NATO STANDARD

AOP-4700

ENERGETIC MATERIALS, SPECIFICATIONS FOR GUDN (GUANYLUREA DINITRAMIDE)

Edition A Version 1

NOVEMBER 2016

NORTH ATLANTIC TREATY ORGANIZATION

ALLIED ORDNANCE PUBLICATION

Published by the
NATO STANDARDIZATION OFFICE (NSO)

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NORTH ATLANTIC TREATY ORGANIZATION (NATO)

NATO STANDARDIZATION OFFICE (NSO)

NATO LETTER OF PROMULGATION

29 November 2016

1. The enclosed Allied Ordnance Publication AOP-4700, Edition A, Version 1, ENERGETIC MATERIALS, SPECIFICATION FOR GUDN (GUANYLUREA DINITRAMIDE), which has been approved by the nations in the CNAD AMMUNITION SAFETY GROUP (AC/326), is promulgated herewith. The agreement of nations to use this publication is recorded in STANAG 4700.

2. AOP-4700 Edition A, Version 1 is effective upon receipt.

3.

4. This publication shall be handled in accordance with C-M (2002)60.

Edvardas MAŽEIKIS
Major General, LTUAF
Director, NATO Standardization Office

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RECORD OF RESERVATIONS

CHAPTER	RECORD OF RESERVATION BY NATIONS

Note: The reservations listed on this page include only those that were recorded at time of promulgation and may not be complete. Refer to the NATO Standardization Document Database for the complete list of existing reservations.

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RECORD OF SPECIFIC RESERVATIONS

[nation]	[detail of reservation]

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TABLE OF CONTENTS

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CHAPTER 1 INTRODUCTION

1.1. CHEMICAL REQUIREMENTS AND TEST PROCEDURES FOR GUDN (Guanylurea Dinitramide).

1.1.1 The aim of this agreement is to establish common chemical requirements and test procedures for GUDN.

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ANNEX A Specification for GUDN (Guanylurea Dinitramide)

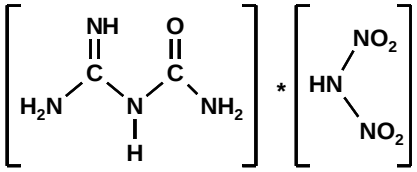
Table with specification for GUDN

Properties	Specification	Procedure
GUDN content	min 98%	B-1
Nitrate content	max 0.1%	B-2
Volatile matter	max 0.1%	B-3
Acidity	pH value of a 0.2% solution >4.0	B-4
Insoluble matter in DMSO	<0.03%	B-5
Gritty matter :		B-6
On sieve US 40 (0.425 mm)	Nil	
On sieve US 60 (0.250 mm)	max 1 piece/10 g	
Peak decomposition temperature by DSC	min 210°C	B-7
Vacuum thermal stability 120°C, 40 h	max 1.5 ml/g	B-8

Abbreviations

Abbreviation	
GUDN or FOX-12	Guanylurea dinitramide

Structural formula of GUDN : The compound is also named FOX-12



ANNEX A TO
AOP-4700

Safety requirements for GUDN

Refer to the information given in the safety data sheet and national regulations for each of the components used throughout this AOP.

ANNEX B Test procedures

CONTENTS OF ANNEX B

1. GUDN content

1.1 Principle

The GUDN sample is dissolved in distilled water. The purity of GUDN is calculated based on the dinitramide content. In this protocol, a calibration curve is used. Alternatively an internal standard consisting of e.g. benzoic acid can be used.

1.2 Chemicals

Acetonitrile (CH_3CN), HPLC grade
Lithium hydroxide (suprapure)
Ammonia solution 25-30%
Distilled water
Ammonium dinitramide (ADN), >99%

Crude ADN can be purified by fractional crystallization from 2-propanol, preferably by evaporation. The second fraction should be >99%. The ADN crystals are separated by filtration and dried at 40°C.
Dissolve 40 g crude ADN in 180 g 2-propanol (IPA) at 50°C. Cool to room temperature stirring the mixture. Separate crystallized ADN saving the mother liquid. (Separated ADN at this stage could be used for future purifications.) Evaporate approximately 100 g IPA of the mother liquid or to half its original volume stirring. Separate the ADN crystals, wash with a little IPA followed by

pure ethyl acetate. Dry the ADN crystals until constant weight. The yield should be approximately 10 g purity >99%.

1.3 Apparatus

HPLC system with variable UV detector
Anion column 4.6 x 50 mm

1.4 Instrument setup

Flow rate: 1.8 ml/min (equipment dependent)
Detector: 214 nm for nitrate and 284 nm for dinitramide ion
Injection: 10 μL
Mobile phase: LiOH 3 mM (H_2O)/CH_3CN 80/20

1.5 Preparation of references

Dinitramide reference: Weigh in 0.12 g ADN (with 0.1 mg accuracy) to a 100 ml volumetric flask. Add 5 ml of ammonia solution (for stabilizing the ADN) and fill to the mark with distilled water. Dilute 2 ml of the dinitramide solution to 100 ml (50 times), alternative 0.2 ml to 10 ml, using automatic pipette. This solution contains about 20 mg dinitramide/L and 0.03 vol% ammonia.

1.6 Sample preparation

Dissolve 0.05 g GUDN in 25 ml water. Let the sample solution stand in an ultrasound bath for about 1 h until all GUDN is completely dissolved. Dilute 2 ml of the dinitramide solution to 100 ml (50 times), alternative 0.2 ml to 10 ml, using automatic pipette.

1.7 HPLC analysis

Inject the reference solutions and the sample solution several times and calculate the percentage content of dinitramide and GUDN according to the formulas below.

1.8 Calculations

$$Dinitramide(\%) = \frac{C(r) \times A(s) \times V(s) \times D \times 100}{A(r) \times W \times 10^6}$$

Where *C(r) = concentration of dinitramide in reference solution in mg/l*
A(s) = area of dinitramide in the sample solution
V(s) = volume of the sample solution before dilution in ml
D = dilution factor
A(r) = area of dinitramide in the reference solution
W = sample amount in gram

$$GUDN(\%) = \frac{dinitramide(\%) \times Mw(GUDN)}{Mw(dinitramide)}$$

Where *Mw(GUDN) = molecular weight of GUDN, 209 g/mole*
Mw(dinitramide) = molecular weight of dinitramide, 106 g/mole

2. Nitrate Content

2.1 Principle

The nitrate content in GUDN is determined by liquid chromatography. In this protocol, a calibration curve is used. Alternatively an internal standard consisting of e.g. benzoic acid can be used.

2.2 Chemicals

Acetonitrile (CH_3CN), HPLC grade
Lithium hydroxide (suprapure)
Ammonia solution 25-30%
Distilled water
Sodium nitrate PA grade

2.3 Apparatus

HPLC system with variable UV detector
Anion column 4.6 x 50 mm

2.4 Instrument setup

Flow rate:	1.8 ml/min (equipment dependent)
Detector:	214 nm for nitrate
Injection:	10 μL
Mobile phase:	LiOH 3 mM (H_2O)/CH_3CN 80/20

2.5 Preparation of references

Nitrate reference: Dissolve 0.14 g of dry $NaNO_3$ (with 0.001 g accuracy) in 100 ml distilled water. This solution contains about 1000 mg/l nitrate.
By further dilution in water, prepare standards that bracket the expected concentration of nitrate in the sample.

2.6 Sample preparation

Dissolve 0.05 g GUDN in 25 ml water. Let the sample solution stand in an ultrasound bath for about 1 h until all GUDN is completely dissolved. Dilute 2 ml of the dinitramide solution to 100 ml (50 times), alternative 0.2 ml to 10 ml,

using automatic pipette. Another suitable dilution grade can be acceptable depending on the response from the actual detector.

2.7 HPLC analysis

Inject the reference solutions and the sample solution several times and calculate the percentage content of nitrate according to the formula below.

2.8 Calculations

$$Nitrate(\%) = \frac{C(r) \times A(s) \times V(s) \times D \times 100}{A(r) \times W \times 10^6}$$

Where *C(r) = concentration of nitrate in reference solution in mg/l*
A(s) = area of nitrate in the sample solution
V(s) = volume of the sample solution before dilution in ml
D = dilution factor
A(r) = area of nitrate in the reference solution
W = sample amount in gram

3. Volatile Matter

3.2 Principle

The moisture is determined gravimetrically. Karl Fisher is not applicable due to difficulties to dissolve GUDN in appropriate solvents and reagents.

3.3 Apparatus

Glass weighing bottle, 35 x 60 mm (H x D)
Drying oven, 110±1°C

3.4 Procedure

Into a tared weighing bottle, weigh approximately 4 g sample (m1) to an accuracy of 0.1 mg. Tare the balance and weigh the bottle with sample (m2). Place the bottle with sample in the oven for 2 hours. Let the bottle cool down in a desiccator for at least 20 min. Weigh the bottle with sample (m3) and calculate the percentage volatile matter according to the following formula :

$$Volatile\ matter(\%) = \frac{(m2 - m3) \times 100}{m1}$$

where *m1 = weight of the sample in gram*
m2 = weight of the bottle and sample before drying in gram
m3 = weight of the bottle and sample after drying in gram

4. Acidity

pH value of a 0.2% solution

4.1 Principle

The acidity of GUDN is determined by measuring the pH value of a 0.2% solution. (A pH value <4.0 corresponds to an acid content >0.005% H_2SO4). Acid-base titration is not recommended as a method since GUDN as an acid in itself would interfere with the titration of acidic impurities.

4.2 pH meter with pH electrode with a 2-decimal resolution.

4.3 Procedure

Weigh 0.10 g of a GUDN sample into a 50 ml volumetric flask and fill up to the mark with previously boiled and cooled distilled water. Let the flask with sample stand in an ultrasound bath until all GUDN is dissolved.

Transfer about 20 ml to a glass beaker and add a magnetic stirrer. Start the stirrer and measure the pH value with a calibrated pH meter.
Report the result with 1 decimal.

5. Insoluble matter in DMSO

5.1 Principle

Insoluble matter is determined by dissolving GUDN in dimethyl sulfoxide and filtering the solution through a glass filter crucible. The insoluble matter on the glass filter crucible is dried and weighed.

5.2 Apparatus

Glass filter crucible, porosity G3 (10-20 micron)
Vacuum filtering equipment suitable for the glass filter crucible
Water bath
Beaker
Oven at 105°C
Desiccator

5.3 Chemicals

Dimethyl sulfoxide, PA grade
Acetone, technical grade

5.4 Procedure

Weigh 10 g GUDN (to an accuracy of 0.01 g) in a beaker and add 20 ml dimethyl sulfoxide. Heat the solution on a water bath until all GUDN is dissolved in the dimethyl sulfoxide. Weigh accurately an empty glass filter crucible and connect it to the filtering equipment. Filter the solution through the funnel. Rinse the beaker with hot dimethyl sulfoxide and pour it through the filter. Wash the residue on the filter with acetone. Dry the crucible in the oven until constant weight is obtained. Cool the crucible in a desiccator and weigh it to an accuracy of 0.1 mg.

5.5 Calculation

$$Insoluble\ matter\ in\ DMSO(\%) = \frac{(W2 - W1) \times 100}{W}$$

Where W1 = weight of the empty filter crucible in gram
W2 = weight of the filter crucible with residue in gram
W = sample weight in gram

6. Gritty matter

6.1 Principle

The gritty matter is determined by dissolving GUDN in dimethyl sulfoxide and filtering the solution through sieves. The number of gritty particles is then determined.

6.2 Apparatus

US sieve no. 40 (0.425 mm) and US no. 60 (0.250 mm), 3-inch diameter water bath, beaker or erlenmeyer-flask, oven at 105°C

6.3 Chemicals

Dimethyl sulfoxide, PA grade
Acetone, technical grade

6.4 Procedure

Weigh 10±0.1 g GUDN in a beaker and add 20 ml dimethyl sulfoxide. Heat the solution on a water bath until all GUDN is dissolved in the dimethyl sulfoxide. Connect the US sieve 40 to sieve 60 and pour the solution through the sieves. Rinse the beaker with hot dimethyl sulfoxide and pour it through the sieves. Wash the residue on the sieves with acetone. Dry the sieves in the oven. The number of particles on the sieves is then determined.

7. Peak decomposition temperature

Differential Scanning Calorimetry

7.1 Principle

Decomposition of explosives often leads to strong exothermal reaction. In this method, GUDN is analysed with Differential Scanning Calorimetry (DSC) to measure the decomposition temperature.

7.2 Apparatus

Differential Scanning Calorimeter
Crimping press
Tool for levelling phial base
Mortar
Sealed capsule of inert materials to GUDN
Nitrogen gas

7.3 Sample preparation:

If the sample is not finely grained, it shall be ground as follows:
Transfer about 100 mg sample to a small agate mortar and carefully crush the crystals. Grind the sample carefully with the mortar pestle until it becomes finely grained.

Weigh 1.0 - 1.2 mg GUDN, to an accuracy of 0.1 mg, in a capsule so that the GUDN is evenly distributed in the capsule. Seal the capsule using the associated equipment.

7.4 Instrument setup

Scan speed:	10°C / min. (Temperature increase °C / min.)
Start temperature:	30°C
Final temperature:	400°C
Gas pressure:	2.0 bar
Plot:	30 - 400°C

See associated manual for more detailed information regarding the use of the instrument.

7.5 Measurement procedure:

When the instrument is ready, run the sequence from 30°C to 400°C.

When the measurement is complete, use the thermograph to evaluate the decomposition temperature.

7.6 Calculation

Find the strongest exothermal peak and evaluate the onset point (T_i) for the exothermal peak using the guidelines from STANAG 4515. Report the onset temperature as the decomposition temperature for the sample. Evaluation can normally be performed using the software running the DSC.

8. Vacuum thermal stability

8.1 Definition

The vacuum stability test is used to assess the thermal stability of an explosive by measuring the volume of gas evolved on heating the explosive under specified conditions. This method is based on STANAG 4556 where a test temperature of 120°C and a duration of 40 hours are used.

8.2 Test Apparatus

Equipment that fulfils the STANAG 4556, transducer method procedure 2A.
Metal thermostatic bath 120±0.5°C
Vacuum pump with capacity <10 mbar

8.3 Sample Preparation

The sample shall be dried at 110°C for 2 hours. Weigh 5.0±0.01 g of the dried sample and transfer it to the glass tube using a powder funnel. A minimum of two tests shall be conducted on each material to be tested

8.4 Procedure

Connect the glass tube to the test equipment. Evacuate the equipment until the pressure is below 6.7 mbar. Let the equipment stabilize for a minimum of 30 minutes. Check the pressure regularly during this time to be sure that the equipment does not leak. Register the start pressure and the temperature near the glass tube and put the glass tube into the bath. After 40 hours, remove the glass tube from the bath and let the equipment cool down for a minimum of 30 minutes. Register the final pressure and temperature.

8.5 Calculation

Calculate the volume of gas V (at 273 K and 1.013 bar) liberated during the test, as follows:

$$V = \left[V_c + V_t - \frac{m}{d} \right] x \left[\frac{P_2 x 273}{273 + t_2} - \frac{P_1 x 273}{273 + t_1} \right] x \frac{1}{1.013}$$

Where:
V = volume of gas liberated from the sample (in cm^3, at STP)
V_c = volume of the transducer and adapter (in cm^3)
V_t = volume of the heating tube (in cm^3)
m = mass of the sample (in g)
d = density of the sample (in g/cm^3), for GUDN the density is 1.76 g/cm^3
P_1 = calculated pressure at the beginning of the test (in bar)
P_2 = calculated pressure at the end of the test (in bar)
t_1 = room temperature at the beginning of the test (in °C)
t_2 = room temperature at the end of the test (in °C)

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