NATO STANDARD

AOP-4776

ENERGETIC MATERIALS, SPECIFICATION FOR DNAN (2,4-DINITROANISOLE)

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NORTH ATLANTIC TREATY ORGANIZATION

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NORTH ATLANTIC TREATY ORGANIZATION (NATO)

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NATO LETTER OF PROMULGATION

24 May 2018

1. The enclosed Allied Ordnance Publication AOP-4776, Edition A, Version 1, ENERGETIC MATERIALS, SPECIFICATION FOR DNAN (2,4-Dinitroanisole), 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 4776.

2. AOP-4776 Edition A, Version 1, is effective upon receipt.

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

Zoltán GULYÁS
Brigadier General, HUNAF
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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CHAPTER 1 INTRODUCTION

1.1. CHEMICAL REQUIREMENTS AND TEST PROCEDURES FOR DNAN (2,4 – DINITROANISOLE).

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

1.1.2 2,4-Dinitroanisole (DNAN) is a key insensitive munition (IM) melt-phase ingredient that is currently featured in several IM melt-pour formulations developed by NATO Countries.

1.1.3 Since DNAN is processed essentially the same as TNT, it allows for analogous explosive formulations to be processed using identical procedures.

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ANNEX A Specification for DNAN (2,4 – Dinitroanisole)

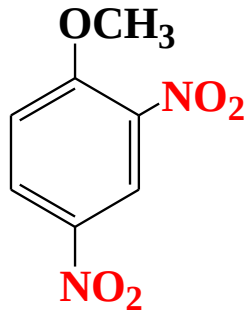
A.1. Table with specification for DNAN

Properties	Specification	Procedure
DNAN Purity	>98%	B-1
Total Impurities, % Undissolved Solids Impurities	<2 0.15 Max < (% total impurities - % undissolved solids)	B-1 B-3
Melting Point (°C)	>90	B-2
Trace Metals Content (dry basis), ppm	<300	B-4
Physical Form	Flake or granular	B-5

Abbreviation

Abbreviation	
DNAN	2,4-dinitroanisole

Structural formula of DNAN:



A.2. Safety requirements for DNAN

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. DNAN Purity

B.1.1. Principle

DNAN purity is determined via HPLC (High Performance Liquid Chromatography).

B.1.2. Test description

This method utilizes High Performance Liquid Chromatography (HPLC) to determine the purity of 2,4-Dinitroanisole (2,4-DNAN), and to quantify the amount of impurities present such as the structural isomer, 2,6-Dinitroanisole (2,6-DNAN), and the possible by-products, 2,4-Dinitrophenol (2,4-DNP), 2,5-Dinitroanisole (2,5-DNAN), and 1-Chloro-2,4-Dinitrobenzene (CDNB). Acetonitrile solutions of accurately weighed samples of 2,4-DNAN are diluted to a concentration of 50 ppm and analyzed via Reverse Phase HPLC. The analyses are compared to a linear regression generated from a series of standards made from purified components. Pure, HPLC-grade solvents and trifluoroacetic acid shall be used, as well as clean and calibrated equipment. Figure 1 shows sample HPLC results trace.

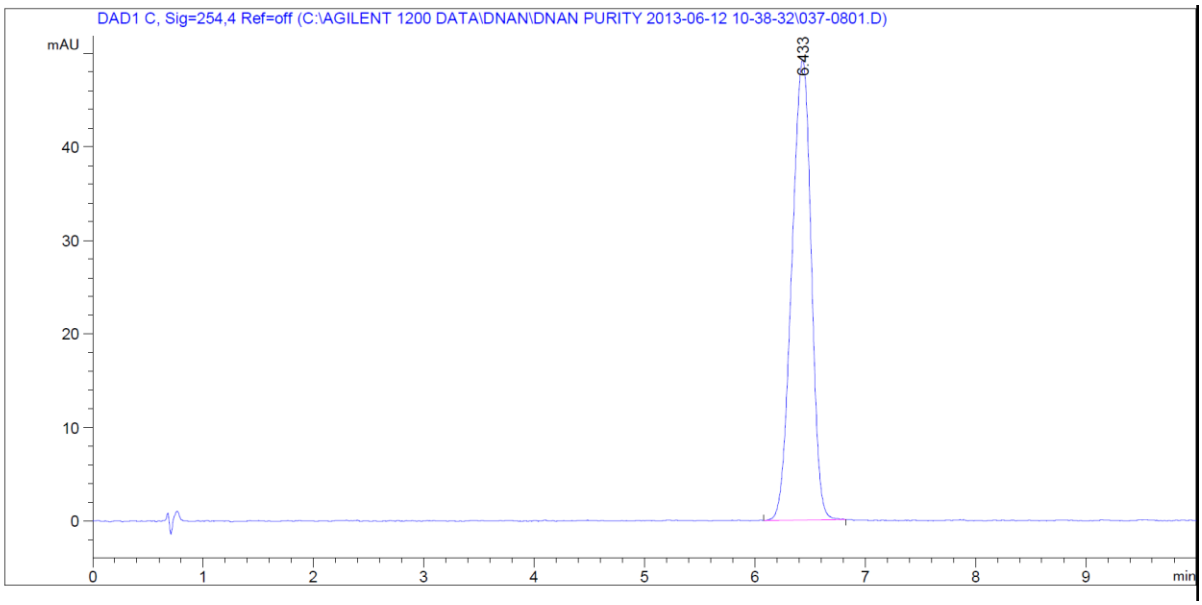


Figure 1. HPLC DNAN Purity Trace

Apparatus and reagents.
a. High Performance Liquid Chromatograph (HPLC).

b. Acetonitrile, HPLC-grade.

c. Methanol, HPLC-grade.

d. Deionized Water, HPLC-grade.

e. Trifluoroacetic Acid, High Purity.

f. Purified 2,4-DNAN, 2,6-DNAN, 2,4-DNP, 2,5-DNAN, and CDNB.

B.1.3. HPLC conditions.

a. A reverse phase column that yields suitable peak shape, resolution and retention (e.g. C18 150x4.6mm, 5µm particle size.)

b. Mobile phase is an isocratic mixture of 55% deionized water (acidified with 0.1% (v/v) of trifluoroacetic acid) and 45% HPLC-grade methanol. HPLC parameters (e.g. flow rates, mobile phase ratios, injection volumes, run times) may be adjusted to maintain adequate resolution and shape of the DNAN peak and any impurities.

c. Relative Standard Deviation between runs is <3%.

B.1.4. Standard preparation.

2,4-DNAN, 2,4-DNP, 2,6-DNAN, 2,5-DNAN and CDNB shall be purified using at least 3 total recrystallizations to ensure absolute purity*.
* Note: Samples with lower purity values (e.g. min 98.0%) may also be used as long as the actual purity value is known. Standard mass values will then be adjusted accordingly for the purity of the material.

Standard solution preparation: Prepare three working dilutions of the 2,4 DNAN standard in HPLC grade acetonitrile with the following approximate concentrations in parts per million:

	Standard 1	Standard 2	Standard 3
2,4-DNAN	10	50	100

B.1.5. Sample preparation.

a. Obtain samples of 2,4-DNAN that have been dried to constant weight in a 60°C steam-heated oven.

b. For each batch to be tested, prepare three 50ppm samples in HPLC grade acetonitrile.

B.1.6. Run samples

Verify all HPLC parameters are correct and allow the system to equilibrate. Enter necessary information into data acquisition program. Run analysis on standard vials. The three standards shall be used to generate a linear equation using a least-squares regression. The R2, or the fraction of the total squared error of the linear equation, shall not be less than 0.990. If this is not the case, analysis of further samples shall not be continued until a series of standards can be analyzed to provide such a linear equation. Enter necessary information into data acquisition program. Run analysis on sample vials. Collect the automatically printed chromatograms and reports.

B.1.7. Impurities

If any impurity peaks are present in the sample chromatograms, they must be identified and quantified where possible. Using previous chromatography data, identify which impurities are present by correlating peak retention times of the known potential impurities. Once the peak(s) have been identified, prepare 3 working dilutions of the particular impurity standard with the approximate concentrations in parts per million of 1, 5 and 10. Test these standards as above.

B.1.8. Calculation to determine purity and concentration

Computer software package is used to establish a calibration equation based on the concentration of 2,4-DNAN, 2,6-DNAN, 2,5-DNAN, 2,4-DNP, and CDNB in the three calibration standards and the HPLC chromatographic peak areas obtained from the analyses of these standards. Using the calibration equation, and the peak areas obtained for the test samples, the concentrations of the components can be determined using Microsoft Excel (or equivalent) to analyze data. This includes using the chromatographic peak areas to determine the component percentages in the DNAN samples. Results will be reported as % purity DNAN and % impurities.

Calculation of DNAN Purity:

%DNAN= sample/reference x 100

Where:
Sample = Peak area from sample of DNAN lot reference=Peak area from reference standard

Calculation of Impurities:

%(W / w) = (sample/(reference× slope)) ×100

Where: sample = Peak area of impurity in sample
reference = 10,000 micrograms/mL
W/w = Constituent
slope = Impurity calibration curve, peak area/microgram/mL

B.2. Melting Point

B.2.1. Principle

A Differential Scanning Calorimeter will be used which is capable of meeting the heating rate and sample size parameters as specified below and shown in Figure 2.

a. Place 1.0 ± 0.5 mg of the DNAN sample in a suitable sized aluminum crucible. Heat at a rate of 5°C/min to a temperature of 150°C.

b. Determine the melting point based on the peak max of the endotherm.

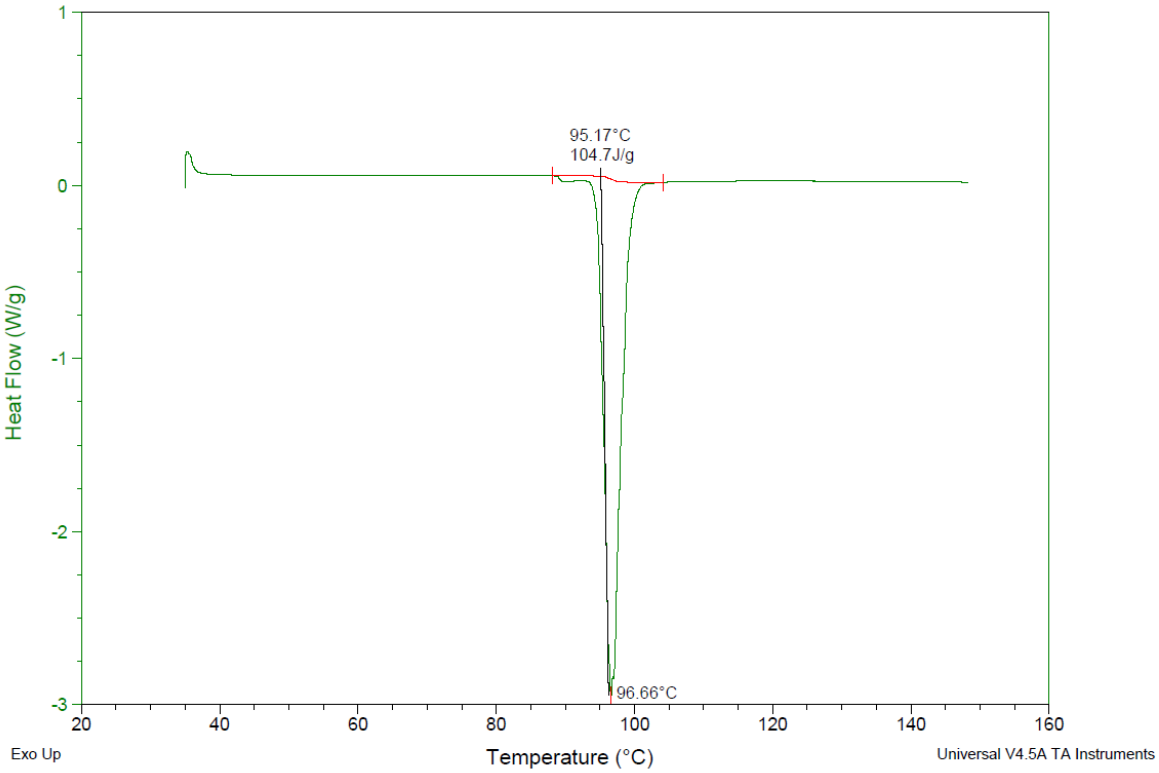


Figure 2. DNAN DSC Thermogram

B.3. Undissolved Solids

B.3.1. Principle

a. Place 1.0 ± 0.001 grams of DNAN in a 200 mL beaker.

b. Add 100 mL of methanol to this DNAN and stir for a minimum of 10 minutes.

c. Screen material through a pre-tarred medium porous crucible.

d. Calculation of undissolved solids:

% Undissolved Solids = (Wt-Tare)/St x 100

Where:

Wt = Weight of tare and undissolved solids, gram
Tare = Weight of the crucible, gram
St = Weight of DNAN, gram

B.4. Trace Metals Content

B.4.1. Principle

Test Description

This method shall be performed in accordance with ASTM D 7303. The user shall modify the ASTM method for trace metal testing of DNAN. Metals analyzed in this test include: Aluminum (Al), Calcium (Ca), Chromium (Cr), Iron (Fe), Magnesium (Mg), Sodium (Na) and Zinc (Zn). The sum of individual metal content will be reported as the trace metal content. Total sum of the trace metals content should be less than 300 ppm. The recommended solvent for the analysis is DMSO-d6. All solution sources, test equipment, and standards shall be noted. All calibrations and test data shall be noted.

Apparatus and reagents.

a. An inductively coupled plasma-atomic emission spectrometer (ICP-AES) that is capable of operating in a simultaneous or sequential mode and uses ionized argon gas as the plasma. System must be capable of fulfilling and complying with the requirements and description of the technique outlined above. System and processing of background corrected signals must be computer controlled.

b. Liquid argon gas supply.

c. Variable peristaltic pump capable of delivering sample and standard solutions to the nebulizer.

d. Assortment of digital air displacement pipetters that cover the range from 0.1 to 2500 μL with suitable tips and Repipet II dispensers or equivalent that cover the 0.0 to 10.0 mL range of volume.

e. Labware and the laboratory work area must be clean to avoid significant errors in determining trace levels of the analytes.

f. Assorted volumetric flasks.

g. Nitric and hydrochloric acid, concentrated. Required dilutions should be made using distilled water.

h. All water used in sample preparation and dilutions should be distilled water.

i. Stock metal solutions should be purchased from a reputable commercial vendor. All stock solutions are 1000 µg/mL with the exception of the potassium and sodium stock solutions, which should be 10,000 µg/mL.

j. Mixed calibration standards can be prepared by mixing appropriate volumes of the stock solutions in 500 mL volumetric flasks. Prepare by adding 20 mL of (1:1) nitric acid and 20 mL of (1:1) hydrochloric acid to the flask, followed by the aliquots of the required stock standard solutions and dilute with distilled water. Transfer each mixed standard to a clean polyethylene bottle that has not been previously used. The following recommended concentrations and combinations of metals for each standard are given below and may be used as is or modified to standardize the instrument for the quantitative determination of trace materials in the material.

k. Mixed Calibration Standard I is prepared by adding 0.25 mL of the stock solution of Ag, 0.5 mL of the stock solution of Ba, 1.0 mL of the stock solutions of B, Cd, Cu, and Mn, 2.5 mL of the stock solutions of Sb and Se, and 5.0 mL of the stock solutions of As and Ca to a 500 mL volumetric flask as prepared above and diluting as above.

NOTE: If the silver precipitates initially, add 15 additional mL of water and warm until the solution clears.

l. Mixed Calibration Standard II is prepared by adding 0.5 mL of the stock solution of Sr, 1.0 mL of the stock solution of K, 2.5 mL of the stock solution of Na, and 5.0 mL of the stock solution of Mo to a 500 mL volumetric flask as prepared above and diluting as above.

m. Mixed Calibration Standard III is prepared by adding 1.0 mL of the stock solutions of Co and V and 5.0 mL of the stock solution of P to a 500 mL volumetric flask as prepared above and diluting as above.

n. Mixed Calibration Standard IV is prepared by adding 2.0 mL of the stock solution of Sn, 2.5 mL of the stock solutions of Cr and Zn, and 5.0 mL of the stock solutions of Al and Si to a 500 mL volumetric flask as prepared above and diluting as above.

o. Mixed Calibration Standard V is prepared by adding 0.5 mL of the stock solution of Be, 1.0 mL of the stock solution of Ni, 2.5 mL of the stock solution of Tl, and 5.0 mL of the stock solutions of Fe, Mg, and Pb to a 500 mL volumetric flask as prepared above and diluting as above.

p. A calibration blank that is used to establish the analytical curve is prepared by adding 20 mL of (1+1) nitric acid and 20 mL of (1+1) hydrochloric acid to a 500 mL flask and diluting to volume with deionized distilled water. This solution should be stored in a polyethylene bottle. Finally, the rinse blank should be prepared as the

calibration blank and is used to flush the instrument sample uptake system and reduce memory interferences.

q. A laboratory performance check solution should be prepared from the stock standard solutions in a 2% nitric and hydrochloric acid matrix. Appropriate dilutions of the stock solutions should be made that will result in a concentration of 2.0 ppm for all elements except for K and P, which should be 10 ppm, and Na which should be 20 ppm.

r. A quality control sample should be prepared in the same acid matrix as the calibration standards at appropriate concentrations such as 1.0 ppm for most elements. This sample should likewise be stored in a polyethylene bottle and be obtained from a source independent of that from which the calibration standards were prepared.

s. A microwave unit that is capable of providing programmable power of at least 574 W and which can be programmed to be within ± 10W of the required power. The microwave unit cavity should be corrosion resistant and well ventilated. All electronics should also be protected against corrosion for safe operation. The unit should use temperature feedback control to provide the primary control performance mechanism for the method, but it may also be pressure controlled and monitored. Temperature feedback control is necessary for reproducible microwave heating allowing flexibility in the reagents used to achieve total decomposition for the analysis. The microwave unit should meet temperature performance requirements that allow the temperature to be sensed to within ± 2.5°C and to automatically adjust the microwave field output power within 2 seconds of sensing if this is not the case. Temperature sensors should be accurate to ± 2°C. A temperature calibration control mechanism should be developed for each specific set of reagent(s) combination(s), quantity, and specific vessel type and number. The system requires fluorocarbon digestion vessels with a volume of at least 45 mL and capable of pressures of at least 30 atm (30 bar or 435 psi) and having a controlled pressure relief. A rotating turntable should also be employed to ensure homogeneous distribution of microwave radiation in the unit. The speed of the turntable should be a minimum of 3 rpm. Follow the manufacturer's recommendations regarding the proper and safe operation of the microwave equipment and vessels.

Procedure

a. Sample preparation requires digestion of approximately 100 milligrams of 2,4-dinitroanisole. Weigh and record the amount of material weighed into each digestion vessel. Add 5.0 mL of concentrated nitric acid to all the digestion vessels. The determination may be performed in triplicate for each sample lot. Samples may also be spiked with known amounts of trace metals, blank spikes may be included, or blanks containing only nitric acid may be added to fill the digestion set. Digest using a microwave program that uses 1200 W of power if all twelve vessels are included in the

microwave carousel. The program should ramp to a temperature of 200°C with a pressure limit of 400 psi and hold at the temperature of 200°C. After completion of the digestion, allow the vessels to cool, and add 20 mL of distilled water to complete sample preparation. The sample is now ready for analysis by ICP-AES.

b. Specific instrument operating conditions will be those recommended by the instrument manufacturer. Typical conditions are as follows: Incident rf power – 1100 watts, Reflected rf power - < 5 watts, Viewing height above the work coil – 15 mm, Injector tube orifice i.d. – 1 mm, Argon supply – liquid, Argon pressure – 60 psi, Coolant Ar flow rate – 19 L/min, Aerosol carrier Ar flow rate – 620 mL/min, Auxiliary (plasma) Ar flow rate – 300 mL/min, and Sample uptake rate – 1.2 mL/min. The instrument should become thermally stabilized for a period of thirty minutes before use and optimization.

c. Optically profile the plasma following the manufacturer's instructions.

d. The instrument should be calibrated for operation following the manufacturer's instructions using the calibration blank and standards previously prepared.

e. Standards and samples should be introduced to the instrument's nebulizer using the peristaltic pump.

f. Equilibrium should be reached in the plasma by aspirating the samples and standards into the plasma 30 seconds before integration of the background corrected signal.

g. Use at least three 5 second background corrected integration periods to obtain the atomic emission signal for use in the calculation of the standard curve and concentration data. The nebulizer and sample uptake system should be flushed with calibration blank between each sample and the standards for a minimum of sixty seconds to ensure that analyte memory effects are not occurring.

h. Immediately following the calibration of the instrument, the calibration blank and laboratory performance check solution should be analyzed. This solution should be also analyzed at the end of the sample run and after every tenth sample. The quality control sample should be analyzed with each daily analytical run.

Quality control

The laboratory performance check and quality control sample values for each analyte should be within 90% to 110% of the expected values. If this condition is not met, the solution should be reanalyzed and if results for an analyte of interest are again outside ±10%, the instrument should be recalibrated. If a laboratory performance check fails, all samples analyzed following the last acceptable check should be reanalyzed.

Calculation

Instrument results for the targeted analytes should be multiplied by the volume (0.025 L), divided by the weight in grams, and by the dilution factor when appropriate to calculate the concentration of a given element in units of parts per million in the DNAN. If final results for trace elements in DNAN are desired in weight percent, divide the previous result by 10,000.

B.5. Physical Form

B.5.1. Principle

Visual examination. The DNAN sample shall be examined with unaided eyes by personnel with normal vision or normal corrected vision.
Workmanship for DNAN. The DNAN shall be uniform in quality and free from lumps, grit, visible impurities, foreign matter, or other defects that would render the DNAN unsuitable for the intended use.

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