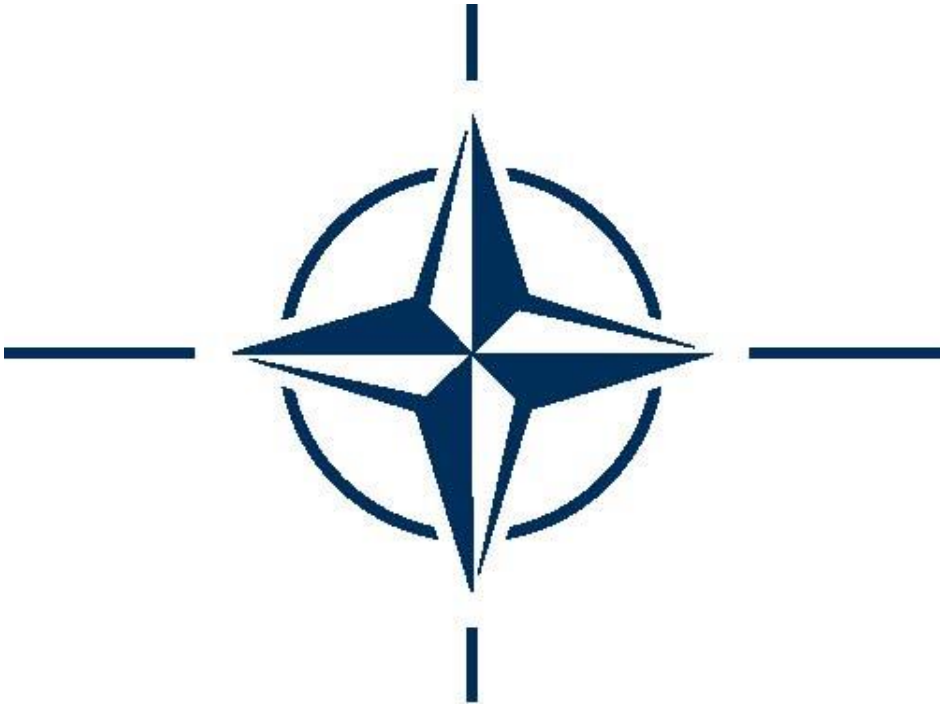
NATO STANDARD

AOP-4543

ENERGETIC MATERIAL, SPECIFICATION FOR NTO [3-NITRO-1,2,4-TRIAZOL-5-ONE]

Edition A, Version 1

MARCH 2023



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NATO LETTER OF PROMULGATION

10 March 2023

1. The enclosed Allied Ordnance Publication AOP-4543, Edition A, Version 1, ENERGETIC MATERIAL, SPECIFICATION FOR NTO [3-NITRO-1,2,4-TRIAZOL-5-ONE, which has been approved by the nations in the CNAD AMMUNITION SAFETY GROUP (CASG - AC/326), is promulgated herewith. The agreement of nations to use this publication is recorded in STANAG 4543.

2. AOP-4543, Edition A, Version 1, is effective upon receipt.

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

Dimitrios SIGOULAKIS
Lieutenant General, GRC (A)
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

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TABLE OF CONTENTS

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CHAPTER 1 INTRODUCTION

1.1. AIM

The aim of this agreement is to ensure that 3-nitro-1,2,4-triazol-5-one (NTO) shall possess properties which make it suitable for military use and to provide, within NATO, an acceptable basis for the procurement and certification of NTO.

1.2. AGREEMENT

Participating nations agree that NTO, proposed for military use, shall meet all the physical and chemical requirements of ANNEX A, Table 1 of this document. The test procedures used to verify the requirements of ANNEX A, Table 1 are described in ANNEX B and the rejection criteria shall be in accordance with ANNEX B, Paragraph 1.2 of this document.

1.3. USE

NTO is intended for use in secondary explosive main fill and booster formulations as well as gun propellants.

1.4. IMPLEMENTATION

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

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ANNEX A REQUIREMENTS FOR NTO

A.1. SPECIFICATION FOR NTO

The requirements for the physical and chemical properties for NTO shall be as specified in Table A-1. Testing Procedures are given as ANNEX B of this document.

Property	Specification	Procedure
Appearance	White to yellow-white	
Decomposition Temperature by DSC		B-2
3°C/min	Min. 271 °C	B-2
5°C/min	Min. 277 °C	B-2
10°C/min	Min. 281 °C	B-2
NTO Purity	(1) ≥99% NTO by HPLC or	B-3
	(2) ≥99% NTO, by potentiometric method	B-4
Chlorine (as Chloride)	≤0.02%	B-5
Nitric Acid	≤ 0.05%	B-6
Volatile Substances	≤0.1%	B-7
Particle Size Distribution	Manufacturer will provide data and documentation of method used	

Table A-1. Specification for NTO.

Compound	Abbreviation
3-nitro-1,2,4-triazol-5-one	NTO

Table A-2. Abbreviation of compounds.

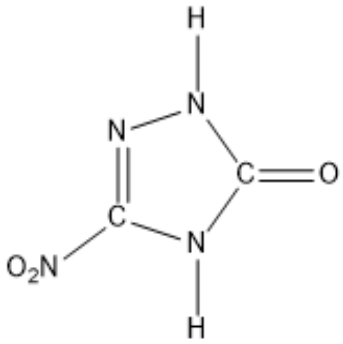

Figure A-1. Structural formula of NTO.

A.2. SAFETY REQUIREMENTS

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

B.1. SAMPLING AND REJECTION

B.1.1. Sampling

A lot of NTO shall consist of the quantity of material produced in a single batch; or when manufactured by a continuous process, a lot shall consist of the total quantity offered for the acceptance at one time. A minimum of two (2) representative samples of at least 200 grams each shall be taken from each container (e.g., drum or bag) of NTO by a sampling procedure which has been agreed upon by the purchasing authority. It will be necessary to dry samples before testing if the NTO was shipped wet.

B.1.2. Rejection Criteria

Failure of either of the samples will result in rejection of a container of NTO. If more than 30% of the samples from any given lot do not satisfy the requirements of this document, the entire lot will be rejected.

B.2. DETERMINATION OF DECOMPOSITION TEMPERATURE

B.2.1. Definition

The temperature at which the solid material chemically breaks down into simpler compounds at atmospheric pressure as determined by differential scanning calorimetery (DSC). This decomposition temperature is reported along with the heating rate.

B.2.2. Sample Preparation

A sample weight of between 0.5 and 1.0 milligram shall be used. The sample shall be prepared in accordance with the procedures detailed in the instruction manual of the specific DSC instrument used.

B.2.3. Test Procedure and Results

The sample shall be run in a nitrogen atmosphere in a sealed pan vented with a pin hole. The start temperature will be 50^{o}C and the stop temperature will be 300^{o}C with a heating rate no greater than 10^{o}C per minute. In Table A-1, temperatures have been provided for heating rates of 3, 5, and 10^{o}C per minute. The operation, analysis, and calculational procedures of the DSC instrument shall be followed for maximum

accuracy and precise measurement of the DSC curve. The peak exotherm temperature shall be reported as the decomposition temperature.

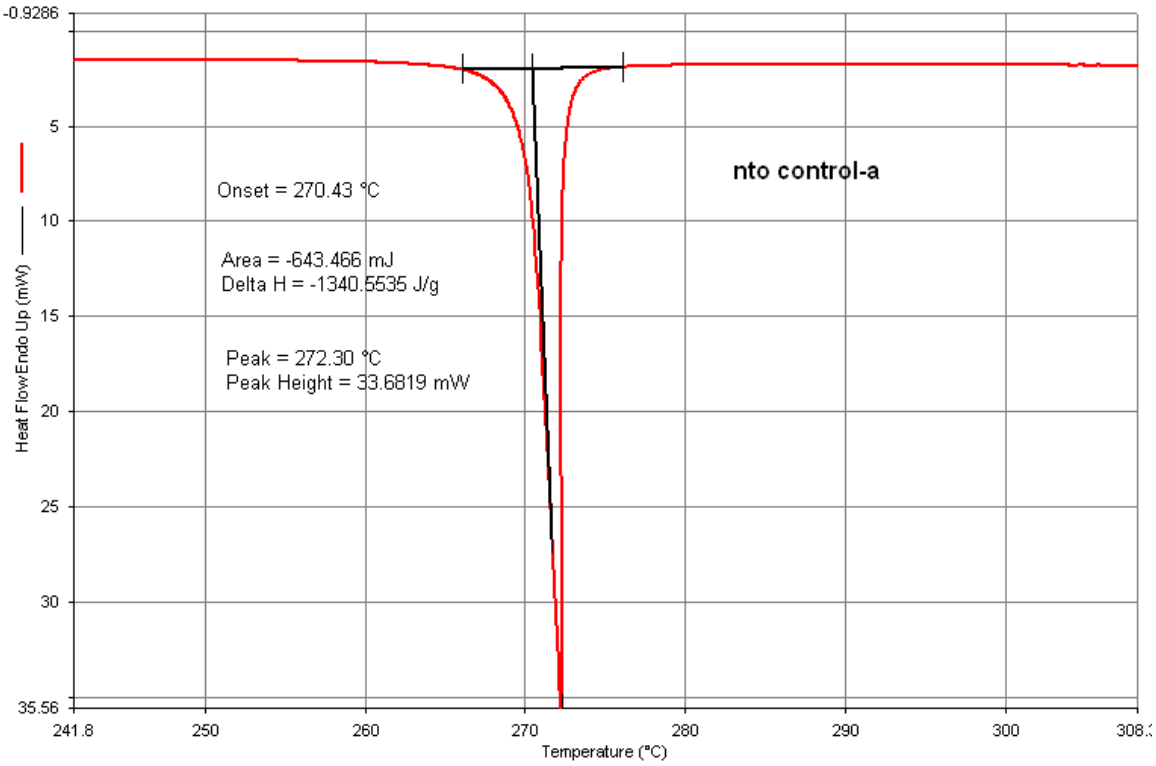

Figure B-1. Representative DSC Data for the Decomposition of NTO at 5°C/min

B.3. DETERMINATION OF NTO PURITY VIA HPLC ANALYSIS

B.3.1. Principle

NTO purity shall be measured by either High Performance Liquid Chromatograph (HPLC) analysis or a potentiometric technique. The HPLC method shall be performed to determine the NTO concentration in a sample from its peak area. The total NTO concentration will be be reported as a single value of weight percent.

B.3.2. Test Description

HPLC shall be used to analyze injections of standardized solutions of pure NTO in order to create a calibration table. This table will be used to determine the purity of a sample of NTO based on the observed peaks.

B.3.3. Sample Preparation for HPLC Analysis

B.3.3.1. Preparation of Standard NTO Solution

A standard sample of pure NTO shall first be made and analyzed for comparison of peak area. Add 1.0 gram of pure NTO to a 100 mL volumetric flask. [The purity of the NTO standard should be ≥99%, as determined by either the potentiometric technique or by using a photodiode array detector to verify the UV spectrum (i.e. purity) of NTO.] Add 1.0 gram of an appropriate internal standard (such as diethyl phthalate, ethyl centralite, or other compound that does not interfere with the analysis of the peaks for NTO) of analytical reagent quality. Add enough HPLC grade water to ensure dissolution. Dilute to mark with additional HPLC grade water.

B.3.3.2. Preparation of Calibration Solutions

Three (3) or more calibration standards spanning the anticipated NTO concentration range contained in the sample shall be prepared to generate a calibration curve/calibration table. Transfer an appropriate amount of the prepared standard NTO solution into a 10mL volumetric flask. Dilute to mark with HPLC grade water and mix well. Repeat with two (2) additional flasks, utilizing different amounts of standard NTO solution to vary the concentration.

B.3.3.3. Preparation of NTO Sample Solution

The sample solution shall be prepared by accurately weighing 0.25 gram of the NTO sample into a 50 mL volumetric flask. Dilute to mark with HPLC grade water and ensure that sample is uniformly mixed before performing analysis. Prepare in triplicate.

B.3.4. HPLC Analysis

a. The following HPLC operating conditions are given for information only.

Mobile phase/eluent	100 percent HPLC grade water plus IPCA (ion pairing agent); also, various proportions of acetonitrile and water could be used
Flow rate	1.0 to 2.0 mL/minute
UV wavelength	214 nm
Column	Reverse phase column or cartridge C-18
Run time	15 minutes
Sample size	1.0 to 5.0 microliters
Temperature	30°C

Table B-1. HPLC Instrument Parameter Guide for NTO Purity Analysis.

b. The concentration of NTO is calculated from its peak area, using the peak of pure NTO for comparison. The operation, analysis, and calculational procedures of the HPLC equipment used shall be followed for maximum accuracy and precise area measurements of the HPLC trace.
c. Standard and sample solutions are introduced into the system using a syringe or autosampler – a 5 µL injection volume is recommended. All standard and sample injections must be performed under the same operating conditions.
d. For statistical control, a sufficient number of injections of each solution must be made to ensure reproducibility of the system. It is recommended that at least two (2) injections be performed for the working calibration standards and samples
e. A calibration heck standard should be run before and after samples with no more than six (6) hours between calibration and verification.

B.4. DETERMINATION OF NTO PURITY VIA POTENTIOMETRIC METHOD

B.4.1. Principle

This method shall be performed to determine the NTO purity via the potentiometric method with a TBAH solution, according to AOP-4682. The NTO purity shall be reported as an average value of weight percent.

B.4.2. Test Description

An automatic potentiometric titrator shall be used to titrate both an NTO sample and a blank sample. The NTO purity is calculated based on the volume of titration.

B.4.3. Equipment

An automatic potentiometric titrator assembly comprised of a recording potentiometer fitted with an automatic burette and equipped with 20 mL syringe and a combination glass-Ag/AgCl electrode can be used.

B.4.4. Reagents

a. Tetrabutlyammonium hydroxide (TBAH) 0.1 N (This is a commercial solution in methanol or in an isopropanol/methanol mixture. This solution must be stored between 16 and 24°C).
b. Isopropanol/distilled water solution (97/3 percent ratio by volume).
c. Benzoic acid, analytical grade, dried at 65.5°C.

B.4.5. Procedure

The temperature of the TBAH solution should not vary by more than +/-1°C during both the determinations of the TBAH titer and the NTO purity.

a. Determination of TBAH Titer:

Transfer a weighed portion of approximately 0.1 gram of benzoic acid (weighed to +/- 0.1 mg) to a 150 mL beaker. Add 100 mL of the aqueous isopropanol solution. Stir until completely dissolved. Then, using the potentiometric titrator, titrate with the TBAH 0.1 N solution. A minimum of three tests with benzoic acid and three tests without benzoic acid (blank tests) shall be conducted. The titrator determines the equivalence point, which is the point where the addition of a minimum amount of TBAH titration solution leads to a maximum change in potential.

The normality of TBAH is calculated as follows:

$$\text{Normality of TBAH} = \frac{(1000) \cdot (\text{m})}{(122.1) \cdot (V_1\text{-}V_0)},$$

Where: m = weight of benzoic acid used (grams),
V_1 = volume in mL of TBAH solution used to reach the equivalence point in the benzoic acid test (the average of three tests is used),
V_0 = volume in mL of TBAH solution used to reach the equivalence point for the blank test (the average of three tests is used),
122.1 = molecular weight of TBAH.

b. Determination of NTO Purity:

Transfer a weighed portion of approximately 0.1 gram of NTO (weighed to +/- 0.1 mg) to a 150 mL beaker. Add 100 mL of aqueous isopropanol. Stir until the NTO is completely dissolved. Then, using the titrator, titrate with the 0.1 N TBAH solution. A minimum of three tests shall be conducted. The titrator determines the equivalence point, which is the point where the addition of a minimum amount of TBAH titration solution leads to a maximum change in potential.

The NTO purity is calculated as follows:

$$\text{NTO purity} = \frac{(130) \cdot (V_1 - V_0) \cdot (\text{N}) \cdot (100)}{(\text{m}) \cdot (1000)},$$

Where: m = weight of NTO (grams).
V_1 = volume of TBAH solution used to reach the equivalence point (the average of three tests is used),
V_0 = volume in mL of TBAH solution used to reach the equivalence point for the blank test (the average of three tests is used),
N = normality of TBAH solution (obtained above),
130 = molecular weight of NTO.

B.5. DETERMINATION OF CHLORINE CONTENT (AS CHLORIDE)

B.5.1. Principle

This method shall be performed to determine the chloride content of the NTO via direct titrimetry with AgNO3, according to AOP-4682. The chloride content shall be reported as an average value of weight percent.

B.5.2. Test Description

An automatic potentiometric titrator shall be used to titrate both an NTO sample and a blank sample. The chloride concentration is calculated based on the volume of titration.

B.5.3. Equipment

a. An automatic potentiometric titrator assembly comprised of a recording potentiometer fitted with an automatic burette and equipped with a 5 mL syringe.
b. Ag shall be the working electrode
c. Ag/AgCl in KCl/K_2SO_4 shall be the reference electrode

B.5.4. Reagents

a. 0.02 N $AgNO_3$ aqueous solution
b. 0.3 g/L NaCl aqueous solution
c. 30% concentrated HNO_3 Nitric Acid solution (1:1 ratio of concentrated nitric acid to water)
d. Distilled water

B.5.5. Procedure

Transfer a weighed portion of 5 +/- 1.0 gram of NTO (weighted to +/-0.1 mg) to a 150 mL beaker. Add 100 mL of distilled water and stir until the NTO is completely dissolved. Add precisely 5 mL of the 0.3 g/L NaCl solution with a pipette. Add 5 mL of the 30% concentrated HNO_3 solution. Then, using the potentiometric titrator, titrate with 0.02 N $AgNO_3$ solution. The titrator determines the equivalence point, which is the point where the addition of a minimum amount of $AgNO_3$ titration solution leads to a

maximum change in potential. A minimum of three tests shall be conducted. A minimum of three tests without NTO shall also be conducted. Then Chloride Concentration is calculated as follows:

$$\% \text{ Cl} = \frac{35.5 \times (V_1 - V_0) \cdot (100) \cdot (0.02)}{(m) \cdot (1000)},$$

Where: m = weight of NTO (grams),
V_1 = volume in mL of $AgNO_3$ solution used to reach the equivalence point with weight "m" of NTO (average of a minimum of three tests is used),
V_0 = volume in ml of $AgNO_3$ solution used to reach the equivalence point without NTO (average of a minimum of three tests is used),
0.02 = Normality of $AgNO_3$ solution,
35.5 = atomic weight of chlorine.

B.6. DETERMINATION OF NITRIC ACID CONCENTRATION

B.6.1. Principle

This method shall be performed to determine the nitric acid content of the NTO. The nitric acid content shall be reported as an average value of weight percent.

B.6.2. Test Description

An automatic potentiometric titrator shall be used to titrate both an NTO sample and a blank sample. The nitric acid concentration is calculated based on the volume of titration.

B.6.3. Apparatus and Reagents

a. An automatic potentiometric titrator assembly comprised of a recording potentiometer fitted with an automatic burette and equipped with a 5 ml syringe and a combination glass-Ag/AgCl electrode
b. 0.1 N Tetrabutylammonium hydroxide (TBAH) commercial solution in methanol or in an isopropanol/methanol mixture. This solution must be stored between 16 and 24°C.
c. Isopropanol/distilled water solution in a 97/3 percent ratio by volume
d. 0.1 N Nitric acid in aqueous solution

B.6.4. Procedure

Transfer a weighted portion of 5-10 grams of NTO (weighted to ± 0.1 mg) to a 150 ml beaker. Add precisely 1 ml of the 0.1N nitric acid solution with a pipette. Add 100 ml of aqueous isopropanol. Stir until the NTO is completely dissolved. Use the titrator to titrate the NTO with the 0.1 N TBAH solution. The titrator determines the equivalence point, which is the point where the addition of a minimum amount of TBAH titration solution leads to a maximum change in potential. A minimum of three (3) tests shall be conducted with NTO. Three (3) tests at minimum shall be conducted without NTO as the blank tests. Calculate the nitric acid concentration from the results of the 6 titrations.

B.6.5. Calculation of Nitric Acid Concentration

The nitric acid concentration is calculated as follows:

$$\%\mathrm{HNO_3} = \frac{(63)\cdot(\mathrm{V_1}-\mathrm{V_0})\cdot(100)\cdot(0.1)}{(\mathrm{m})\cdot(1000)},$$

Where: m = weight of NTO used (grams),
V_1 = volume in ml of TBAH solution used to reach the equivalence point with “m” weight of NTO (the average of three tests is used),
V = volume in ml of TBAH solution used to reach the equivalence point for the blank test (the average of three tests is used),
0.1 = Normality of TBAH solution,
63 = molecular weight of HNO_3.

B.7. DETERMINATION OF VOLATILE SUBSTANCES

B.7.1. Principle

This method shall be performed to determine the content of volatile substances in NTO via heating and reweighing, according to AOP-4682. The total content will be reported as a value of weight percent.

B.7.2. Test Description

A sample of NTO will be heated in an air oven to drive off volatile substances. The volatiles content is calculated based on the weight loss of the sample.

B.7.3. Sample Procedure

Add 5.0 grams of NTO in a 100 ml beaker; record the weight of the beaker with the NTO. Transfer the beaker and its contents to an air oven and heat at 103 ± 2°C for 2 hours. Remove the beaker from the oven and place in desiccator until cool. Weigh the beaker with the NTO. Calculate the volatiles content.

B.7.4. Calculation of Volatile Substances

The volatiles content shall be calculated by the difference in weight before and after heating and reported on a percentage basis per the following equation:

$$\text{Weight percent volatiles} = \frac{(W_0 - W_1) \cdot (100)}{m},$$

Where: m = weight of NTO used in grams (g),
W_0 = weight of beaker plus NTO initially in grams (g),
W_1 = weight of the beaker plus NTO after drying in grams (g).

B.8. GENERAL NOTES AND INFORMATION

NTO is usually prepared by nitrating Triazolone (TO). Since there is significant difference between manufacturers for the particle size and particle size distribution of NTO, the manufacturer will provide particle size distribution data and documentation of the test method used when NTO is purchased.

AOP-4543(A)(1)