NATO STANDARD

AOP-4719

ENERGETIC MATERIALS, SPECIFICATION FOR TEGDN (TRIETHYLENE GLYCOL DINITRATE)

Edition A Version 1
NOVEMBER 2016

NORTH ATLANTIC TREATY ORGANIZATION

ALLIED ORDNANCE PUBLICATION

Published by the
NATO STANDARDIZATION OFFICE (NSO)

INTENTIONALLY BLANK

NORTH ATLANTIC TREATY ORGANIZATION (NATO)

NATO STANDARDIZATION OFFICE (NSO)

NATO LETTER OF PROMULGATION

29 November 2016

1. The enclosed Allied Ordnance Publication AOP-4719, Edition A, Version 1 ENERGETIC MATERIALS, SPECIFICATION FOR TEGDN (TRIETHYLENE GLYCOL DINITRATE), 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 4719.

2. AOP-4719, Edition A, Version 1 is effective upon receipt.

3. No part of this publication may be reproduced, stored in a retrieval system, used commercially, adapted, or transmitted in any form or by any means, electronic, mechanical, photo-copying, recording or otherwise, without the prior permission of the publisher. With the exception of commercial sales, this does not apply to member or partner nations, or NATO commands and bodies.

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

EdvardasMAŽEIKIS
Major General, LTUAF
Director, NATO Standardization Office

INTENTIONALLY BLANK

RESERVED FOR NATIONAL LETTER OF PROMULGATION

INTENTIONALLY BLANK

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.	

INTENTIONALLY BLANK

RECORD OF SPECIFIC RESERVATIONS

[nation]	[detail of reservation]
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.	

INTENTIONALLY BLANK

TABLE OF CONTENTS

INTENTIONALLY BLANK

CHAPTER 1 INTRODUCTION

1.1 AIM OF AGREEMENT

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

1.2. RELATED DOCUMENTS

MIL-N-246B Military Specification Nitroglycerin, 19 Feb 1962

Ti Application Note No. T- 37 Nitrogen content of nitrocellulose, Metrohm

ASTM D 6304-07, “Standard Test Method for Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fisher Titration”

STANAG 4515 Ed. 1, Explosives, Thermal Characterization by Differential Thermal Analysis, Differential Scanning Calorimetry and Thermogravimetric Analysis

STANAG 4491 Ed.1, Explosives, Thermal Sensitiveness and Explosiveness Tests

STANAG 4582 Ed. 1, Explosives, Nitrocellulose Based Propellants, Stability Test Procedure and Requirements Using Heat Flow Calorimetry

1.3. NOTE ON STANDARD DEVIATION

In all the test procedures, the standard deviation is calculated using formula:

$$s = \sqrt{\frac{1}{\mathrm{n}-1}\sum_{\mathrm{i}=1}^{\mathrm{n}}(\mathrm{x_i}-\bar{\mathrm{x}})^2}$$

where,

s	*Standard deviation*
n	*Number of degrees of freedom*
x_i	*Value*
$x;^{-}$	*Average*

INTENTIONALLY BLANK

ANNEX A REQUIREMENTS FOR TRIETHYLENEGLYCOLDINITRATE (TEGDN)

A.1. TABLE WITH REQUIREMENTS FOR TEGDN

Properties	**Requirements**	**Test procedure**
TEGDN purity by HPLC by NMR, alternative method	min 97 %	B.1 B.2
Acidity Alkalinity	max 0.002% max 0.002%	B.3
Nitrogen content	min 11.5%	B.4
Water content , Karl Fisher titration coulometric volumetric	max 1%	B.5 B.6
Decomposition temperature by Differential Scanning Calorimetry (DSC)	Decomposition Onset min 183ºC @ 5 K/min	B.7

A.2. TABLE WITH OTHER INFORMATIVE PROPERTIES FOR TEGDN

Properties	**Test procedure**
Quantitative analysis of inorganic impurities	B.8
Temperature of Ignition	B.9
Thermal Stability by Heat Flow Calorimetry (HFC)	B.10

A.3. ABBREVIATION FOR TEGDN

Abbreviation	**Explanation**
TEGDN	Triethylene Glycol Dinitrate $C_6H_{12}N_2O_8$

A.4. STRUCTURAL FORMULA OF TEGDN

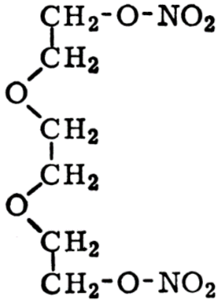


Figure 1: Structural formula of TEGDN

A.5. CHARACTERISTICS OF TEGDN

TEGDN (CAS number 111-22-8) is classified as a transparent, oily liquid. The melting point of TEGDN is -19°C. It is miscible in any proportion with for example acetone, benzene, carbon tetrachloride, chloroform, diethyl ether, ethanol, methanol, toluene, trichloroethylene. The molecular weight of TEGDN is 240.1 g/mole. TEGDN has an oxygen balance -66.7 %.[1]

A.6. SAFETY REQUIREMENTS FOR TEGDN

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

---

[1] Meyer, R., Köhler, J., Homburg, A., Explosives, Sixth Edition, 2007, Wiley-VCH VerlagGmbH& Co. KGaA, (343-345)

INTENTIONALLY BLANK

ANNEX B TEST PROCEDURES

CONTENTS OF ANNEX B

Test procedures page

B.1. TEGDN PURITY (HPLC)

1.1. PRINCIPLE

The determination of TEGDN purity is performed by using high performance liquid chromatography (HPLC).

The sample is dissolved in acetonitrile (ACN) or any other suitable solvent. The qualitative recognition is based on the retention time. The quantitative content of TEGDN is calculated based on the peak height or area by using internal or external standard procedure.

1.2. CHEMICALS

Acetonitrile (CH_3CN) or other suitable solvent, HPLC grade
H_2O (HPLC grade)
TEGDN calibration standard (purity by NMR > 99 %)
Internal Standard e.g. 2,4-DNT (purity > 98 %)

1.3. APPARATUS

Analytical balance with precision of 0.1 mg
Standard laboratory equipment and glassware
HPLC system with variable PDA or UV-detector
Analytical Column: RP C-18

1.4. EXAMPLE HPLC CONDITIONS

Column:	XBridge C18 3.5 µm, 4.6x250mm or Kinetex C18 2.6 µm 4.6x150mm
Eluent:	ACN/ H_2O (65/35 by volume)
Flow rate:	1.0 ml/min (equipment dependent)
Injection volume:	10 µl
Detector wavelength:	UV at 220 or 230 nm
Temperature:	20 – 22ºC

1.5. STANDARD PREPARATION

Prepare the TEGDN standard stock solution by weighing accurately 500-550 mg of TEGDN standard into a 50 ml flask. Fill in with ACN, or any suitable solvent.

Prepare the internal standard stock solution accurately weighing 50-100 mg of the internal standard e.g. 2,4-DNT into a 50 ml flask. Fill in with ACN, or any suitable solvent.

Prepare the standard solutions by pipetting 0.4, 0.8, 1.2 and 1.6 ml of the TEGDN stock solution into a 25 ml flask. When using internal standard procedure, add accurately 1.0 ml internal standard stock solution. Fill the flask to the 25 ml mark. Calculate the exact TEGDN and internal standard concentrations of the standard solutions.

NOTE: *The internal standard can be introduced by weighing or by pipetting of a stock solution. The standard solution should be stored in cool dark conditions for no more than one week.*

1.6. SAMPLE PREPARATION

Weigh approximately 40 mg of TEGDN sample into 50 ml flask with precision of 0.1 mg. When using internal standard procedure, add accurately 2.0 ml internal standard stock solution (e.g. 2,4-DNT). Fill the flask to the mark with ACN. Prepare at least three parallel sample solutions. Mix thoroughly and ensure proper dilution.

1.7. HPLC ANALYSIS

The injections of standard solutions and solutions to be analyzed must be done under the same operating conditions. At least two injections of each solution should be performed to ensure the reproducibility of the chromatographic system.

1.8. RESULTS/CALCULATIONS

Results are calculated based on calibration curve using internal standard or external standard procedure and expressed as percentage of TEGDN present in the sample.

Example of calculation by using internal standard procedure

$$\% TEGDN = \frac{\mathrm{Hs\ x\ Wint\ x\ RF}}{\mathrm{Hint\ x\ Ws}}\ \mathrm{x100\ \%} \qquad (1)$$

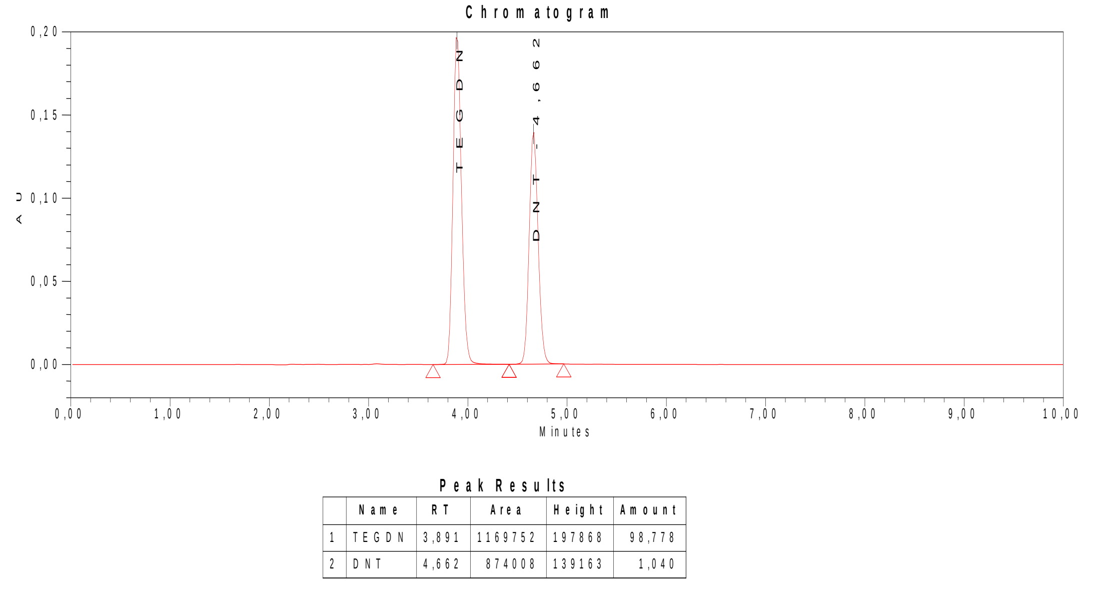
where

RF = response factor of TEGDN, as determined by calibration standards
Hs = sample peak height (mAU)
Hint = internal standard peak height (mAU)
Wint = weight of internal standard (mg)
Ws = sample weight (mg)

1.9. ACCURACY AND PRECISION

Accuracy of calibration curve: ±3 %
Precision: < 1.0 % based on standard deviation of 10 measurements (s= max 0.5 multiplied by factor k=2; confidence interval is 95 %).

1.10. EXAMPLE OF CHROMATOGRAM



Peak Results

	Name	RT	Area	Height	Amount
1	TEGDN	3,891	1169752	197868	98,778
2	DNT	4,662	874008	139163	1,040

Figure 2: HPLC chromatogram of TEGDN and Internal Standard 2,4-DNT

B.2. TEGDN PURITY (NMR)

2.1. PRINCIPLE

The determination of TEGDN purity is performed by ^{1}H-NMR Spectrometry using an internal standard procedure. At least two parallel measurements are made using a standard e.g. 2,4,6-trinitrotoluene (TNT) and deuterated chloroform ($CDCl_3$) as solvent.

2.2. CHEMICALS

Deuterated chloroform ($CDCl_3$) ≥ 99.8 % D, containing 0.1 % tetramethylsilane (TMS)
Internal standard e.g. TNT purity ≥ 99.8 %

2.3. APPARATUS

Analytical balance with precision of 0.01 mg
Standard laboratory equipment and glassware
NMR spectrometer ^{1}H frequency at least 400 MHz

2.4. INSTRUMENT SETUP

Field gradient adjusted so that ^{1}H linewidth of TMS signal (0.0 ppm) is ≤ 0.5 Hz at half height.

2.5. PREPARATION OF REFERENCES

Internal standard procedure is described in section 2.6.

2.6. SAMPLE PREPARATION

15 mg of the TEGDN sample and 30 mg of the internal standard e.g. 2,4,6-trinitrotoluene (TNT) are weighed accurately to a 5 ml glass tube and dissolved into 0.8 ml $CDCl_3$. The liquid sample is filtered directly into a NMR tube and the ^{1}H-NMR spectrum is measured under quantitative conditions using the repetition time which is at least $5T_1$ (T_1 = relaxation time).

2.7. ANALYSIS

NMR signals of the internal standard e.g. TNT (methyl triplet, 2.7 ppm) and TEGDN (multiplet, 3.8 ppm and singlet 3.7 ppm) are integrated using integration ranges from

2.9 to 2.5 ppm and from 4.2 to 3.2 ppm (Figure 3). The amount of impurities such as triethyleneglycol which is used as the starting compound (multiplet to 3.5-3.7 ppm) and decomposition products have to be taken into account during integration if they exist.

2.8. CALCULATIONS

Weight of the TEGDN is calculated using formula:

$$m_a = \frac{M_a \cdot N_s \cdot I_a \cdot m_s}{M_s \cdot N_a \cdot I_s} \qquad (2)$$

where,
M_a molar mass of analyte (*g/mol*)
N_s number of protons (standard) producing analytical line/s
I_a integral of analyte
m_s exact weight of standard (*g*)
M_s molar mass of standard (*g/mol*)
N_a number of protons (analyte) producing analytical line/s
I_s integral of standard

Formula above gives amount of analyte in milligrams and mass percentage is calculated with formula:

$$Mass\ percentage = \frac{m_a}{m_{weighed}} \cdot 100\% \qquad (3)$$

where, $m_{weighed}$ exactly weighed amount of analyte (*g*)

Result is calculated as average of the measurements and accuracy of the determination is ± 0.5 % (weighing 0.3 % and integration 0.2 %).

2.9. EXAMPLE OF QUANTITATIVE ^{1}H NMR MEASUREMENT

This example spectrum (Figure 3) illustrates quantitative ^{1}H NMR measurement of TEGDN.

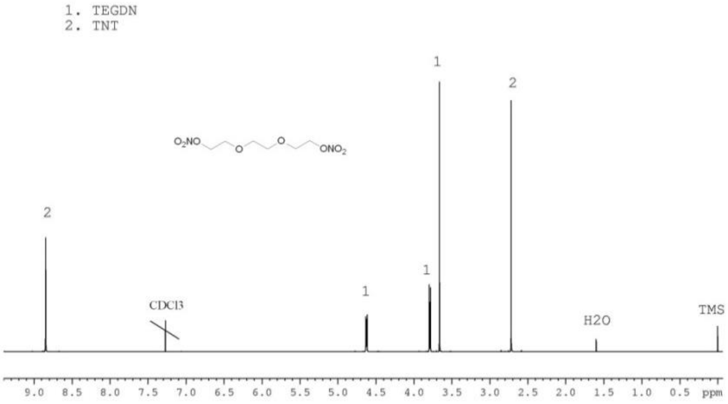


Figure 3: Quantitative ^{1}H NMR measurement of TEGDN.

B.3. ACIDITY OR ALKALINITY

3.1. PRINCIPLE

For the acidity/alkalinity measurement, TEGDN is dissolved in toluene and extracted with water in a separation funnel. The water layer is separated and titrated with dilute NaOH or H_2SO_4 using bromothymol blue as an indicator.

3.2. CHEMICALS

Toluene, for analysis
Water, CO_2- free, resistivity 18.2 MΩ cm or equivalent
Bromothymol blue, 1 % in ethanol (pK_{In}= 7.1, pH range 6.0- 7.6)
0.01 N NaOH
0.01 N H_2SO_4

3.3. APPARATUS

Analytical balance with precision of 0.1 mg
Weighing pipette or syringe
Separationfunnel 250 ml
Burette, capable of dispensing 20 µl portions
Titration vessel 150 ml
Magnetic stirrer and stir bar

3.4. PREPARATION OF REFERENCES

A blank determination is done with 100 ml water extracted with toluene. The indicator (0.5 ml) is added to the water extract. If the colour turns yellow, it is titrated to blue with 0.01 N NaOH. If the colour turns blue, a measured amount of 0.01 N H_2SO_4 is added dropwise until it turns light yellow. An equal amount of 0.01 N H_2SO_4 is added to the water extracts of all samples.
The blanks and samples must be extracted with the same bottle of toluene because of the different acidities of toluene in the various bottles.

3.5. SAMPLE PREPARATION

Approximately 10 g TEGDN is accurately weighed with a precision of 0.1 mg and dissolved in 100 ml toluene. The mixture is extracted two times with 50 ml of water. Three parallel samples (and blanks) are done.

3.6. ANALYSIS

The water extracts are combined and 0.5 ml of indicator is added. Acid addition must be done depending of the blank determination in 3.4. If the color turns yellow, it is titrated to light yellow with 0.01 N NaOH. If blue or green, it is titrated with 0.01 N H_2SO_4 to light yellow.

3.7. CALCULATIONS

Results are calculated and expressed as % H_2SO_4 or % Na_2CO_3.
The minimum detectable quantity is based on the titration method. It should be confirmed prior to the measurement.

$$Acidity\ \%\ \mathrm{H_2SO_4} = \frac{(a-b)\cdot n\cdot 49.04\cdot 100}{w} \qquad (4)$$

Where,
a ml NaOH for sample
b ml NaOH for blank
n normality of NaOH
w sample weight (mg)

$$Alkalinity\ \%\ \mathrm{Na_2CO_3} = \frac{(a-b)\cdot n\cdot 52.99\cdot 100}{w} \qquad (5)$$

Where,
a ml H_2SO_4 for sample
b ml H_2SO_4 for blank
n normality of H_2SO_4
w sample weight (mg)

3.8. RESULTS

The percentage of acidity or alkalinity is reported to the nearest 0.001 %. The standard deviation of three parallel samples is 0.0002 %.

3.9. REFERENCES

MIL-N-246B Military Specification Nitroglycerin, 19 Feb 1962

B.4. NITROGEN CONTENT

4.1. PRINCIPLE

Determination of the nitrogen content of TEGDN by potentiometric titration with Fe(II) using a combined Pt electrode. In sulphuric acid the nitrate ion is reduced to nitrocyl acid and Fe(III) is oxidized to Fe(II) according to the reaction:

$$NO_3 + 2Fe^{3+} + 3H^+ + H_2SO_4 \rightarrow HSO_3NO_2 + 2Fe^{2+} + 2H_2O \qquad (6)$$

4.2. CHEMICALS

Sulfuric acid, 98 % for the determination of nitrogen
$(NH_4)_2Fe(SO_4)_2$ x $6H_2O$, 99 %, for analysis
Deionized water, resistivity 18.2 MΩ cm or equivalent
KNO_3,99.995 % for standardization of titrant

4.3. APPARATUS

Analytical balance with precision of 0.1 mg
Weighing pipette or syringe
Graduated bottle 1000 ml
Titrator
Combined Pt electrode
Titration vessel
Magnetic stirrer
Ice cooled bath or cryostat

4.4. PREPARATION OF REFERENCES

The titrant (0.4 M) is prepared by dissolving 157 g $(NH_4)_2Fe(SO_4)_2$ x $6H_2O$ in 400 ml water in a 1000 ml graduated bottle. The bottle is filled to the mark with sulfuric acid (1:1).

The titrant is standardized with dried KNO_3 (nitrogen content 13.855 %).
Sulfuric acid, a 15 ml portion, is dispensed to the bottom of the titration vessel. Weighed KNO_3 amount (0.20-0.23 g with a precision of 0.1 mg) is added. A volume of 35 ml sulfuric acid is then added along the edges of the vessel. Using magnetic stirrer, dissolving the sample takes six minutes.

4.5. SAMPLE PREPARATION

Sample (0.2 g) is weighed with a precision of 0.1 mg in the titration vessel and 50 ml of concentrated sulfuric acid is added slowly along the edges of the vessel.

4.6. ANALYSIS

Before starting the titration, the titration vessel is cooled down below 10°C. During cooling, the liquid is mixed six minutes with the magnetic stirrer to dissolve the sample. Sample solution is titrated with standardized $(NH_4)_2Fe(SO_4)_2$ (Iron(II) ammonium sulphate), stirring solution with magnetic stirrer using a combined Pt electrode to measure the titration curve.

4.7. CALCULATIONS

Nitrogen content is calculated using formula:

$$N\% = \frac{V_t \cdot c_t \cdot M_N}{m_s \cdot 2} \cdot 100\% \qquad (7)$$

where,

where,	V_t	titrant consumption (*L*)
	c_t	titrant concentration (*mol/L*)
	M_N	Molar mass of nitrogen (*g/mol*)
	m_s	sample weight (*g*)

4.8. RESULTS

The percentage of nitrogen is reported to the nearest 0.01 %. The standard deviation of three parallel samples is 0.05 %. The literature value for the nitrogen content of TEGDN is 11.67 %.

4.9. REFERENCES

Ti Application Note No. T- 37 Nitrogen content of nitrocellulose, Metrohm

B.5. WATER CONTENT, COULOMETRIC TITRATION

5.1. PRINCIPLE

This method uses the Karl Fischer titration technique to quantify the moisture content of TEGDN. The Karl Fischer titration is based on the oxidation of sulfur dioxide by iodine in a methanolic hydroxide solution. In principle, the following chemical reaction takes place:

$$H_2O + I_2 + SO_2 + CH_3OH + 3RN \rightarrow [RNH]SO_4CH_3 + 2[RNH]I \qquad (8)$$

The titration can be performed volumetrically or coulometrically. In the coulometric procedure, the iodine participating in the reaction is generated directly in the titration cell by electrochemical oxidation of iodine until again a trace of unreacted iodine is detected. Water determination is based on measurement of time and current (in coulombs) used to generate the iodine. This method is good for low level moisture determinations. Faraday’s law can be used to calculate the amount of iodine generated from the quantity of electricity required.

5.2. APPARATUS

Automatic coulometric Karl Fisher titrator consisting of a control unit, titration vessel, dual platinum sensing electrode, generator assembly, and magnetic stirrer.

Syringe, 50 µl, gas tight
Serum bottles
Oven, temperature 100 ± 5ºC
Desiccator
Analytical balance with precision of 0.1 mg.

5.3. REAGENTS

Commercial Generator Titrant Solution (catholyte)
Commercial Solvent Titration Solution (anolyte)

5.4. INSTRUMENT SETUP

Clean, dry and assemble the titration chamber as described in the manufacturer’s instructions. Add the anolyte. Add the catholyte. Allow to stabilize as directed in the manufacturer’s instructions.

5.5. SAMPLE PREPARATION

Dry the sample bottles and caps overnight in an oven at 100ºC before using. Allow to cool in a desiccator before filling and sealing. Fill the sample bottle as rapidly as possible and immediately seal.

5.6. PROCEDURE

Withdraw 30 to 50 µL of the sample into the syringe and discard the contents into a waste container. Withdraw into the syringe 30 µL of sample and weigh the syringe and the contents to the nearest 0.1 mg. Start titration and inject the sample slowly into the titration solution. Weigh the syringe to the nearest 0.1 mg to determine the exact sample mass. Allow the titration to proceed until the end point is indicated. Record the micrograms of water determined.

5.7. CALCULATIONS

Calculate the water content in percent in the sample, if the sample weigh was keyed in, or as in formula:

$$Water\ content = \frac{m_w}{m_s \cdot 10\,000} \qquad (9)$$

where, m_W Water found (*µg*)
m_S Sample mass (*g*)

5.8. REPORT

Report the percentage of water to the nearest 0.01 %.

5.9. PRECISION

The precision of the method according the reference ASTM D 6304-07:

repeatability	0.03813 $x^{0.6}$ mass %
reproducibility	0.4243 $x^{0.6}$ mass %

where x is the mean of duplicate measurements.

5.10. REFERENCES

ASTM D 6304-07, “Standard Test Method for Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fisher Titration”

B.6. WATER CONTENT, VOLUMETRIC TITRATION

6.1. PRINCIPLE

This method uses the Karl Fischer titration technique to quantify the moisture content of TEGDN. The Karl Fischer titration is based on the oxidation of sulfur dioxide by iodine in a methanolic hydroxide solution. In principle, the following chemical reaction takes place:

$$H_2O + I_2 + SO_2 + CH_3OH + 3RN \rightarrow [RNH]SO_4CH_3 + 2[RNH]I \qquad (10)$$

The titration can be performed volumetrically or coulometrically. In the volumetric method, a Karl Fischer solution containing iodine is added until the first trace of excess iodine is present. The amount of iodine converted is determined from the burette volume of the iodine-containing Karl Fischer solution. Water determination is based on volumetric measurement of reagent.

6.2. APPARATUS

Automatic volumetric Karl Fisher titrator consisting of a control unit, titration vessel, platinum electrode, generator assembly, and magnetic stirrer.

Analytical balance with precision of 0.1 g.

6.3. REAGENTS

Commercial Titrant Solution
Commercial Solvent Titration Solution
Commercial standard for methanol-water

6.4. INSTRUMENT SETUP

Sample solution is titrated with standardized solution, stirring solution with magnetic stirrer using a combined Pt electrode to measure the titration curve.

6.5. SAMPLE PREPARATION

Dry the sample bottles and caps overnight in an oven at 100ºC before using. Allow to cool in a desiccator before filling and sealing. Fill the sample bottle as rapidly as possible and seal immediately.

6.6. PROCEDURE

Withdraw into the syringe about 0.3 ml of sample and weigh the syringe and the contents to the nearest 0.1 mg. Add about 0.3 g of the sample into a vessel. Start the titration and inject the sample slowly into the titration solution. Weigh the syringe to the nearest 0.1 mg to determine the exact sample mass. Allow the titration to proceed until the end point is indicated. Record the micrograms of water determined.

6.7. CALCULATIONS

Calculate the water content in percent in the sample, if the sample weigh was keyed in, or as in formula:

$$\text{Water content} = \frac{m_w}{m_s \cdot 10\,000} \qquad (11)$$

where, m_W Water found (µg)
m_S Sample mass (g)

6.8. REPORT

Report the percentage of water to the nearest 0.01 %.

B.7. DECOMPOSITION TEMPERATURE BY DIFFERENTIAL SCANNING CALORIMETRY (DSC)

7.1. PRINCIPLE

Analysis of thermal properties of TEGDN is performed by DSC. This technique measures the heat flow to/from a sample as it undergoes transitions in a thermally controlled environment. The STANAG 4515 method is used to determine the decomposition temperature.

7.2. APPARATUS

DSC
Analytical balance, with precision of 0.01 mg
Nitrogen (purge and protective gas) and/or Helium in case the melting point is measured
Gas flow controller
Sample crucibles (Aluminum)
Crucible sealing press

7.3. INSTRUMENT SETUP

A heating rate of 5 K/min is used on the DSC apparatus to determine the decomposition temperature of TEGDN. The measurement starts no higher than 100ºC and ends no lower than 250ºC. Nitrogen is used as purge gas and as protective gas.

7.4. SAMPLE PREPARATION

Sample weighing e.g. about 5 mg is placed in an aluminum crucible equipped with pin holes in the lid. The lid can be crimped.

7.5. ANALYSIS

The onset temperature and the peak temperature of the exotherm shall be reported as the decomposition of TEGDN.

T_{onset}, is measured as the point of intersection of two tangents: one drawn to the curve before commencement of the event, the other to a point on the steepest part of the transition.

T_{peak}, is the temperature at which the peak maximum is observed.

7.6. CALCULATIONS

Measurements are performed with the help of the apparatus software. All exothermic events, endothermic events and temperatures (T_{onset} and T_{peak}) are determined from the DSC curve.

The standard deviation of the obtained temperature result with the heating rate 5 K/min is < 1.0°C.

7.7. EXAMPLE OF THERMOGRAM

This example of thermogram (figure 6) illustrates DSC measurement of TEGDN.

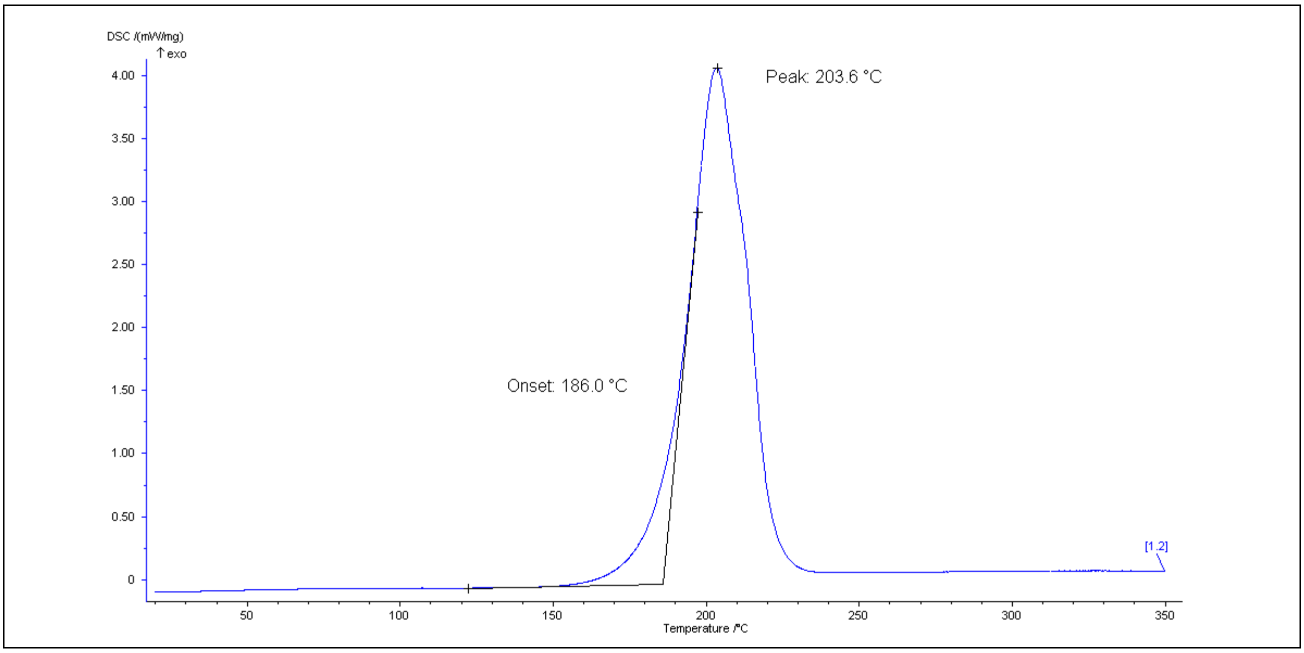


Figure 6: The decomposition temperature of TEGDN

B.8. QUANTITATIVE ANALYSIS OF IMPURITIES

8.1. PRINCIPLE

For the measurement of the inorganic impurities, TEGDN is dissolved in toluene and extracted with water in a separation funnel. The water layer is separated and analyzed by Ion Chromatograph (IC) for the anions (chloride, nitrite, nitrate, sulfate) and by Inductively Coupled Plasma (ICP) for the elements.

8.2. CHEMICALS

Toluene, for analysis
Deionized water, resistivity 18.2 MΩ cm or equivalent
ICP:
Nitric acid 65 % Suprapur® or equivalent
Element standard solutions 1000 mg/l for ICP
Multi-element standard solutions for ICP
IC:
Sodium hydroxide, 50 % (w/w) for analysis
Eluent 28 mMNaOH prepared by diluting 50 % NaOH purchased as certified solution or prepared from analytical grade or equivalent NaOH pellets
Anion stock standard solutions 1000 mg/l for IC (Cl^-, NO_2^-, SO_4^{2-}, NO_3^-) may be purchased as certified solutions or prepared from analytical grade or equivalent potassium or sodium salts

8.3. APPARATUS

Analytical balance with precision of 0.1 mg
Weighing pipette or syringe
Separation funnel 250 ml
ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometer) or ICP-MS (Inductively Coupled Plasma Mass Spectrometer)
IC (Ion Chromatograph) with conductivity detector and suppressor
Analytical column and guard column for analysis of inorganic anions

NOTE: *The glassware and auto-sampler tubes must be rinsed carefully several times with deionised water just before use. The insufficient rinsing can be seen in the concentrations of sample blanks.*

8.4. INSTRUMENT SETUP

ICP (example of operating conditions):

RF power	1150 W (metals)/950 W (alkali metals)
Plasma gas flow (Ar)	12 L/min/10 L/min
Nebulizer gas flow (Ar)	0.5 L/min/0.65 L/min
Auxiliary gas flow (Ar)	0.5 L/min
Spray chamber	Cyclonic
Nebulizer	Concentric

IC (example of operating conditions):

Columns	IonPac AG18 Guard, IonPac AS18 Analytical (quaternary ammonium phase)
Eluent	28 mMNaOH
Eluent flow	1 ml/min
Sample loop	100 µl
Detector	Suppressed conductivity detector
Suppressor	Electrolytically regenerated suppressor (low background level), current 75 mA
Total analysis time	15 min

8.5. PREPARATION OF REFERENCES

8.5.1. ICP

For screening method, only blank and 1000 µg/l multi-element standard solutions are prepared by diluting 1000 mg/l stock solution.

For quantitative analysis, 10 000 µg/l stock standard solution, containing all analytes found with the screening method, is prepared from single element standard solutions. The standard solutions, blank and five different concentrations, are prepared by diluting stock solution. The nitric acid (HNO_3) content is the same as in samples (1- 5 %).
The control sample(s) is/are made from the multi-element standard solution by diluting near to the concentration of the samples.

8.5.2. IC

Depending on the anion concentration expected, use anion stock solutions to prepare five to ten calibration solutions covering the expected working range as evenly as possible.

8.6. SAMPLE PREPARATION

Approximately 10 g TEGDN is accurately weighed with a precision of 0.1 mg and dissolved in 50 ml toluene. This mixture is extracted two times with 10 ml of water. Three parallel samples are made.

Sample blank determinations, the first extraction and after every set of three parallel samples, are done with toluene extracted two times with 10 ml of water.

The water extracts are divided in two parts directly into the rinsed auto-sampler tubes, one is for ICP analysis and the other for IC analysis.
For the ICP measurement, the samples are made to the same acid content ascontrols and standards (acid content 1- 5 %).

For the IC measurement, the sample (water extract) is analysed as it stands.

8.7. ANALYSIS

8.7.1. ICP

First the samples are analysed with the qualitative screening method to find out the possible analytes. For the quantitative analysis, the concentrations of analytes in the standards and the control samples can be estimated by the results of the screening method.

8.7.2. ICP & IC

Standards and controls are analysed first, then the extracts of the sample blanks and samples in the same order as they were extracted.

8.8. CALCULATIONS

The detection and quantitation limits are instrument and method specific and should be confirmed prior to the measurement. The sample blanks should contain only trace amount of analytes and this amount should be nearly the same in all sample blanks.

8.8.1. ICP

$$\text{Analyte mg/kg} = \frac{c \times df \times V}{m} \qquad (12)$$

where,
c ICP result for the analyte (µg/L)
df dilution factor (because of acid addition)
V volume of water in the extraction (L)
m sample mass (g)

8.8.2. IC:

$$\text{Analyte mg/kg} = \frac{c \times V \times 1000}{m} \qquad (13)$$

where,		
	c	IC result for the analyte (mg/l)
	V	volume of water in the extraction (L)
	m	sample mass (g)

B.9. TEMPERATURE OF IGNITION

9.1. PRINCIPLE

The thermal sensitivity of TEGDN is assessed by determining the deflagration/ignition temperatureof the sample. The sample is heated at constant heating rate until it is ignited. The procedure given in STANAG 4491 section B1 shall be used.

9.2. CHEMICALS

TEGDN

9.3. APPARATUS

Balance with precision of 1 mg
Heating block
Temperature controller with accuracy ±0.2 ºC
Glass test tubes

9.4. SAMPLE PREPARATION

The sample is kept at standard room temperature for one day prior to the analysis.

9.5. ANALYSIS

200 mg of TEGDN is heated in the glass tube placed in a steel block. The start temperature for the sample is 90ºC. The block is heated at constant heating rate 5°C/min, until an event occurs.

9.6. CALCULATIONS

The reaction is either burning of the sample with flame or rapid decomposition (puff or smoke). The result of the test is reported as a ‘’Temperature of ignition’’ and is the lowest temperature at which the reaction is observed of at least three parallel tests.

B.10. THERMAL STABILITY BY HEAT FLOW CALORIMETRY (HFC)

10.1. PRINCIPLE

The test is based on measuring heat flow (µW) and heat energy (J) from a sample heated at a constant temperature for a specified time. A maximum cumulative heat is used as a criterion for sufficient chemical stability. The procedure is based on STANAG 4582.

10.2. CHEMICALS

TEGDN

10.3. APPARATUS

Heat flow calorimeter equipment with a measuring range corresponding to 10 to 500 µW/g
Glass ampoules with a minimum volume of 2 cm^3 which can be hermetically sealed
Appropriate data collecting and calculating system
Analytical balance with precision of 1 mg
Standard laboratory glassware

10.4. INSTRUMENT SETUP

The sample material is placed in a vessel, which is placed in close contact with a heat flow detector. Two identical measuring units of equal sensitivity (one for reference) are used. The bath is heated to the appropriate test temperature and allowed to stabilize for a few hours. The test temperature is either 70ºC, 80ºC or 85ºC. The corresponding length of the test is 34.8 d, 10.6 d or 5.98 d, respectively.

10.5. SAMPLE PREPARATION

Fill the sample ampoule up to the top so that the amount of air inside is minimal. A minimum of two tests shall be conducted. As an example, a weight of 5.1 g was used with a 4 ml ampoule.

10.6. ANALYSIS

Heat the bath up to desired temperature. Allow the bath to stabilize for a few hours. Place the test sample and reference ampoule into the apparatus according to the equipment manufacturer's manual. Temperature equilibration must be attained before actual measurement is started. Measure the heat generation rate of the TEGDN sample for the time period corresponding to the test temperature.

10.7. CALCULATIONS

The data must be normalised to one gram of TEGDN. Determine the maximum cumulative heat at the end of the test, which must not exceed a limit value of 10 J/g. The standard deviation for 24 identical samples measured at 85ºC was 0.8.

10.8. EXAMPLES OF HEAT FLOW AND CUMULATIVE HEAT CURVES

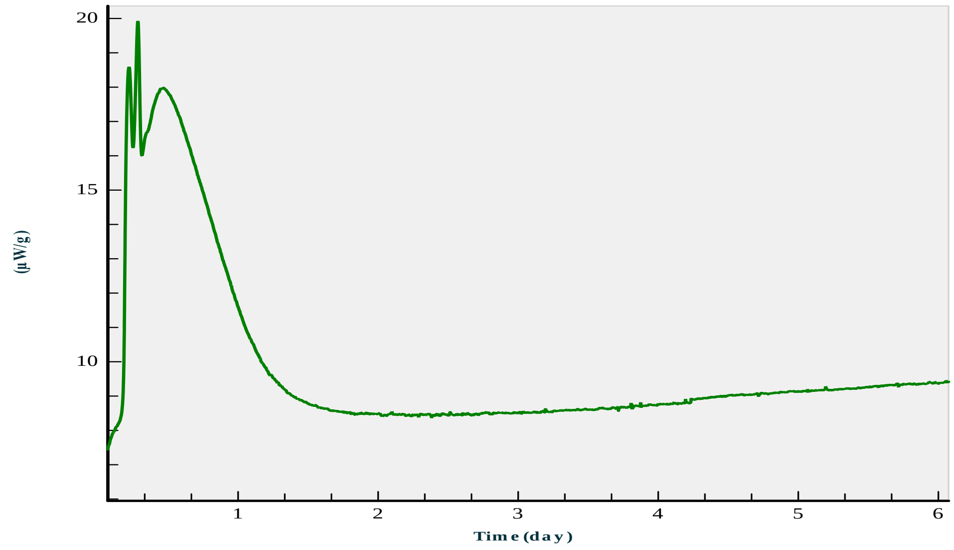


Figure 4.The heat flow curve for TEGDN at 85ºC.

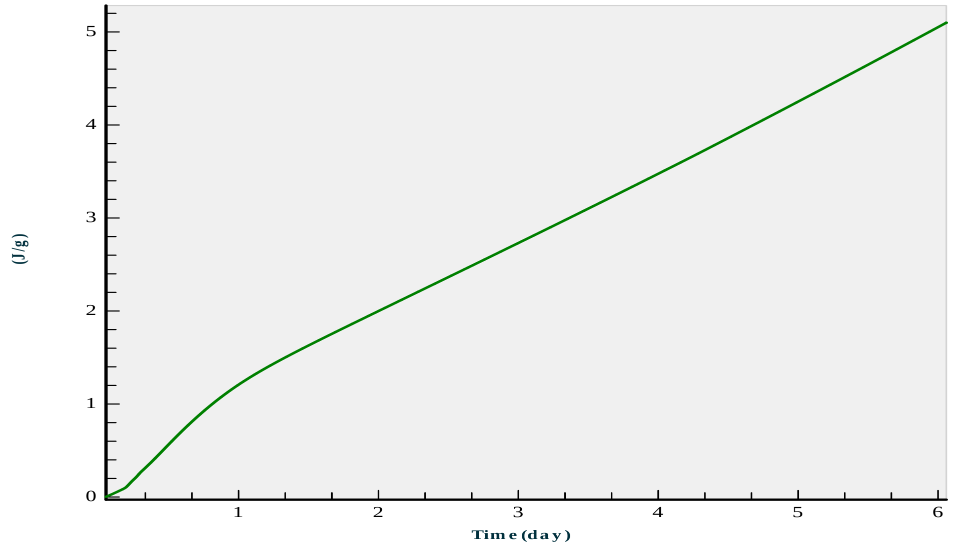


Figure 5.The cumulative heat curve for TEGDN at 85ºC.

INTENTIONALLY BLANK

AOP-4719(A)(1)