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STANAG 4582 JAS (EDITION 1) – EXPLOSIVES, NITROCELLULOSE BASED PROPELLANTS, STABILITY TEST PROCEDURE AND REQUIREMENTS USING HEAT FLOW CALORIMETRY

Reference: PFP(AC/326)D(2004)0007 dated 3 March 2004

1. The enclosed NATO Standardization Agreement, which has been ratified by nations as reflected in the **NATO Standardization Document Database (NSDD)**, is promulgated herewith.

2. The reference listed above is to be destroyed in accordance with local document destruction procedures.

ACTION BY NATIONAL STAFFS

3. National staffs are requested to examine **their ratification status of the STANAG** and, if they have not already done so, advise the Defence Investment Division through their national delegation as appropriate of their intention regarding its ratification and implementation.

J. MAJ
Major General, POL(A)
Director, NSA

Enclosure:
STANAG 4582 (Edition 1)

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STANAG 4582
(Edition 1)

NORTH ATLANTIC TREATY ORGANIZATION
(NATO)

NATO STANDARDIZATIONAGENCY
(NSA)

STANDARDIZATION AGREEMENT
(STANAG)

SUBJECT: EXPLOSIVES, NITROCELLULOSE BASED PROPELLANTS, STABILITY TEST PROCEDURE AND REQUIREMENTS USING HEAT FLOW CALORIMETRY

Promulgated on 09 March 2007

J. MAJ
Major General, POL(A)
Director, NSA

RECORD OF AMENDMENTS

No.	Reference/date of Amendment	Date Entered	Signature

EXPLANATORY NOTES

AGREEMENT

1. This NATO Standardization Agreement (STANAG) is promulgated by the Director NATO Standardization Agency under the authority vested in him by the NATO Standardization Organisation Charter.

2. No departure may be made from the agreement without informing the tasking authority in the form of a reservation. Nations may propose changes at any time to the tasking authority where they will be processed in the same manner as the original agreement.

3. Ratifying nations have agreed that national orders, manuals and instructions implementing this STANAG will include a reference to the STANAG number for purposes of identification.

RATIFICATION, IMPLEMENTATION AND RESERVATIONS

4. Ratification, implementation and reservation details are available on request or through the NSA websites (internet http://nsa.nato.int; NATO Secure WAN http://nsa.hq.nato.int).

FEEDBACK

5. Any comments concerning this publication should be directed to NATO/NSA – Bvd Leopold III - 1110 Brussels - BE.

STANAG 4582
(Edition 1)
NAVY/ARMY/AIR

NATO STANDARDISATION AGREEMENT
(STANAG)

EXPLOSIVES, NITROCELLULOSE BASED PROPELLANTS, STABILITY TEST PROCEDURE AND REQUIREMENTS USING HEAT FLOW CALORIMETRY

Annexes:
A. Theoretical Considerations
B. Test Procedure
C. Criteria of Acceptance
D. Test Data Sheet
E. Typical heat flow curves and evaluation

AIM

1. The aim of this agreement is to standardize a stability test procedure for single base (SB), double base (DB), and triple base (TB) propellants using heat flow calorimetry.

2. The test procedure was developed to facilitate cross procurement and provide a means by which countries can satisfy themselves that propellants received from abroad will remain chemically stable for a minimum of ten years if stored at temperatures equivalent to an isothermal storage at 25°C.

3. This agreement is intended for use by the NATO Participating Nations.

AGREEMENT

4. Participating Nations agree to adopt the test procedure described in Annex B for the heat flow calorimetry (HFC) measurement of propellants, to adopt the limits of acceptance in Annex C, and to use the data sheets at Annex D for reporting test results.

GENERAL

5. This STANAG describes a method for establishing the chemical stability of SB, DB and TB propellants for a minimum of 10 years when stored at 25°C or to an equivalent degree as defined in A-4 paragraph 4.

The test can be applied for qualification, quality control or for prolongation of service life time for further 10 years using unchanged criteria of acceptance as defined in Annex C.

However, since the heat flow depends on reactions differing in enthalpy for different stabilizers it is not an absolute measure of stability. Comparison is only meaningful for propellants of similar composition. This STANAG does not imply that a propellant with a higher heat flow is less stable than one with a lower heat flow.

The procedure, based primarily on measurements and safety simulations of diphenylamine (DPA) stabilized propellants, has been found to be equally applicable to propellants containing other stabilizers like 2-nitro-DPA, akardite II, MNA and ethyl centralite.

In spite of the quite different shapes of the HFC curves due to nitration and nitrosation of the stabilizers it can be assumed that the temperature dependence will be dominated mainly by the slower decomposition reactions of nitrocellulose and nitroglycerin (NG). Consequently the same test conditions can be used for different types of stabilizers.

The ageing method tests propellants in a gas-tight closed vessel. The conditions in this vessel are considered to be equivalent to the conditions in most ammunition articles containing propellants. The results may therefore differ from those using other procedures.

WARNING

6. This STANAG calls for the use of substances and test procedures that may be injurious to health if adequate precautions are not taken. It refers only to technical suitability and in no way absolves the user from the statutory obligations relating to health and safety at any stage during use.

IMPLEMENTATION OF THE AGREEMENT

7. This STANAG will be considered implemented when ratifying countries comply with the test procedure described for assessing the chemical stability of SB, DB, and TB propellants.

THEORETICAL CONSIDERATIONS

1. GENERAL ASPECTS

This STANAG gives a basic outline description of the proposed HFC method. A more detailed description of associated experimentation and theory has been presented at the 31st ICT Conference [1].

Quantitative estimation of the chemical stability of propellants means calculation of the critical conditions of time and temperature for thermal explosion. Whether the stability will be sufficient depends on the composition (including moisture) of the propellant and its geometry, storage temperature and time and thermal insulation of the ammunition. The main problems in data acquisition for the calculation are the estimation of the heat conductivity of the propellant and its surrounding materials and the determination of the heat generation rate of decomposition as function of temperature and time. This “kinetic model“ must be valid at least up to the highest isothermal reaction rate of the reactions.

Due to nitration and nitrosation of different stabilizers the shapes of HFC curves vary on a large scale. The temperature dependence of these reactions however, varies only in a small range, because they all are controlled by the slower decomposition of nitrocellulose and nitroglycerin. Therefore a one temperature heat flow method is sufficient to detect propellants “out of range“ if two conditions are realized:

1. A conservative theory for extrapolation of test duration to ambient temperature times must be established. Then a test duration at least equivalent to the thermal stress of a 10 years isothermal storage at 25°C can be calculated.
2. For shorter periods in the service life time the temperature of a propellant may rise considerably above ambient temperature. Assuming the highest expected stress a heat flow limit that keeps the system nearly isothermal should be estimated. This ensures that storage near ambient temperatures remains isothermal in any case and no accelerated ageing occurs.

An equivalent of this likewise conservative heat flow limit can be calculated for the measuring temperature and used as criterion for sufficent chemical stability.

2. EXTRAPOLATION THEORY

A typical heat flow curve of a DB propellant stabilized with DPA beyond the time of the maximum rate is shown in Fig A-1.

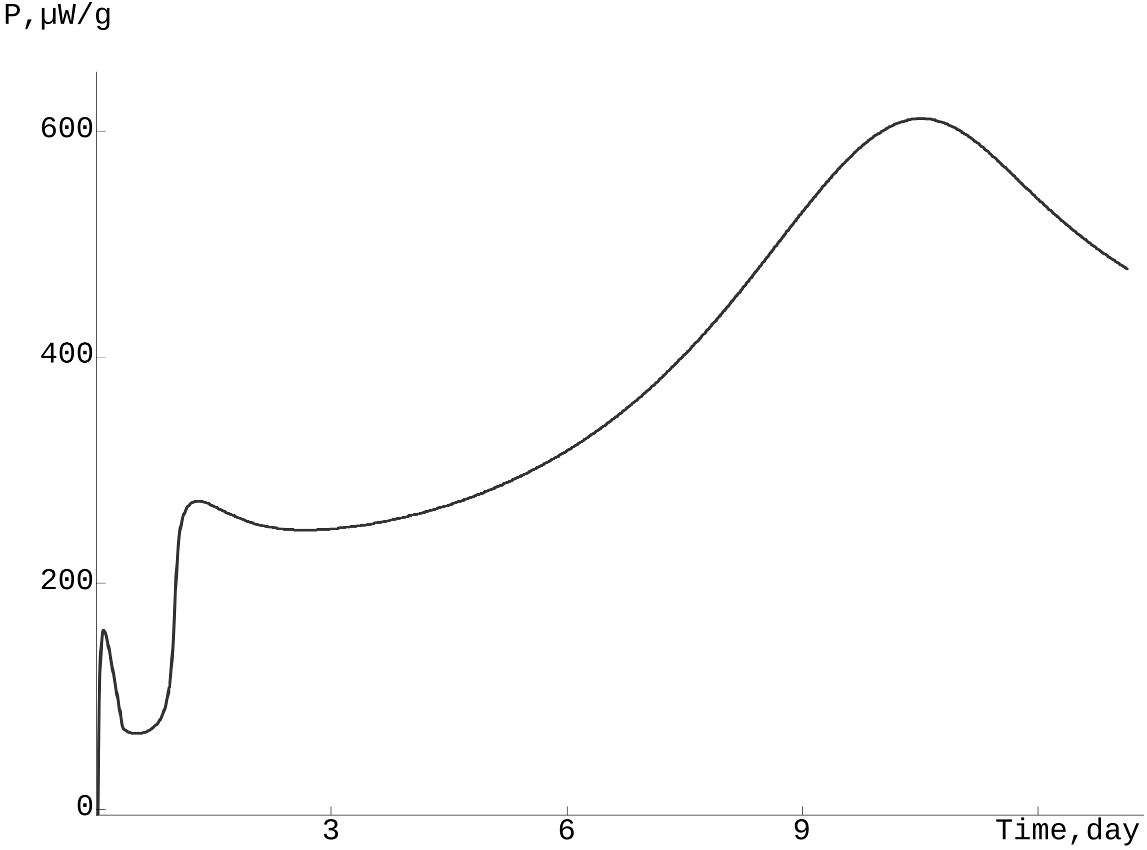

Fig. A-1. Heat flow curve of a DB propellant at 89°C (stabilized with DPA)

The decomposition region up to 4 days is equivalent to a storage at 25°C for at least 10 years. Therefore it is sufficient to evaluate the kinetics of this part. This was done by heat flow measurements of the same propellant resulting in an approximately constant activation energy (AE) of 130-140 kJ/mole in the temperature range from 50 to 89°C [2].

Some other propellants, however, show a change between 50 and 60°C corresponding to about 90 kJ/mole in the lower temperature range (see Fig. A-2).

Setting the levels at 80 kJ/mole for temperatures below 60°C and at 120 kJ/mole in the range above this temperature is assumed to be conservative enough for extrapolations. (This means that the decomposition of the propellants after 10 years storage will mostly be considerably lower than in the measurement).

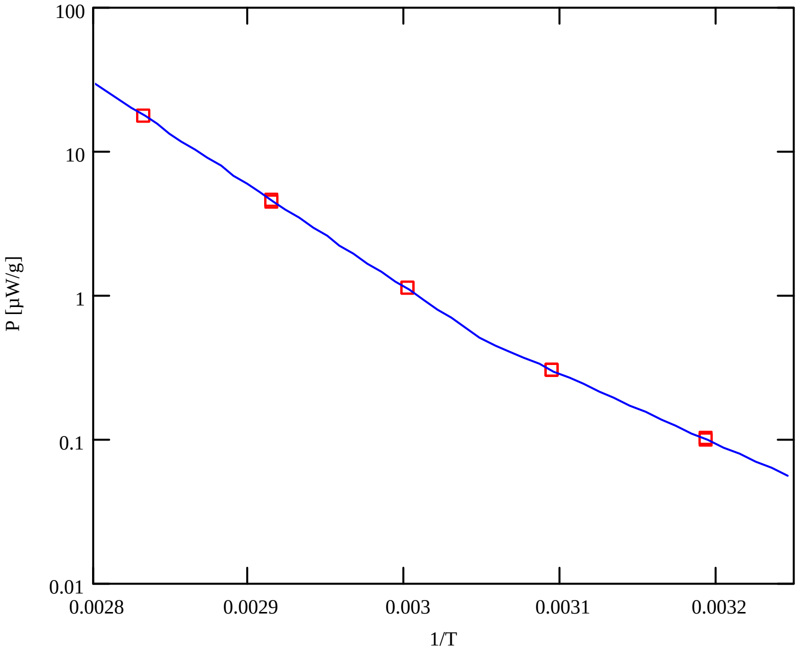

Fig. A-2. Arrhenius plot of a SB propellant (stabilized with DPA)

Apart from the different temperature dependence the reactions are assumed to be identical below and above 60°C.

The duration of the experiment leading to the same decomposition degree as a ten years storage at 25°C can then be calculated from

$$t_m = t_{25} * e^{[E_1 \cdot (1/T_m - 1/T_{60}) + E_2 \cdot (1/T_{60} - 1/T_{25})]/R} \qquad (1)$$

t_m = test duration [days]
t_{25} = duration of storage at 25°C (3652.5 days = 10 years)
T_m = test temperature [K]
T_{60} = temperature of change of the activation energy (AE) (333.15 K = 60°C)
T_{25} = storage temperature (298.15 K = 25°C)
E_1 = AE of the higher temperature range (120 kJ/mole)
E_2 = AE of the lower temperature range (80 kJ/mole)
R = gas constant (0.0083143 kJ/(K·mole))

By introduction of the constant values $T_{25} = 298.15$ K, $T_{60} = 333.15$ K and $E_2 = 80$ kJ/mole eq. (1) simplifies to

$$t_m = t_{25} * e^{E_1/(R*T_m) - C} \qquad (2)$$

C = 46.713

Eq. (2) is used for calculation of the test duration for different temperatures (see table C-1).

3. ESTIMATION OF HEAT FLOW LIMIT

A thermally well insulated cartridge of 230 mm inner diameter and a maximum storage temperature of 71°C was assumed to be the worst case during the service life of a gun propellant incorporated into ammunition. For storage of propellants in bulk or large rocket motors a diameter of 1000 mm and a temperature of 50°C were considered as upper limits.

Varying the heat generation rate by the frequency factor of a zero order reaction these conditions were simulated using the heat transport model of Thomas [3]. It was found that a heat generation rate of 39 µW/g at 71°C causes a temperature increase of about 1.5°C in the center of the propellant loaded into the 230 mm cartridge. The same effect is achieved by a heat generation rate of 2.6 µW/g at 50°C in both 1000 mm systems (grained gun propellant and compact rocket propellant).

This means that up to these limits the propellant remains approximately at ambient temperature and the extrapolation theory outlined in paragraph 2 is valid. Assuming an activation energy of 120 kJ/mole both heat generation rates are kinetically equal (39 µW/g at 71°C correspond to 2.56 µW/g at 50°C, see eq. (3))

Therefore a unit limit for the heat generation rate can be derived from eq. (3). It is valid for all worst cases considered, but, of course, different for different test temperatures.

$$P_l = P_{71} * e^{E_1 * (1/T_{71} - 1/T_m)/R} \qquad (3)$$

T_m = test temperature [K]
T_{71} = 344.15 K (= 71°C)
E_1 = activation energy (120 kJ/mole)
P_{71} = heat flow limit at 71°C (39 µW/g)
P_l = heat flow limit at T_m [µW/g]

In the first part of the measurement some propellants show an initial high rate due to aerobic decomposition reaction until the supply of air which is sealed within the sample vessel is consumed. The total heat of this reaction is small and cannot cause a temperature rise of more than a few degrees centigrade, even if released instantaneously. To allow for this effect the P_l criterion should be used only in the region between the time corresponding to a heat release of 5 J/g and the test time defined by eq. (2).

Even though DB, SB, and TB propellants are considerably different in stability there is no reason to choose different safety levels. Therefore the same heat flow limit should be used for all types. Values for different test temperatures are given in table C-1.

4. ASSESSMENTS FOR NON ISOTHERMAL STORAGE

In practice an isothermal storage will not often be realized. However, if a temperature and time profile of storage can be predicted, it is possible to check whether the equivalent degree of thermal ageing will be less or more than a storage at 25°C. For temperatures below 50°C any storage durations can be added up as storage times equivalent to 25°C.

$$t_{25} = t_s * e^{E_2 (1/T_{25} - 1/T_s)/R} \qquad (4)$$

T_s = storage temperature [K]
t_s = storage duration [y]
t_{25} = storage duration at 298.15 K [y]
E_2 = 80 kJ/mole

An example is given in table A-1.

Table A-1: Calculation of 25°C times for a storage profile

T_s [°C]	**t_s [y]**	**t_{25} [y]**
40	0.1	0.47
35	0.4	1.14
30	1.5	2.55
25	3	3.00
20	4	2.31
15	1	0.33
SUM	10	9.80

This procedure contains an additional conservative aspect if the high temperature periods are short, e.g. in a cyclic storage situation (high ambient temperature during day and low temperature during night). In this case only the outer regions of a propellant in a large diameter article reach ambient temperature, whereas the major part remains close to mean temperature.

Literature

[1] U. Ticmanis, S. Wilker, G. Pantel, P. Guillaume, C. Balès, N. van der Meer „Principles of a STANAG for the estimation of the chemical stability of propellants by Heat Flow Calorimetry“, *Proc. Int Annu. Conf. ICT* 31, 2 (**2000**).

[2] P. Guillaume, M. Rat, S. Wilker, G. Pantel, „Microcalorimetric and Chemical Studies of Propellants“, *Proc. Int Annu. Conf. ICT* 29, 133 (**1998**).

[3] P.H. Thomas, *Trans. Faraday. Soc.* 54, 60-65 (**1942**).

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TEST PROCEDURE

1. DEFINITIONS

Heat flow signal is the sum of the heat flows that are produced during the ageing of a propellant by chemical and physical reactions.

2. GENERAL DESCRIPTION

Samples are measured at a constant temperature between 60°C and 90°C for a specified time dictated by the temperature chosen. This time is considered to be equivalent to at least a 10 years storage at 25°C. A maximum permissible heat flow limit, also dictated by the experimental temperature employed is used as a criterion for sufficient chemical stability.

Due to an AE considerably above the assumed value of 120 kJ/mole some propellants may fail the stability criteria when measured at temperatures close to 90°C. In such cases the test can be repeated at a lower temperature (e.g. at 60°C). To give more information the results of both measurements should be reported.

3. APPARATUS

3.1 Heat flow calorimeter with a measuring range corresponding to 10 to 500 µW/g. The error must be less than 2% during the total measuring time. If necessary to reach this level the drift of the baseline must be estimated and used for correction.

3.2 Sample vessels with a minimum volume of 2 cm^3 that can be hermetically sealed. It must be proved that the vessel material does not react with propellants and their decomposition products.

3.3 Appropriate data collecting and calculating system including integration.

4. PREPARATION OF PROPELLANTS

4.1 As far as possible the propellant should be measured in its original condition. The sample should be representative for the batch or lot of propellant in test. If the volume of the sample vessel is too small to fulfill this a sufficiently large amount of the propellant should be ground or cut and the sample should be taken from a well mixed fraction as near as possible between 1 - 2 mm.

4.2 Since the heat flow depends somewhat on the moisture content, it is advisable to determine the moisture content by an appropriate method (e. g. Karl Fischer titration) and to test the samples as received without preconditioning.

5. LOADING DENSITY

The sample vessels should be filled up to the top so that the amount of air inside is minimal. The loading density is thus approximately 0.8 to 1.1 g/cm³. In double or multiple measurements approximately the same loading density should be used. Otherwise different atmospheric conditions/ pressure effects may affect the decomposition reaction and thus give slightly different HFC curves. For safety reasons the sample size might be reduced. In this case the free volume should be filled nearly completely with an inert material (for example using a glass rod corresponding to the inner diameter of the ampoule). Filling with grainlike material results in a lower loading density and should be avoided.

Alternatively the loading density of the ammunition defined for the propellant in test may be used for the HFC measurements.

6. DETERMINATION OF HFC SIGNAL

6.1 Procedure

6.1.1 Calibration

The calibration must be done very carefully. In calorimeters where the electrical heating device is placed outside, use empty vessels on the sample and reference side. For calibration of apparatus with heating devices inside the sample vessel follow the instructions of the manufacturer. Before calibrating wait for a stable baseline for at least 12 h. Estimate the maximum heat flow of the measurement and use the most sensitive range which will accommodate this.

6.1.2 Measurement

The test temperature should be in the range from 60°C to 90°C (see table C-1). However, to save time, temperatures close to the upper limit are recommended. Perform the experiment at least in duplicate. The test duration depends on the temperature chosen and is calculated by eq. (2) in Annex A (see table C-1).

For surveillance and quality control of qualified propellants the test duration may be shortened by up to 30%. Experiments where endothermic peaks due to the escape of gas from the ampoule are observed should be discarded (see fig. B-1).

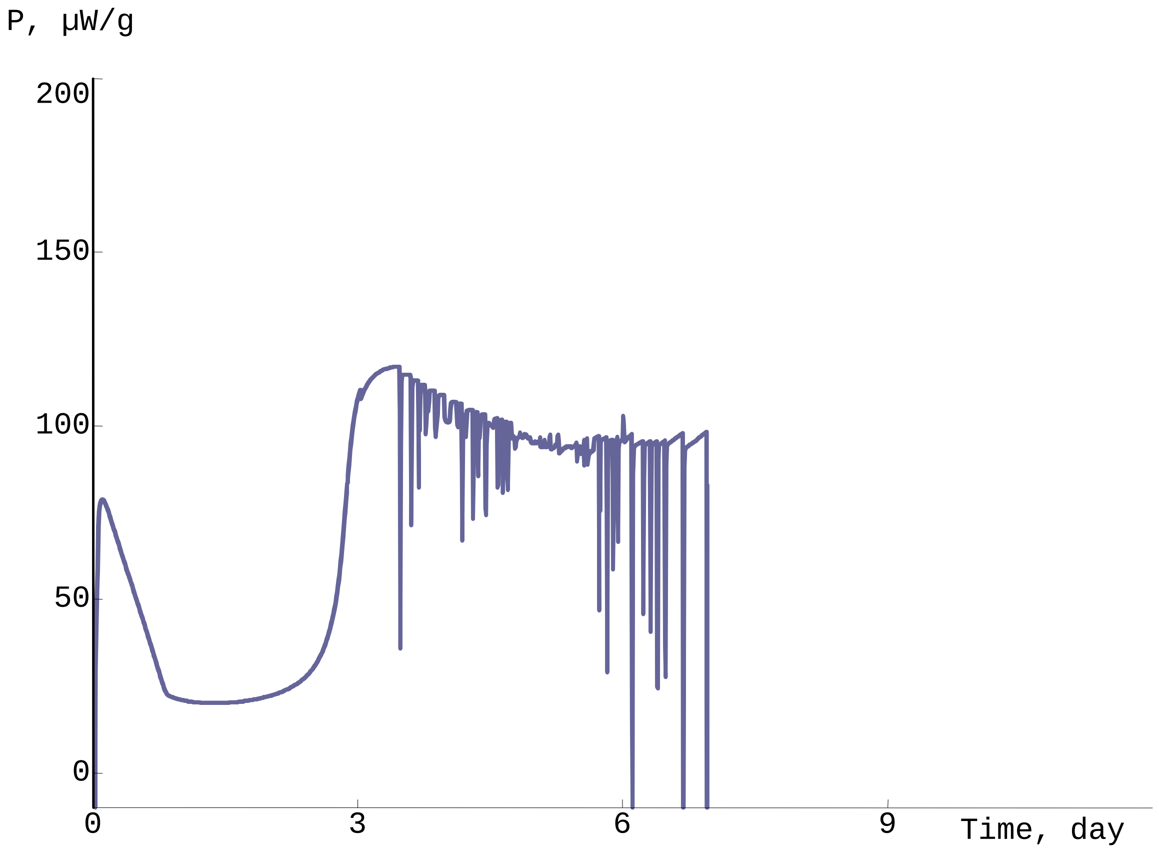

Fig. B-1. HFC measurement of a DPA stabilized DB propellant at 80°C showing gas evolution peaks.

6.1.3 Data evaluation

The data must be normalised to one gram of propellant. Determine the maximum heat flow in the region between the time corresponding to a heat release of 5 J/g and the defined measuring time (table C-1). For information on the decomposition degree calculate the total heat release after the specified time as well. Several examples of evaluation are given in Annex E (All measurements were performed in glass vessels of 3 cm³ volume; loading density 0.8-1.1 g/cm³; for the porous propellants 0.4-0.6 g/cm³).

6.1.4 Reporting

Report the results in the form outlined in data sheet 2 at Annex D. Provide separate copies of the heat flow diagram for each sample.

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CRITERIA OF ACCEPTANCE

1. Propellants will be sentenced according to the following requirements.

2. Propellants stored at temperatures equivalent to an isothermal storage at 25°C (A-5) will remain chemically stable for a minimum of 10 years if the following criterion is met:

   The maximum heat flow in the experimental part between the time corresponding to a heat release of 5 J/g and the time defined by eq. 2 (Annex A) must not exceed a limit calculated from eq. 3 (Annex A). Both measuring times and heat flow limits depend on the test temperature chosen (table C-1).

Table C-1. Calculation of test times t_m (eq. 2) and heat flow limits P_l (eq. 3) for different test temperatures T_m

T_m [°C]	t_m [days]	P_l [µW/g]
60	123	9.8
61	108	11.1
62	95.0	12.6
63	83.6	14.4
64	73.6	16.3
65	64.9	18.5
66	57.2	21.0
67	50.5	23.8
68	44.6	27.0
69	39.4	30.5
70	34.8	34.5
71	30.8	39.0
72	27.3	44.0
73	24.2	49.7
74	21.5	56.0
75	19.0	63.1
76	16.9	71.1
77	15.0	80.0
78	13.4	90.0
79	11.9	101
80	10.6	114
81	9.43	127
82	8.41	143
83	7.50	160
84	6.70	179
85	5.98	201
86	5.35	225
87	4.78	251
88	4.28	281
89	3.83	314
90	3.43	350

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TEST DATA SHEET

NATO STANAG 4582 DATA SHEET 1	
Report Reference Number: (Unique Reference Number)	Page 1 of 2 Page(s)
TEST SITE INFORMATION	**SPECIMEN INFORMATION**
Laboratory: (Name of Laboratory)	Propellant: (Type of propellant)
Date: (Date that form was completed)	Identification: (Trade name and/or Identity code)
	Manufacturer: (Name of Manufacturer)
Date Tested: (Date of test period)	Lot, Batch or Consigment Number:
POC: (Point of contact)	Date of Manufacture or Receipt:
TEST CONDITIONS	**COMPOSITION**
Type of Calorimeter Sample preparation: (Including details of cutting and conditioning) Moisture content (if determined)	(Composition and Percentages)
	Comments:
	Data Sent To: (Name and address of person receiving this information)

NATO STANAG 4582 DATA SHEET 2			
Report Reference Number: (Unique Reference Number)			Page 2 of 2 Page(s)
RESULTS			
Sample No	1	2	3
Material of vessel			
Volume of vessel [cm^3]			
Sample weight [g]			
Calibration range [µW]			
Test temperature [°C]			
Total measurement duration [d]			
Time of evaluation calculated by eq. 2 [d]			
Heat release until time of evaluation [J/g]			
Max. heat flow (P_m) 1) within time of evaluation [µW/g]			
Heat flow limit calculated by eq. 3 [µW/g]			

1) see Annex B-3 (data evaluation)

TYPICAL HEAT FLOW CURVES AND EVALUATION

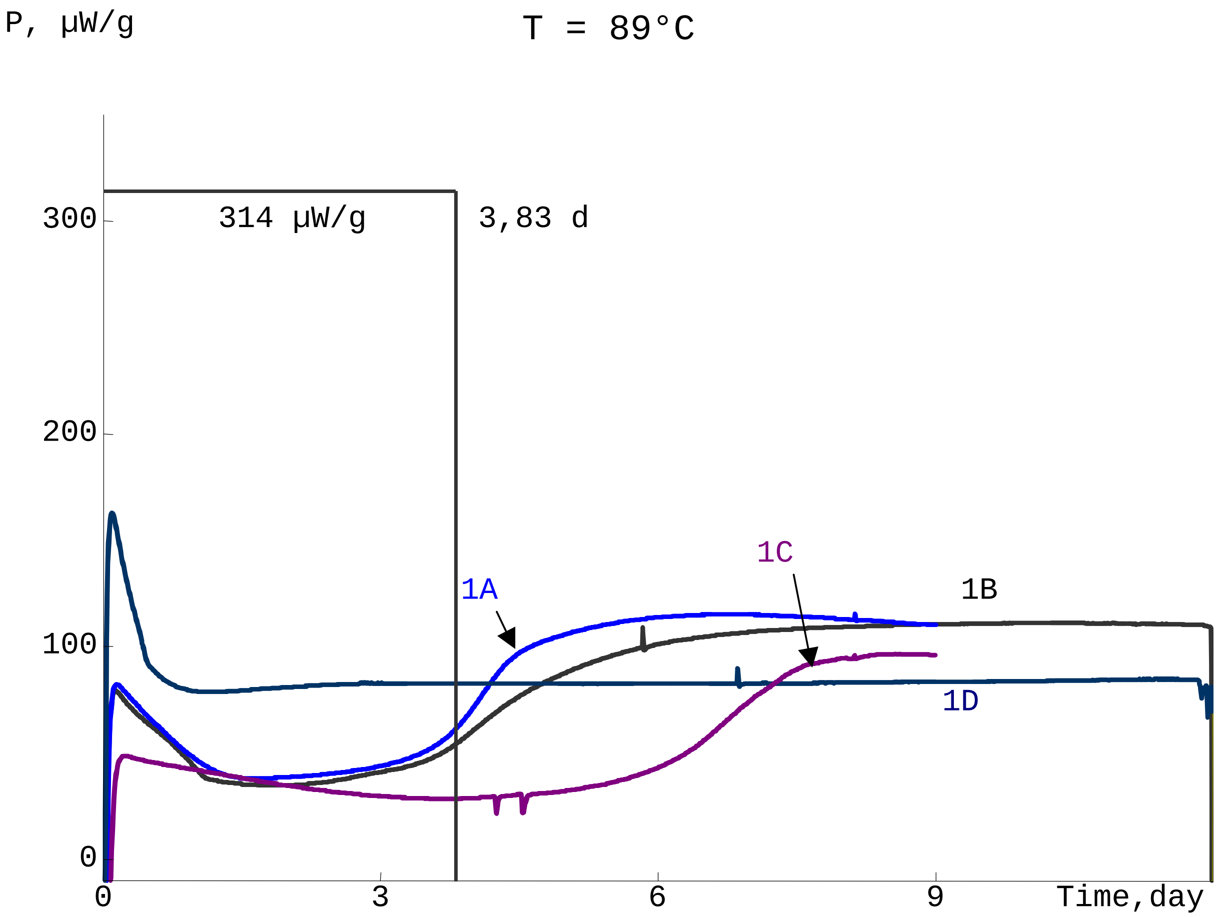

Figure E-1. Heat flow curves and evaluation of SB propellants (I)

Propellant	Propellant type	Stabilizer content	Comments
1A	Single base, DNT contg.	DPA 1.0%	7 hole, original size used
1B	Single base	DPA 0.9%, Centralite I 1.1%	Small grains, original size used
1C	Single base, DNT contg.	DPA 1.5%	19 hole, cut into small pieces
1D	Single base	Centralite I 2.0%	One hole, original size used

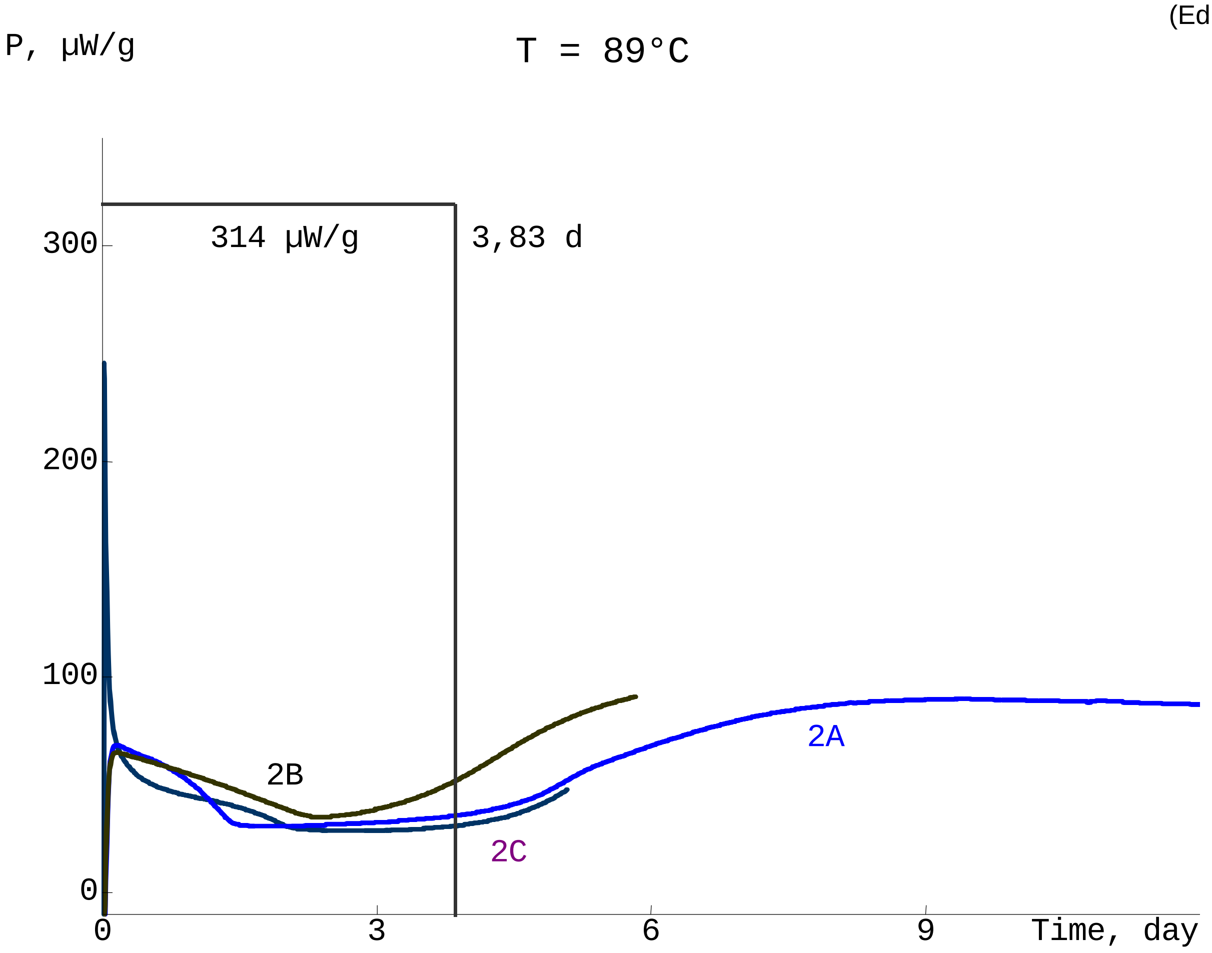

Figure E-2. Heat flow curve and evaluation of SB propellants (II)

Propellant	Propellant type	Stabilizer content	Comment
2A	Single base, DNT contg.	DPA 1.0%	19 hole, original size used
2B	Single base, DNT contg.	DPA 1.3%	19 hole, cut into small pieces
2C	Single base	DPA 1.1%	One hole, original size used

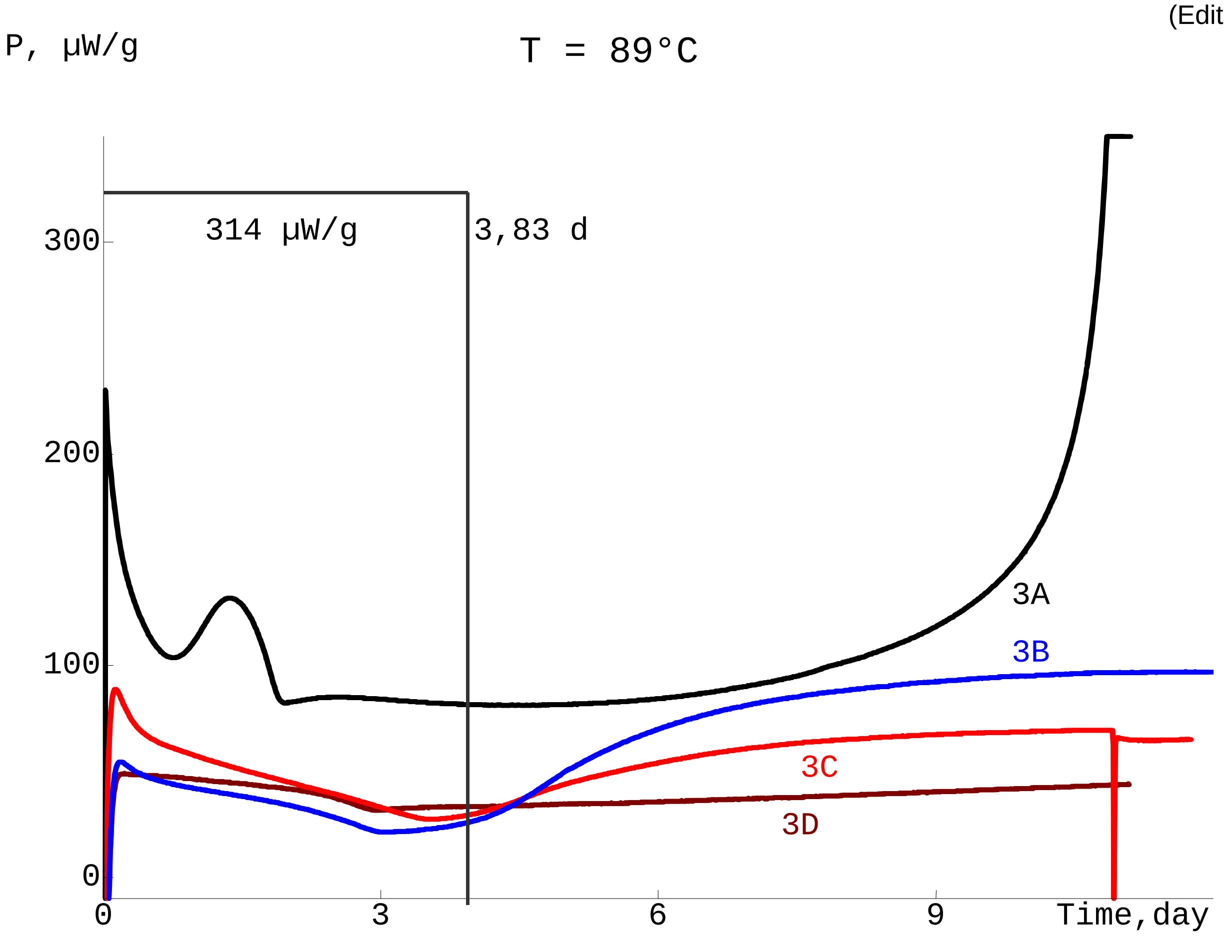

Figure E-3. Heat flow curves and evaluation of SB porous propellants

Propellant	Propellant type	Stabilizer content	Comments
3A	Single base, porous	DPA 1.0%	Small grains, original size used
3B	Single base, porous	DPA 0.9%, Centralite I 0.5%	Small flakes, original size used
3C	Single base, porous	DPA 1.1%, Centralite I 0.5%	Small cylinders, original size used
3D	Single base, porous	Akardite II 1.0%	Small flakes, original size used

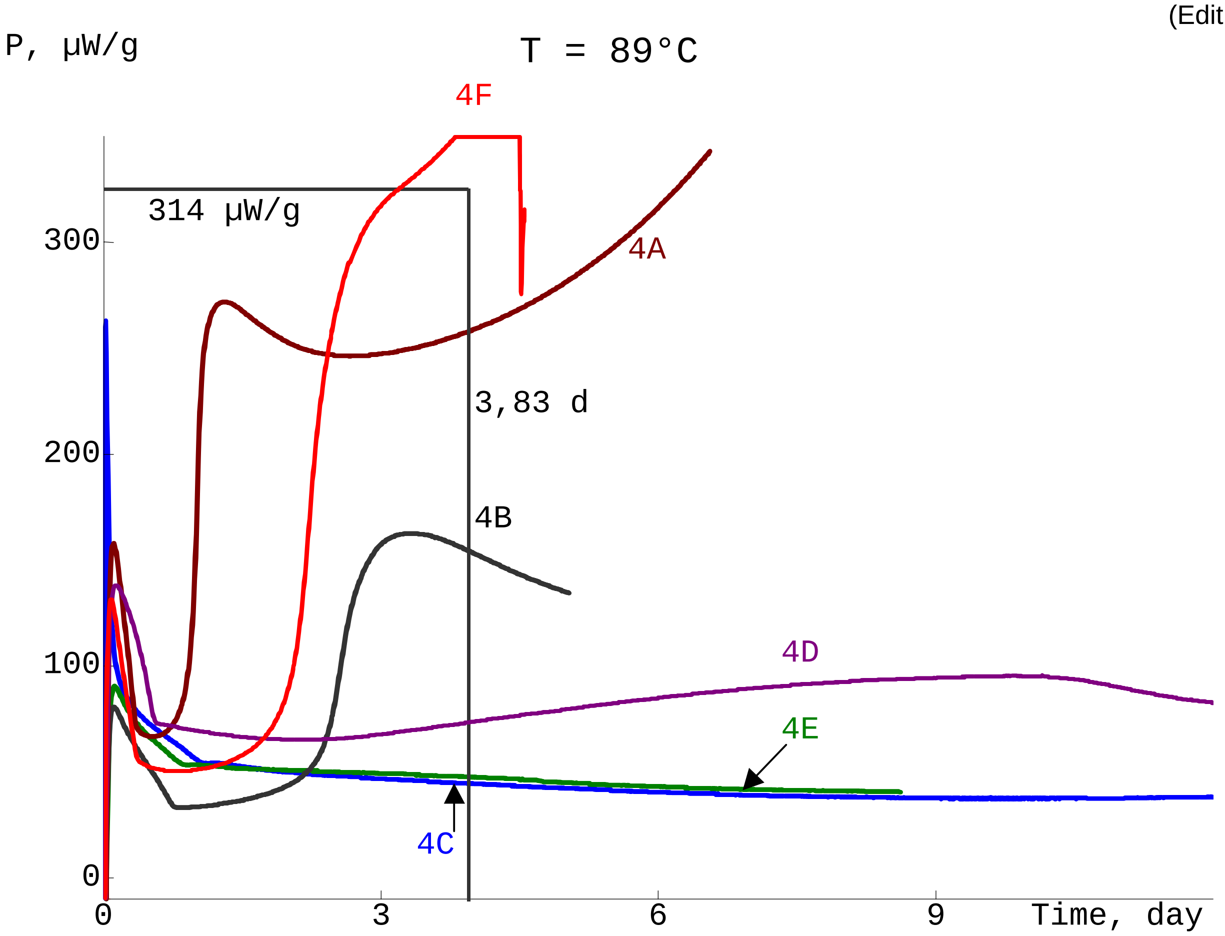

Figure E-4. Heat flow curves and evaluation of DB propellants

Propellant	Propellant type	Stabilizer content	Comments
4A	Double base, NG = 19%	DPA 0.9%	Ball propellant, original size used
4B	Double base, NG = 11%	DPA 0.8%, Centralite I 0.5%	19 hole propellant, original size used
4C	Double base, DEGN = 36%	Centralite 0.25%, Akardite II 0.45%	7 hole propellant, cut into smaller pieces
4D	Double base, NG = 33,5%	2-NDPA 1.7%	Rocket propellant. Cut into small cubes
4E	Double base, NG = 15%, DEGN = 25%	Akardite II 0.7%	Stick propellant, cut into small cylinders
4F	Double base, NG = 15%	DPA 1%, Centralite I 3%	Ball propellant, original size used, **sample fails criterion**

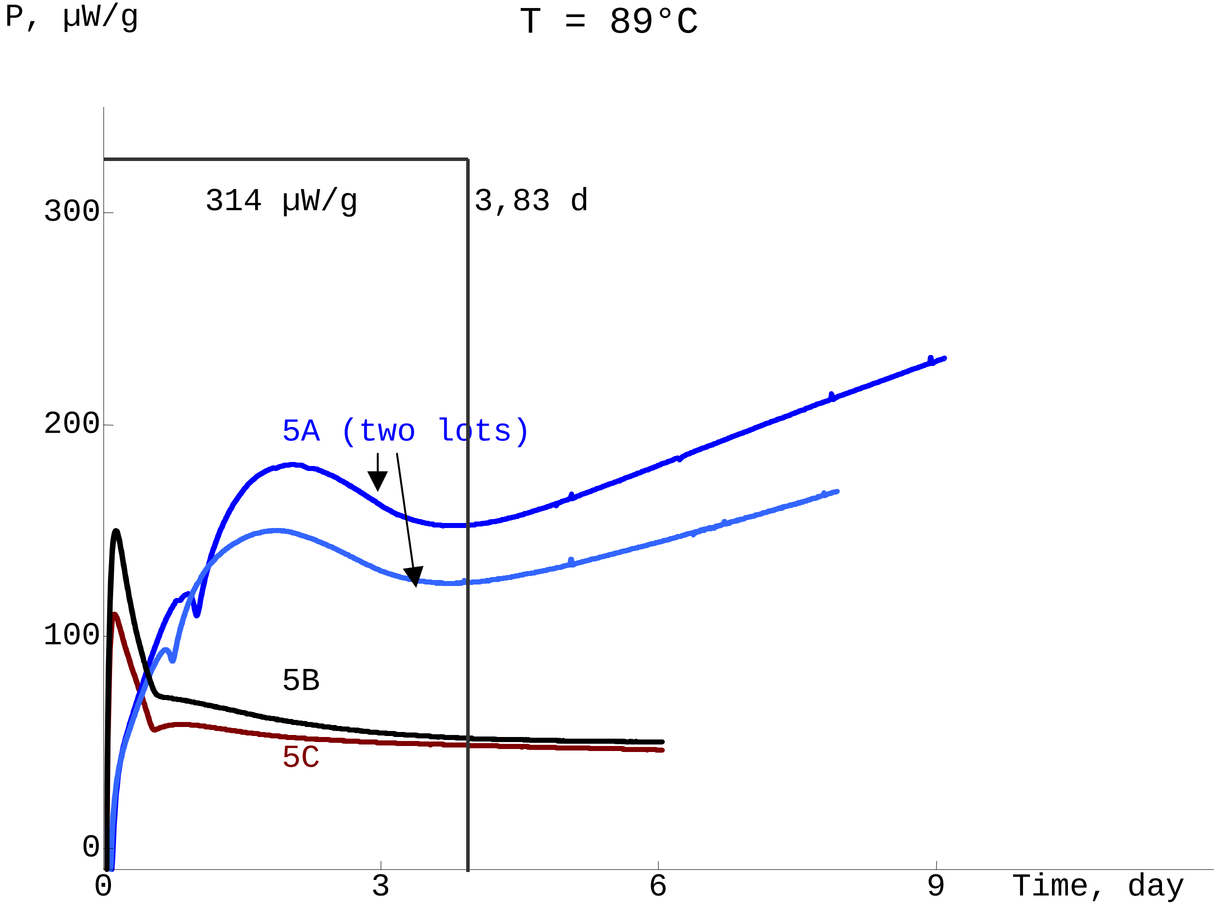

Figure E-5. Heat flow curves and evaluation of TB propellants

Propellant	Propellant type	Stabilizer content	Comments
5A	Triple base, NG = 19%, NQ = 55%	Centralite I 3.5%	One hole long sticks, cut into small cylinders
5B	Triple base, DEGN = 17%, NQ = 5%	Akardite II 0.9%	19 hole, original size used
5C	Triple base, DEGN = 17%, NQ = 5%	Akardite II 0.9%	Stick propellant, original size used