United Nations ST/SG/AC.10/C.3/2014/52

Secretariat

Distr.: General
3 April 2014

Original: English

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

Forty-fifth session
Geneva, 23 June – 2 July 2014
Item 2 (e) of the provisional agenda
Explosives and related matters: miscellaneous

Thermal stability test at 75°C using the simulated bulk auto-ignition temperature (SBAT) apparatus

Transmitted by the expert from the United States of America[1]

Introduction

1. Determination of the thermal stability of a substance is required to ensure the safety of people and protection of property during storage and transport. The current test methodology can present significant hazards during handling of 50 to 100 grams of primary explosive material. We recommend that an additional test be added to Type 3(c) for determining the thermal stability of a substance. The SBAT thermal stability test significantly reduces the hazards during handling, has equivalent or better temperature control and temperature monitoring, and matches the sensitivity of the existing instrumented thermal stability test in Test 3(c).

Discussion

2. The SBAT or "simulated bulk auto-ignition temperature" apparatus is a device that monitors the temperature effects on a substance of approximately 5 grams under isothermal or non-isothermal conditions. It consists of a metal block with six ports (example shown in Figure 1) where up to 5 samples plus a reference can be placed. Each sample is placed in a test tube surrounded by insulation and then that insulated tube is placed in one of the 6 ports of the heating block. Both the heating block and the sample are insulated. The temperature of the sample is monitored and recorded.

[1] In accordance with the programme of work of the Sub-Committee for 2013-2014 approved by the Committee at its sixth session (refer to ST/SG/AC.10/C.3/84, para. 86 and ST/SG/AC.10/40, para. 14).

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Figure 1
Example SBAT oven showing the six ports in a black-anodized cylindrical aluminium oven block. The top insulating cover is not shown.

3. Using the SBAT to determine the thermal stability of a substance can significantly reduce the handling risks of primary explosives or very sensitive substances as compared with the current method:

(a) The Manual Test Series 3 (c): *Thermal stability test at 75 °C* does suggest that when testing a new substance several screening tests should be performed to evaluate the hazards associated with testing. However, the actual test requires that 50 or 100 grams of material be used to evaluate the thermal stability of a substance. Handling 50 to 100 grams of a primary explosive can present a significant safety hazard. The SBAT can be used to reliably evaluate the thermal stability of a substance with a smaller but significant sample size of approximately 5 grams.

(b) Additionally, the SBAT can easily be used to heat the sample to ignition following testing thereby eliminating the hazards of handling a potentially thermally sensitized substance. Under the current method given in Test Series 3(c), hazards from handling following testing can be increased as the sensitivity and reactivity may be greater due to thermal damage to the sample.

4. The SBAT thermal stability test matches the ability of the existing methodology in Test 3(c) to identify self-heating within the sample. The current instrumented test states that if ignition or explosion occurs or a temperature difference of 3 °C or greater is measured then the test is considered "+". The SBAT test would give the same sensitivity as the oven test with a 1.5 °C measurement of temperature rise. The following outlines the principles behind this determination.

(a) In Test 3(c): (Thermal stability test at 75 °C) the temperature of the oven is held at 75 °C for a period of 48 hours. If the sample's temperature increases above that of the oven, the extra heat in the sample is transferred to the oven at a rate determined by the sample's thermal diffusivity and the heat-transfer properties of the sample's environment. Thus the increase in temperature of the sample depends on the heat-transfer rate away from the sample. If the sample is well insulated from the oven environment then the rate of heat transfer from the sample is reduced. If the sample is large then the heat transfer rate is reduced as the heat must be transferred through a greater distance; the increased size of the sample effectively acts as insulation around the center most parts of the sample.

(b) The rate of heat transfer from the sample to the oven can be quantified by measuring the time that it takes an inert material (with similar thermal properties as the sample) to reach the oven temperature given the inert material is at a different initial temperature than the oven and the oven temperature remains constant. The

time it takes for the temperature difference to decay to 36.8 percent of the initial difference is equal to the temperature decay time constant. This time constant, τ, relates a materials ability to respond to an increase or decrease in temperature. The greater the time it takes the sample to equilibrate with the oven temperature (or the greater the time constant) the more sensitive is the testing methodology to identifying internal heating as the heat generated by the sample will be lost to its environment at a slower rate. Below in Table 1 is shown the time constant for multiple cooling scenarios where the sample cools from near 75 °C to room temperature.

Table 1: Time constant for the two configurations associated with the oven and SBAT respectively

Instrument	Container	Contents	Temperature decay time constant, min
Oven	Uninsulated glass tube with stopper	Sand – 100 g	20
SBAT	Insulated 13 x 100 mm glass test tube	Sand – 5 g	12.5

(c) Note that in the proposed submission, instead of specifying the insulation used we chose to detail the characteristics of that insulation under the test configuration and thus give the user greater flexibility in choosing an applicable method to obtain the same outcome. In paragraph 13.6.2.2.1(c), there are explicit instructions on how to readily determine the temperature decay time constant.

(d) The minimum temperature difference that the test uses to specify the occurrence of internal heating together with the temperature decay time constant determines the minimum internal heat generation rate that can be detected. For a 3 °C difference the minimum constant heat generation rate that can be identified is 2.0 W/kg (given a heat capacity of 0.83 kJ/kg/K and a temperature decay constant of 20 min). This was found from the energy balance:

$$m \cdot C_v \frac{dT}{dt} = -h \cdot A(T - T_o) + m \cdot g_{gen},$$

where m is the mass of the sample, T is the temperature of the sample, T_o is the oven temperature, C_v is the sample heat capacity, h is the heat transfer coefficient, A is the heat transfer area, g_{gen} is the heat generation rate in the sample, and t is time. With a test time much greater than the temperature decay time constant the temperature difference between the oven and the sample will approximately be

$$(T - T_o) = \tau \cdot g_{gen}/C_v$$

where τ is the temperature decay time constant. This relationship is plotted in Figure 2 with the minimum detectible heat generation rate plotted as a function of the temperature decay time constant for two temperature differences, 1.5 °C and 3 °C. Also shown is the horizontal line for the minimum detectible heat generation rate for the existing instrumented thermal stability test. Note that with the SBAT temperature decay time constant and a 1.5 °C difference, the minimum detectible heat generation rate is equivalent to the current instrumented thermal stability test. Thus with a criteria of 1.5 °C temperature rise the SBAT thermal stability test is just as sensitive as the existing instrumented thermal stability test.

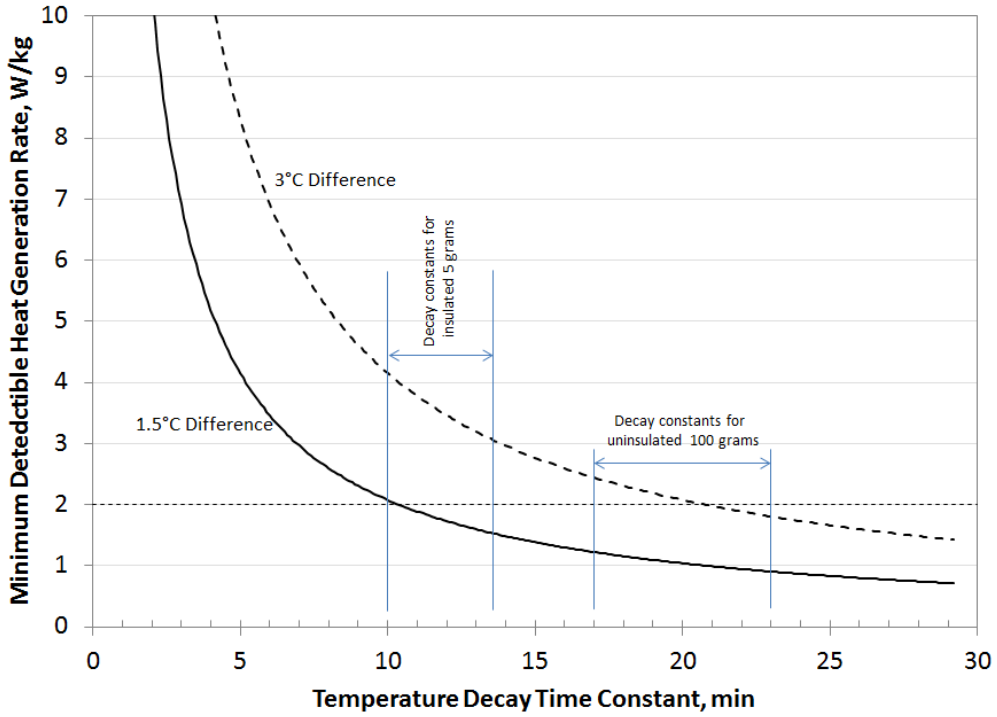


Figure 2

Minimum detectible heat generation rate plotted as a function of the temperature decay time constant for two temperature differences, 1.5 °C and 3 °C. Also shown is the horizontal line for the minimum detectible heat generation rate for the existing instrumented thermal stability test, 2.0 W/kg.

5. The criterion for failure is not based on the sample exceeding a certain temperature. There is a significant difference in accuracy attainable for differential versus an absolute temperature comparison using a thermocouple. A thermocouple is a differential device: it accurately measures changes in temperature and is less accurate at measuring an absolute temperature. Changes in the sample temperature can be accurately assessed to less than 0.25 °C (for example, National Instruments reports that for their NI 9211 thermocouple input module sensitivities are less than 0.1 °C). For an absolute temperature comparison, the accuracy of a thermocouple is typically 1-2 °C depending on multiple factors. The proposed submission is not basing the pass/fail criteria on an absolute temperature measurement; it's based on the change observed in the sample's temperature. As stated below in the proposed submission in paragraph 13.6.2.4 "the result from a test is considered '+' if either the sealed or unsealed sample shows more than a 1.5 °C temperature rise…"

6. In addition to the modeling completed to verify that the SBAT method matches the sensitivity of the existing method, experimental testing comparing the instrumented thermal stability to the SBAT has also been completed. Tests were conducted on a substance that failed the instrumented thermal stability test with a non-sealed container. An 8 °C temperature rise was observed and thus the substance failed the thermal stability test. The substance was a catalyst containing copper acetylide. An SBAT thermal stability test at 75 °C was completed to verify that the SBAT apparatus could also identify the substance as thermally unstable. A temperature rise of greater than 1.5 °C was observed with the SBAT thus it would also be considered to be thermally unstable. Figure 3 shows the plot of the inert reference and the temperature of the catalyst.

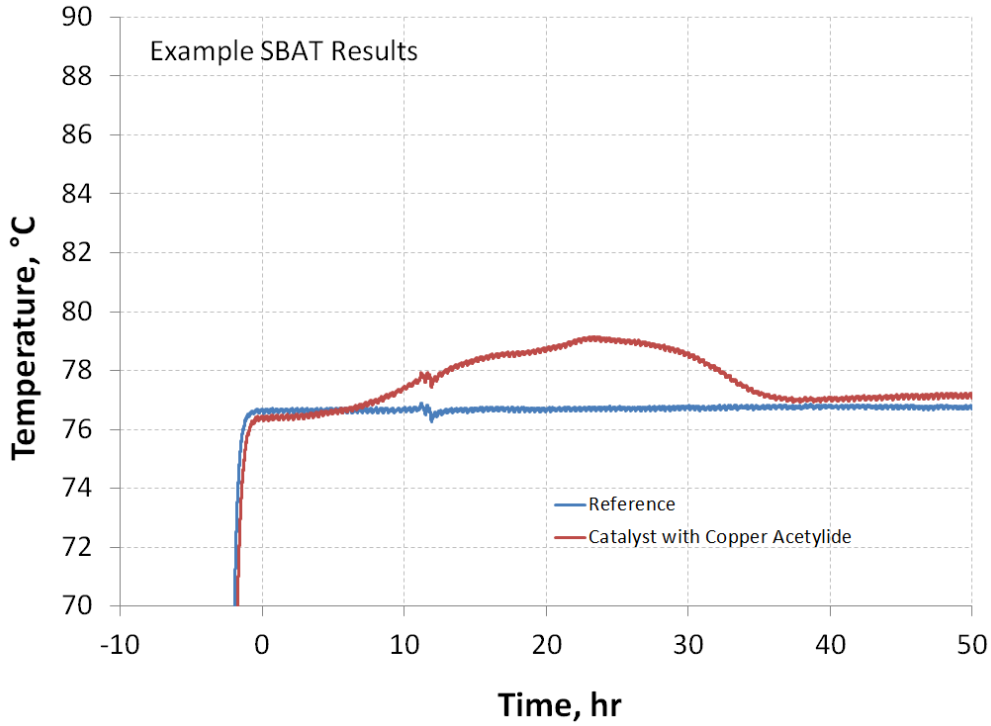


Figure 3

Example SBAT results showing the temperature verus time plot of both the reference temperature (blue) and the catalyst containing copper acetylide (red). The blip in both temperature profiles was a power inconsistency. The temperature rise of the sample was greater than 1.5°C and thus thermally unstable, matching the results observed in the instrumented thermal stability test (shown in Figure 4).

7. The SBAT thermal stability test incorporates the worst case from effects with substances in both unpressurized and pressurized containers. Tests are completed with both an unsealed and sealed glass tube. Increased pressure effects can significantly increase the rate of decomposition. An unsealed tube could result in a worst case should a stabilizing agent volatilize and evaporate from the substance or due to the samples continual exposure to oxygen in the air. Such a result occurred with a catalyst containing copper acetylide. The modified (unsealed) instrumented thermal stability Test 3 (c) failed when the substance self-heated increasing its temperature 8 degrees above that of the oven (temperatures shown in Figure 4). When tested sealed, the substance did not self-heat.

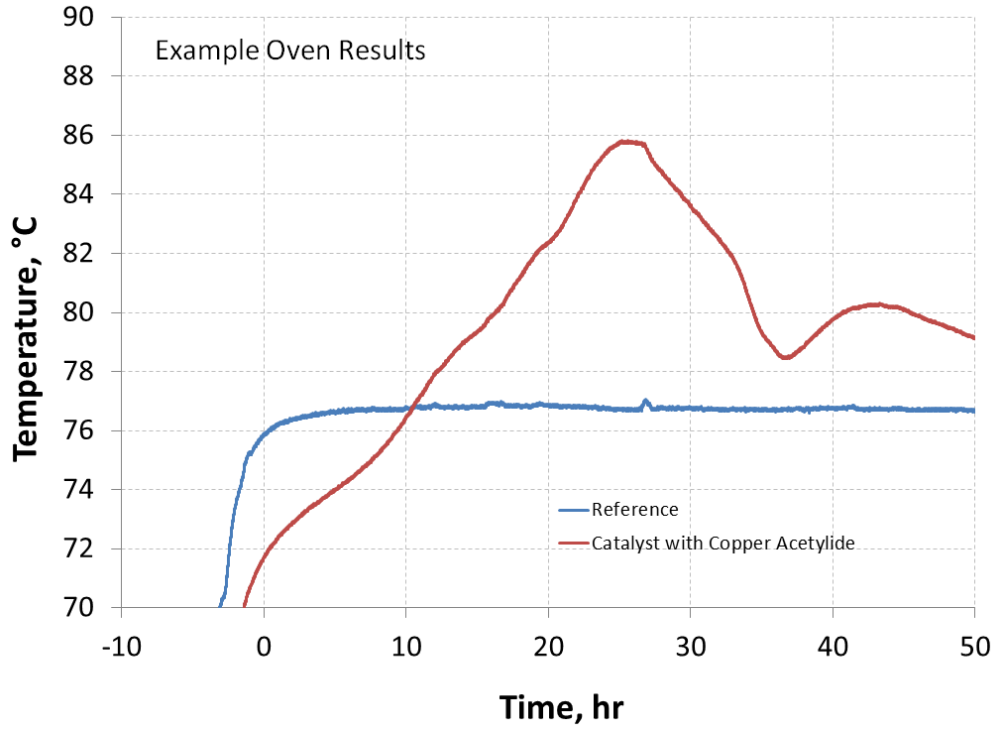


Figure 4

Example oven results showing the temperature versus time plot of both the reference temperature (blue) and a catalyst containing copper acetylide (red, same material as shown in Figure 3 with the SBAT thermal stability test). The temperature rise of the sample was greater than 3°C and thus thermally unstable.

8. In summary, some of the reasons using the SBAT to determine the thermal stability of a substance is advantageous include:

(a) The safety hazards of handling 5 grams of primary explosives are significantly less than handling 50 to 100 grams presently required in Test 3(c).

(b) The SBAT thermal stability test has the same sensitivity in detecting internal heat generation as the current version of the thermal stability instrumented test.

(c) The SBAT thermal stability test uses both open and sealed glass tubes to account for both effects of (1) pressure with a sealed container and (2) evaporation of a stabilizing component or the continued exposure to additional amounts of oxygen with an open container.

(d) The SBAT apparatus is more rugged than many other apparatus. Approximately 5 grams of substance can be ignited in each cell with little to no damage to the equipment. Should the sample explode, the glassware in the sample port would be destroyed but the metallic sample port would receive little to no damage.

(e) The SBAT apparatus has been successfully used for more than 20 years to characterize the thermal stability, auto-ignition temperatures, and critical temperatures of substances.

(f) The SBAT oven can also be used for vacuum thermal stability testing (NATO STANAG 4556) with additional hardware (glassware, vacuum system, and pressure monitoring system).

(g) Kinetic parameters can be estimated from SBAT testing (as can be completed using the differential scanning calorimetry (DSC) as described by N. Sbirrazzuoli, L. Vincent, A. Mija, and N. Guigo in Chemometrics and Intelligent Laboratory Systems 96 (2009) 219 as well as H. Friedman, Journal of Polymer Science C. 6 (1964) 183). The SADT (self accelerating decomposition temperature) can then be readily estimated with the kinetic parameters and the packaging thermal parameters.

Proposal

9. It is proposed to include the SBAT apparatus in the Test Series 3(c) thermal stability options titled Test Series 3(c)(ii) with Test Series 3(c)(i) being the current Thermal stability test at 75 °C.

10. Insert a new sub-section 13.6.2 to read as follows:

"13.6.2 Test 3(c)(ii): SBAT thermal stability test at 75 °C

13.6.2.1 *Introduction*

This test is used to measure the stability of the substance when subjected to elevated thermal conditions to determine if the substance is too dangerous for transport.

13.6.2.2 *Apparatus and materials*

13.6.2.2.1 The following apparatus is required:

(a) Glass sample tubes of 13 x 100 mm inside a larger tube of 25 x 100 mm. Each 13 x100 mm tube is surrounded by insulation and placed into the larger tube. Each larger glass tube has insulation surrounding it further isolating it thermally from the metal oven block. The glass sample tube can be sealed to prevent the escape of gases.

(b) A well-insulated multiport metal block that can be heated with resistance heaters to a temperature of at least 260 °C. The heating of the block must be automated or reliably controlled so that the desired temperature can be maintained within ± 0.5 °C. The heated block should have independent protection against excessively heating the block in the event of a primary control system failure. Each port in the metal block should have a diameter of 2 inches and a depth of 4 inches.

(c) The temperature decay time constant, τ, for the configuration outlined in (a) and (b) should be at least 10 minutes. The decay constant, τ, is found by heating 5 grams of an inert material (e.g. dried silica, alumina, or silicone) in the sample tube (13 x 100 mm test tube) to a temperature 50 °C or more higher than the constant temperature of the SBAT. The heated sample tube is placed into the SBAT apparatus (into the larger glass tube with internal and external insulation as previously described). The sample will cool to the constant temperature of the oven. While cooling, the sample temperature is recorded. The decaying temperature will be exponential in shape and is fit to the following equation:

$$(T - T_a)/(T_i - T_a) = \exp(-t/\tau)$$

where T is the inert reference temperature that varies with time, T_a is the constant oven temperature, T_i is the initial reference temperature, t is time and τ is the temperature decay time constant.

(d) An inert material (e.g. dried silica, alumina or silicone) to be used as a reference which is also placed into insulated glass tubes (13 x 100 mm inside the larger 25 x 100 mm tube) with the same insulation configuration as the sample.

(e) Thermocouples with a data recording system to record the temperature of the reference and sample(s) as well as thermocouple(s) to measure and control the oven temperature.

13.6.2.3 *Procedure*

13.6.2.3.1 Five grams of the sample or an amount that fills the tube to 75 mm height, whichever is less, is placed inside one of the sample tubes. A second sample tube is filled with the same amount of sample. One of the filled sample tubes is not sealed whereas the second filled sample tube is sealed with a screw cap or other method. For the sample tube that is sealed, the thermocouple is attached to the sidewall of the sample tube. For the open sample tube, the thermocouple can be attached to the side of the tube or inserted into the sample.

13.6.2.3.2 Each sample tube is then surrounded with insulation and placed into the larger 25 x 100 mm tube which is also insulated from the side walls of the SBAT oven ports. The approximately 5 gram reference sample must also be present in one of the SBAT ports with the same insulation configuration as the sample. The samples are heated to 75 – 77 °C and maintained at that temperature for 48 hours. Sample and reference temperatures are recorded throughout the test.

13.6.2.3.3 Once the test has been completed, additional test data may be obtained by linearly increasing the temperature of the apparatus to determine the thermal profile of the sample (measuring endotherms and exotherms, as evidenced by departures of the sample from the temperature of the inert reference).

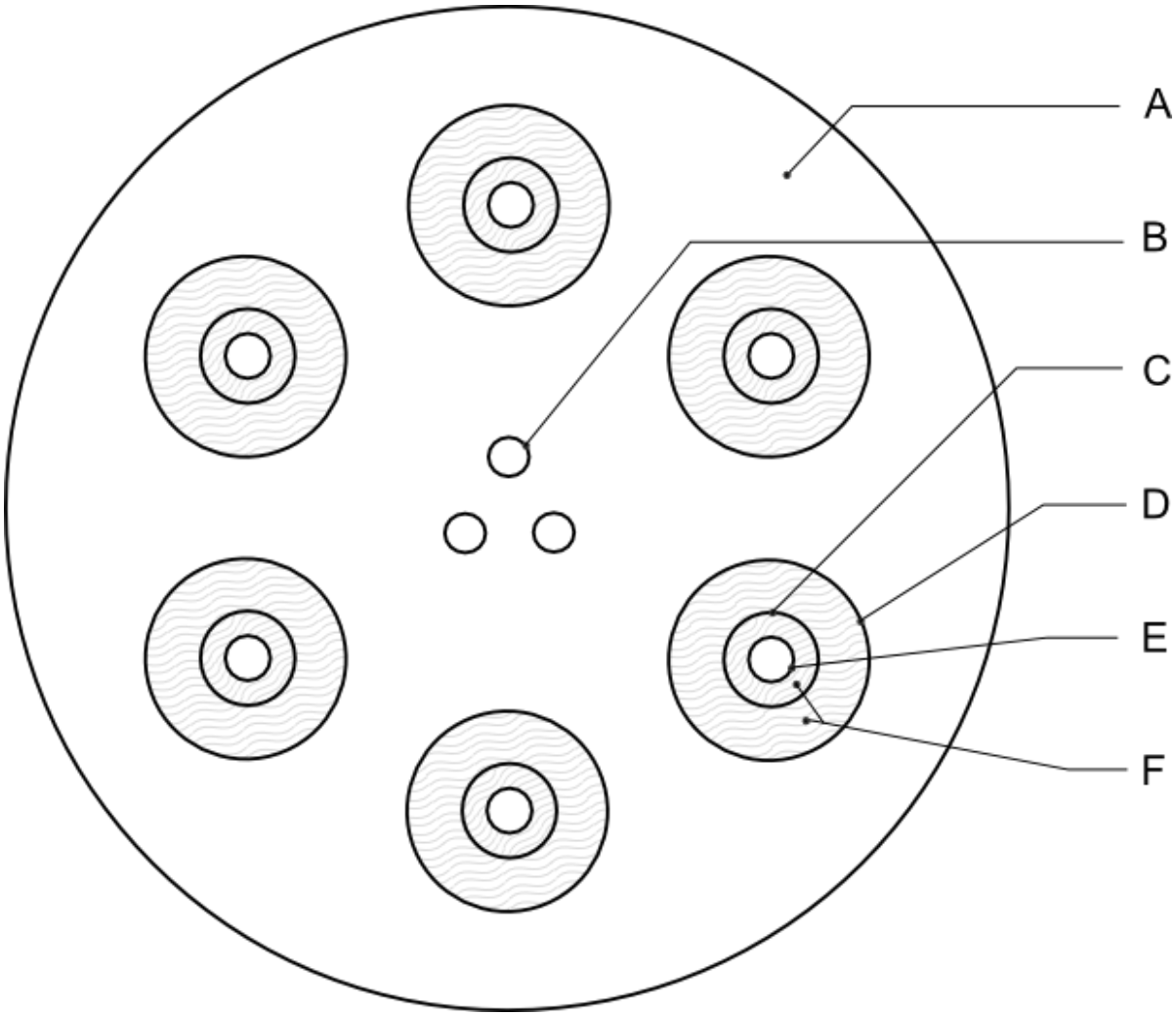
13.6.2.4 *Test criteria and method of assessing results*

13.6.2.4.1 The result from a test is considered "+" if either the sealed or unsealed sample shows more than a 1.5 °C temperature rise during the 48 hour test period indicating self-heating.

13.6.2.4.2 If the test result is "+", the substance should be considered too thermally unstable for transport.

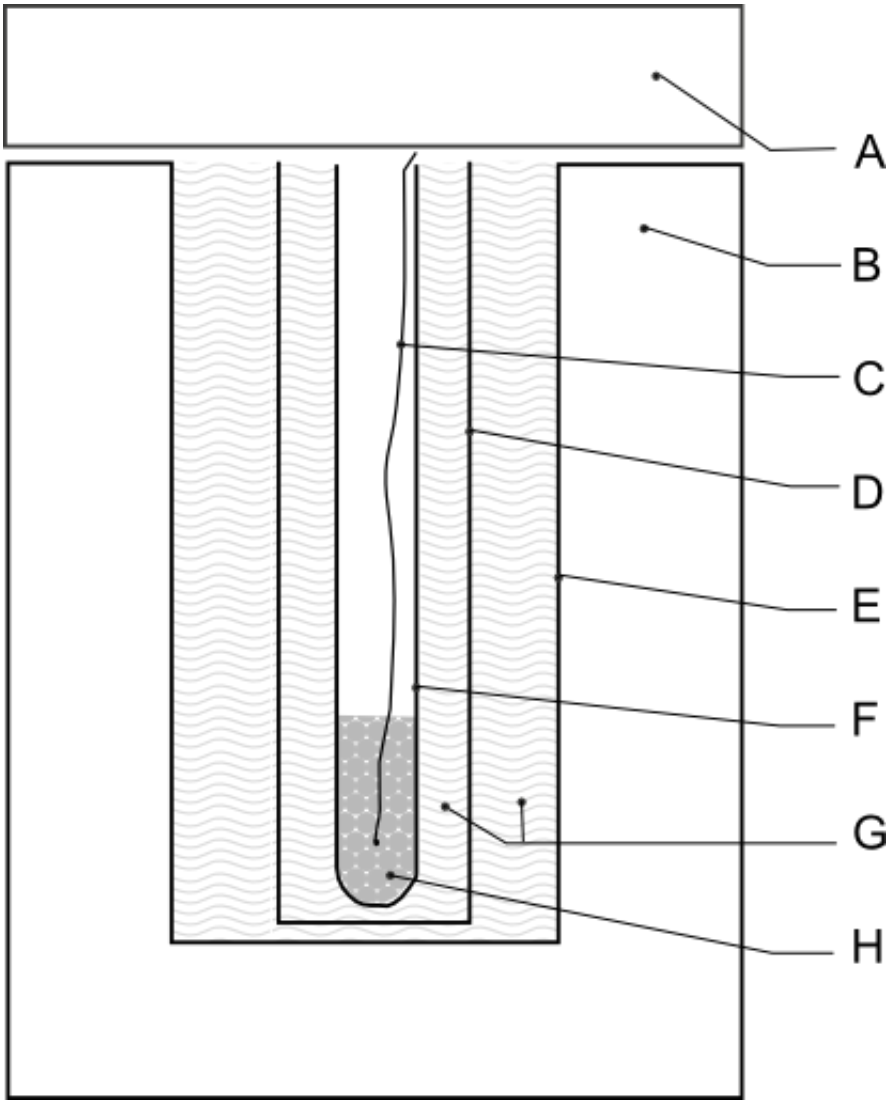
13.6.2.5 *Examples of results*

Substances	**Temperature Rise**	**Result**
PETN	Less than 1.5 °C	–
RDX	Less than 1.5 °C	–
TNT	Less than 1.5 °C	–
Composition B, reclaimed	Less than 1.5 °C	–
Double base smokeless powder, 40% NG	Less than 1.5 °C	–
Black powder	Less than 1.5 °C	–
Barium styphnate	Less than 1.5 °C	–
Rocket motor propellant (60-70% AP, 5-16% Al, 12-30% binder)	Less than 1.5 °C	–
Catalyst containing copper acetylide	Greater than 1.5 °C	+



(A)	Metal block	(B)	Cartridge heaters
(C)	Glassware	(D)	Sample port
(E)	Glass sample container	(F)	Insulation

Figure 13.6.2.1: SBAT Heating Block



(A)	Insulative cap or blanket	(B)	Metal block
(C)	Thermocouple	(D)	Glassware
(E)	Sample port	(F)	Glass sample container
(G)	Insulation	(H)	Sample

Figure 13.6.2.1: SBAT Port