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STANAG 4026 JAIS (EDITION 3) – EXPLOSIVES, SPECIFICATION FOR NITROGUANIDINE (PICRITE)

References:

a. MAS(ARMY)(62)645, dated 25 September 1962
b. PFP(AC/326)D(2008)0001, dated 19 June 2008

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 references listed above are 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.

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Enclosure:
STANAG 4026 (Edition 3)

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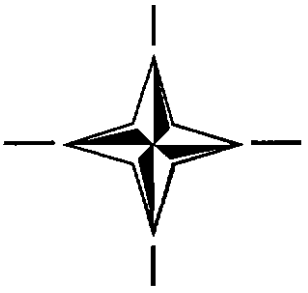
STANAG 4026
(Edition 3)

NORTH ATLANTIC TREATY ORGANIZATION (NATO)



NATO STANDARDIZATION AGENCY (NSA)

STANDARDIZATION AGREEMENT (STANAG)

SUBJECT: EXPLOSIVES, SPECIFICATION FOR NITROGUANIDINE (PICRITE)

Promulgated on 28 April 2009

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Director, NATO Standardization Agency

STANAG 4026
(Edition 3)

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 - Belgium.

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(Edition 3)

NATO STANDARDIZATION AGREEMENT
(STANAG)

EXPLOSIVES, SPECIFICATION FOR NITROGUANIDINE (PICRITE)

Annexes:

A. PHYSICAL AND CHEMICAL PROPERTIES
B. SAMPLE PREPARATION
C. TEST PROCEDURES

AIM

1. The aim of this agreement is to ensure that nitroguanidine shall possess properties which make it suitable for military use and to provide, within NATO, an acceptable basis for the procurement and certification of nitroguanidine.

AGREEMENT

2. Participating nations agree that nitroguanidine, proposed for military use, shall meet all the physical and chemical requirements of ANNEX A of this document. The test procedures used to verify the requirements of ANNEX A are in accordance with the sample preparation described in ANNEX B and test procedures described in ANNEX C.

GENERAL

3. Nitroguanidine is intended for use in gun propellants, high explosives and pyrotechnics.

MANUFACTURING PROCES

4. Any data or information concerning the proposed manufacturing process must be provided in confidence at the request of the purchaser. Any deviation from this accepted process must be noted and the product thus manufactured put aside until the purchaser has determined its approval or rejection.

DEFINITION OF LOT

5. For material manufactured by a continuous process, a lot is defined as the total quantity that is offered for acceptance at one time. For material manufactured by a batch process, a lot may be either the output of a single batch or a blend of several batches that have been combined to give a material of uniform properties throughout the lot.

SAMPLING

6. A representative sample is a sample of at least 200 g, taken at random from each lot by a sampling procedure which has been agreed by the purchaser.

REJECTION CRITERIA

7. Failure of a representative sample of nitroguanidine to meet the requirements specified in Annex A shall cause rejection of the lot of nitroguanidine from which the sample was taken.

WARNING: 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

8. This STANAG is considered implemented when a nation has issued the necessary orders and instructions putting the contents of this agreement into effect.

ANNEX A to
STANAG 4026
(Edition 3)

Physical and Chemical Properties

1. COMPOSITION

Nitroguanidine corresponds to the chemical formula $(NH_2)_2C=NNO_2$.
The following classes of nitroguanidine are specified:

Class a - specific surface between 12000 and 18000 cm^2/cm^3 or an average particle diameter between 3.3 and 5.0 μm

Class b - specific surface more than 18000 cm^2/cm^3 or an average particle diameter less than 3.3 μm

Specific requirements may demand particle sizes or specific surface to be different from class a and class b.

2. APPEARANCE

The material must be in the form of a white crystalline powder.
The processability of nitroguanidine in propellant, high explosive or pyrotechnic formulations is known to depend on its crystal shape (needles, spheres). No requirement for crystal shape can be given, but it is recommended to visually examine the crystal shape and provide crystal microphotographs.

3. REQUIREMENTS FOR PHYSICAL AND CHEMICAL PROPERTIES

a.	Purity	:	minimum 98.5%
b.	Volatile matter (applicable only if nitroguanidine is supplied dry)	:	maximum 0.25%
c.	Ash	:	maximum 0.30%
d.	Water insoluble and gritty particles	:	maximum 0.2%
e.	Gritty particles	:	
	on 0.25 mm aperture sieve	:	no more than 5 particles / 50 gram
	on 0.42 mm aperture sieve	:	no particles
f.	Acidity (as sulphuric acid)	:	maximum 0.06%
g.	Surface area (or average particle size)		
	class a	:	minimum 12,000 cm^2/cm^3 (or maximum 5.0 μm) maximum 18,000 cm^2/cm^3 (or minimum 3.3 μm)
	class b	:	minimum 18,001 cm^2/cm^3 (or maximum 3.3 μm)
	requirement different from class a and b	:	
h.	Sulphates (as sodium sulphate)	:	maximum 0.20%
i.	Chlorides (as sodium chloride)	:	maximum 0.10%
j.	Nitrates (as sodium nitrate)	:	maximum 0.20%
k.	Thermal stability	:	maximum 0.50 cm^3(STP)/gram (48 hours at 120 °C)

Sample preparation

It will be necessary to dry samples before testing if taken from a water wetted supply. The sample is dried in a thin layer in an oven at 60 °C for 8 hours.

Unmilled nitroguanidine
Rub the unmilled picrite gently through a 2 mm sieve into a receiver and transfer the sieved material to a 250 gram rubber-stoppered bottle. The sample is then treated in the same way as if it were milled.

Milled nitroguanidine
No preparation is required, test as received.

Test Procedures

WARNING: Adequate safety precautions shall be taken during the processing, testing, and handling of the nitroguanidine to protect personnel from accidents, fires, or explosions, and to limit damage to equipment and processing areas.

Procedure	Chapter
Purity by HPLC	1
Volatile matter	2
Ash	3
Water insoluble and gritty particles	4
Acidity	5
Surface area by BET	6
Visual inspection	7
Determination of chloride, sulphate and nitrate by ion chromatography	8
Thermal stability	9

Test Procedures
Chapter 1

Purity by HPLC

1.1 Apparatus

A high performance liquid chromatograph (HPLC) with a suitably-sized sample loop, a detection system equipped with a DAD (or UV) detector and an integrator or computerized data acquisition system

1.2 Reagents and materials

Analytical column, such as an Agilent Zorbax eclips C-18 column with 3.5 µm particle size, 4.6 mm inside diameter, and 150 mm length.
Acetonitrile (HPLC grade)
Water (HPLC grade)
Nitroguanidine calibration standard

The standard nitroguanidine has to be taken from normal supply (industrial manufacture), three-times recrystallized from hot HPLC grade water and subsequently dried to less than 0.05 % of volatiles. Its impurities visible in UV at 230 nm must not represent more than 0.5 % of total peak area (solvent peak excluded) on the HPLC chromatogram.

25 and 50 ml volumetric flask
1.0 ml volumetric pipette

1.3 Example HPLC conditions

Eluent:	60/40 acetonitrile/water
Flow rate:	0.8 ml/min
Injection volume:	10 µl
DAD wavelength:	sig = 265 nm, ref = 500 nm
DAD bandwidth:	sig = 10 nm, ref = 100 nm
Slit:	4 nm
Column oven:	30 °C

1.4 Sample preparation

Approximately 50 mg of the dry nitroguanidine sample are weighed to within 0.1 mg and added to a 50 ml volumetric flask. Add 20.00 ml of distilled water and directly add 20.00 ml of acetonitrile. Close the flask and place it in an ultrasonic bath until the nitroguanidine is completely dissolved and the solution is uniformly mixed. After dissolution let the flask cool down to room temperature and add acetonitrile to fill up this 50 ml volumetric flask. V_1 is the total volume of acetonitrile and distilled water. From this solution, 1.0 ml (V_2) is removed by pipette and diluted to 25 ml (V_3) with the eluent solution. This solution is used for injection on the column.
When internal standards are used, sample preparation and procedure have to be changed accordingly.

1.5 Procedure

The calibration of nitroguanidine in the HPLC chromatogram is performed by preparation of at least 3 calibration standards similar to the sample preparation described above. The calibration curve has to include the concentration of the sample to be tested. With the above example HPLC conditions and a typical DAD detector the maximum concentration is limited to 100 mg/l on the basis of spectral response.

The calibration curve is defined by

$$y = A * x + B$$

where
y: area of nitroguanidine peak in standard solution,
x: concentration of standard solution [mg/l],
A, B: constants, values calculated by linear regression.

The nitroguanidine sample is injected into the HPLC using a syringe and sampling loop of the appropriate volume. A blank analysis of the solvent is performed as well to verify absence of contamination from a previous analysis.

Calculate the peak areas obtained from the HPLC chromatogram for the sample using the data collection system (i.e. computer, computing integrator, etc). Perform three injections for each sample analyzed. Average the results of the three injections.

1.6 Reporting

Calculate the purity as follows:

$$purityNQ[\%] = 100 * \frac{(y_{NQ} - B) * V_1 * DF}{A * W}$$

where:

y_{NQ}	=	average peak area of nitroguanidine in the sample,
A,B	=	constants of the calibration curve,
V_1	=	solvent volume used to dissolve nitroguanidine [l],
DF	=	dilution factor equals the ratio V_3/V_2 [l/l],
W	=	weight of nitroguanidine [mg].

Test Procedures
Chapter 2

Volatile matter

2.1 Apparatus
Oven
Balance
Petri dish

2.2 Procedure
A sample of about 5 g is put on a tared petri dish and its weight is determined to the nearest 0.001 g. The petri dish with material is dried for two hours in an oven at 100 °C ± 2°C, and cooled down. The weight after drying is determined.

2.3 Reporting
Calculate the quantity of volatile matter as follows:

$$\text{Volatile matter [\%]} = 100 * \frac{(W_2 - W_1)}{W}$$

where:
W = weight of sample [g],
W_1 = weight of petri dish with sample after drying procedure [g],
W_2 = weight of petri dish with sample before drying procedure [g].

Test Procedures
Chapter 3

Ash

3.1 Apparatus

Evaporating dish, 90 mm silica or chemical porcelain
Steam bath in a well-ventilated hood
Muffle furnace
Desiccator containing an indicating desiccant

3.2 Reagents

Nitric acid, 65-percent solution, Analytical Reagant

3.3 Procedure

The specimen shall consist of approximately 5 g of picrite, weighed to within 0.2 mg.
Place the specimen in a tared evaporating dish that has been previously ignited and cooled. Add 10 – 15 ml of the 65 percent nitric acid solution, and place the evaporating dish on the steam bath until the specimen is disintegrated, and no liquid remains. Ignite the dish and the contents, heating it gently at first until fumes are no longer evolved, then heating it in the muffle furnace (or over a gas flame) at 500 to 700 °C for 2 hours. Cool the dish and contents to room temperature in the dessicator, and weigh.

3.4 Reporting

Percent ash:

$$\text{Ash [\%]} = 100 * \frac{W_2}{W_1}$$

where:
W_1 = sample weight [g],
W_2 = residue weight [g].

Test Procedures
Chapter 4

Water insoluble and gritty particles

4.1 Apparatus
Oven
Tared sintered glass crucible with medium porosity
Sieves with 0.25 and 0.42 mm aperture

4.2 Materials
Distilled water

4.3 Procedure
Weigh approximately 50 g of material to the nearest 0.01 g (W) and dissolve the sample in 2 l of boiling distilled water. Filter all the solution, through a tared sintered glass crucible (W_1) with medium porosity, and transfer the insoluble matter wholly to the crucible. Dry the crucible with insoluble residue for 1 hour in an oven at 110 °C. Cool the crucible in a desiccator, then weigh the crucible to the nearest 0.001 g (W_2).

Brush all particles retained on the crucible on a 0.25 mm aperture sieve, count and examine any that are retained. Gritty particles are indicated by lack of uniformity of the material and the persistence of scratching noise when the material is pressed and rubbed on a smooth glass slide with a smooth steel spatula. From the 0.25 mm sieve, the particles are brushed on a 0.42 mm aperture sieve. The particles retained on the sieve are again counted and examined for their gritty character.

4.4 Reporting
Calculate the quantity of water insoluble matter as follows:

$$\text{Water insoluble [\%]} = 100 * \frac{(W_2 - W_1)}{W}$$

where:
W = weight of sample [g],
W_1 = weight of empty tared crucible [g],
W_2 = weight crucible with water insoluble matter [g].

Report the quantity of water insoluble matter and the number of gritty particles retained on the 0.25 mm and 0.42 mm aperture sieve.

Test Procedures
Chapter 5

Acidity

5.1 Apparatus

Balance
Erlenmeyer flask, 500 ml
Graduated cylinder, 250 ml
Semi-microburette

5.2 Reagents

Distilled water
Methyl red / methylene blue indicator
Ethyl alcohol
0.05 N Sodium hydroxide standardized before use

5.3 Procedure

Weigh a 10 g sample of nitroguanidine (w) to the nearest 0.01 g and place it in a 500 ml Erlenmeyer flask.
Add 200 ml of distilled water measured in a 250 ml graduated cylinder. This water must be freshly boiled and at a temperature of 80 °C. Keep the whole content of the flask at 80 °C until the picrite (nitroguanidine) is completely dissolved. Leave to cool at room temperature (approximately 20 °C).
Add 8 to 10 drops of methyl red / methylene blue indicator (0.1 g of methyl red and 0.03 g of methylene blue in 100 ml of 95% ethyl alcohol) and titrate at once, without filtering, using 0.05 N sodium hydroxide. For this purpose use a 5 ml semi-microburette graduated in 1/50 ml, 1 ml corresponding to a length of 70 to 80 mm. Add the 0.05 N sodium hydroxide solution drop by drop to the flask, shaking until the indicator end-point is reached. Note the volume V_1 of solution used.
Carry out a blank test simultaneously under identical conditions to those of the actual determination. For this purpose, place in a 500 ml Erlenmeyer flask 200 ml of freshly boiled distilled water and 8 to 10 drops of methyl red / methylene blue indicator. Titrate with 0.05 N sodium hydroxide solution. Note the volume V_2 of solution used.

5.4 Reporting

The acidity of the nitroguanidine expressed as percentage of sulphuric acid is given by:

$$\text{Acidity (as sulphuric acid) [\%]} = 100 * \frac{(V_1 - V_2) * N_{NaOH} * 98.08}{1000 * w * 2}$$

where:

V_1	=	volume of NaOH solution needed to reach end-point titration of nitroguanidine [ml],
V_2	=	volume of NaOH solution needed to reach end-point titration of distilled water (blank determination) [ml],
N_{naOH}	=	normality of sodium hydroxide solution [mol/l],
98.08	=	molecular weight of sulphuric acid [g/mol],
1000	=	conversion factor from liter to milliliter,
w	=	weight of nitroguanidine sample [g],
2	=	correction of normality for sulphuric acid vs. sodium hydroxide solution.

Test Procedures
Chapter 6

Surface area by BET

6.1 Apparatus
Nitrogen adsorption instrument
Balance

6.2 Reagents
Liquid nitrogen
Nitrogen gas
Helium gas

6.3 Procedure
Nitroguanidine must be dried in a vacuum oven at around 70 °C for 24 hours prior to analysis.
A clean, dry, and closed sample tube is weighed accurately. A sample of the dried nitroguanidine is introduced into this tube. The sample size depends on the specific adsorption instrument; a typical sample size is 1 – 5 gram. The sample is outgassed according to the Instruction Manual of the specific nitrogen adsorption instrument for 30 minutes at 120 °C. The tube with the outgassed sample is closed and weighed accurately. The weight of the outgassed nitroguanidine sample is calculated.

The nitrogen adsorption is measured at a temperature of 77 K. The procedures in the Instruction Manual of the specific nitrogen adsorption instrument shall be followed. Whenever the sample weight is asked for, the weight of the outgassed sample must be entered. At least 5 data points shall be measured at relative pressures between 0.05 and 0.15.
The nitrogen adsorption is measured in duplicate (on 2 separate samples).

6.4 Calculations and Reporting
The specific surface area is calculated from the measured adsorption data, applying the multipoint B.E.T. method (at least 5 data points at relative pressures in the range 0.05 – 0.15) and assuming a molecular area of adsorbed nitrogen of 0.162 nm^2.
When the instrument reports the B.E.T. surface area in square meters per gram of sample, this result is recalculated in square centimetres per cubic centimetre by the formula:

$$BET_{cm3} = BET_g \times 10000 \times \rho$$

where:

BET_{cm3} = B.E.T. surface area in [cm^2/cm^3],
BET_g = B.E.T. surface area in [m^2/g],
10000 = conversion factor in [cm^2/m^2],
ρ = 1.77, the density of nitroguanidine in [g/cm^3].

Test Procedures
Chapter 7

Visual inspection

7.1 Apparatus
(optical microscope)

7.2 Materials
Sheet of glazed paper

7.3 Procedure
Transfer the sample to a sheet of glazed paper and examine the nitroguanidine for the presence of visible foreign matter or other abnormal features. If available for a more detailed inspection, light microscopy may be used.

7.4 Reporting
The crystal shape has to be reported, preferably with a microphotograph of a representative sample.

Test Procedures
Chapter 8

Determination of chloride, sulphate and nitrate by ion chromatography

8.1 A quantitative analysis of anions can be performed simultaneously by ion chromatography using conductivity as method of detection.
Other methods (e.g. ion-pair chromatography, capillary electrophoresis, direct potentiometry or titration with ion selective electrodes) can be used if they show equivalent precision.

8.2 Apparatus
Analytical balance
Ion chromatograph
Column: IonPac AS 4A or comparable
Suppressor: AMMS-II or comparable
Detector: Conductimeter or comparable

8.3 Reagents and materials
Deionised water
Chloride standard solution of 1000 mg/l
Sulphate standard solution of 1000 mg/l
Nitrate standard solution of 1000 mg/l
Volumetric flasks of 100 ml
Pipettes: 0.1 - 10 ml

8.4 Example ion chromatography conditions

Eluent:	2.2 mM Na_2CO_3 and 0.75 mM $NaHCO_3$
Flow rate:	2 ml/min
Injection volume:	50 µl

8.5 Working standard solutions
Prepare a series of working standards by taking 0, 0.10, 0.25, 0.50, 0.75 and 1.0 ml of each standard solution and dilute each to 100 ml in a series of volumetric flasks. These solutions are equivalent to 0.0, 1.0, 2.5, 5.0, 7.5 and 10.0 mg/l of chloride, sulphate and nitrate respectively.

8.6 Sample preparation
Weigh 0.300 $\pm$ 0.001 g of nitroguanidine and dissolve the sample in approximately 50 ml of warm deionised water and dilute to 100 ml in a volumetric flask with deionised water. The solution with the dissolved anions is used for injection on the column.

8.7 Procedure
Set the optimum conditions for the ion chromatograph being used. Measure the conductivity changes due to the samples and standards and determine the retention times of each anion. By measuring the peak height of each standard solution, prepare a calibration graph for each anion. Determine the concentration of each anion in the sample by reference to the appropriate calibration graph. Carry out a blank determination on the deionised water.

8.8 Reporting
The software of the chromatograph compares the peak height of the anionic standard with the peak height of the sample.
Calculate the content of sodium chloride, sodium sulphate and sodium nitrate as follows:

$$C[\%] = y_{anion} * \frac{V}{W} * \frac{M_{Na-anion}}{M_{anion}} * \frac{1}{10000}$$

where:
C = concentration of the sodium anion in the sample [% *m/m*],
y_{anion} = concentration of the anion in the sample [mg/l],
V = volume of the sample solution [ml],

W = weight of nitro guanidine [g],
10000 = conversion factor,
$M_{Na\text{-}anion}$ = mol mass of sodium anion
NaCl = 58.45 g/mol
Na_2SO_4 = 142.06 g/mol
$NaNO_3$ = 85.01 g/mol
M_{anion} = mol mass of anion
Cl = 35.45 g/mol
SO_4 = 96.07 g/mol
NO_3 = 62.01 g/mol.

Test Procedures
Chapter 9

Thermal stability

9.1 The thermal stability of nitroguanidine shall be assessed in accordance with NATO STANAG 4556 Explosives: Vacuum Stability Test. The following conditions are specific to the thermal stability determination of nitroguanidine: the sample weight is 5 g, the test temperature is 120 °C and the test duration is 48 hours. The test shall be carried out at least in duplicate.

9.2 Reporting
The thermal stability assessed in accordance with STANAG 4556 will be reported as the mean volume of gas evolved, at standard volume and pressure, per unit weight of sample, i.e. in cm^3(STP)/gram.