

INCH-POUND

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SUPERSEDING

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PERFORMANCE SPECIFICATION

PROPELLANTS, DINITROGEN TETROXIDE



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MIL-PRF-26539F

PARAGRAPH	CONTENTS	PAGE
1	SCOPE	1
1.1	Scope.....	1
1.2	Classification.....	1
2	APPLICABLE DOCUMENTS	1
2.1	General	1
2.2	Government documents	1
2.2.1	Specifications, standards, and handbooks.....	1
2.3	Non-Government publications	2
2.4	Order of precedence.....	2
3	REQUIREMENTS.....	2
3.1	Chemical composition and physical properties	2
3.2	Limiting values	2
3.3	Filter	2
3.4	Qualitative	2
3.5	Leakage	3
4	VERIFICATION	4
4.1	Classification of inspections	4
4.2	Quality conformance inspection	4
4.2.1	Individual tests	4
4.2.2	Sampling tests	4
4.2.2.1	Sampling Plan	4
4.2.2.1.1	Sample.....	4
4.2.2.1.1.1	Sampler.....	4
4.2.2.1.2	Cylinders, portable tanks, cargo tanks, tank cars and other containers	5
4.2.2.1.3	Method of taking sample	5
4.2.3	Rejection.....	5
4.3	Test methods.....	5
4.3.1	Examination of product.....	5
4.3.2	Nitric oxide (NO) content	5
4.3.2.1	Nitric oxide assay	5
4.3.2.1.1	Tared sample	5
4.3.2.1.2	Procedure	5
4.3.2.1.3	Calculation	6
4.3.2.2	Alternate procedure	6
4.3.2.2.1	Preparation	6
4.3.2.2.2	Procedure	6
4.3.2.2.3	Calibration curve.....	7
4.3.3	Dinitrogen tetroxide assay	11
4.3.3.1	Preparation of sample	11
4.3.3.1.1	Oxidation state.....	11
4.3.3.1.1.1	NTO composition	11
4.3.3.1.1.2	MON composition	11
4.3.3.1.2	Sample sealing	11
4.3.3.2	Procedure	11
4.3.3.3	Calculation	11
4.3.3.4	Reagents	12
4.3.4	Water equivalent.....	12
4.3.4.1	Near infrared absorption method.....	12
4.3.4.1.1	Preparation	12

MIL-PRF-26539F

4.3.4.1.2	Procedure	13
4.3.4.1.3	Calculations	13
4.3.4.2	Gas chromatographic method	14
4.3.4.2.1	Analytical apparatus	14
4.3.4.2.2	Procedure	16
4.3.4.2.3	Calculation	16
4.3.4.2.4	Calibration	16
4.3.5	Chloride content	17
4.3.5.1	Silver nitrate titration method	17
4.3.5.1.1	Sample preparation	17
4.3.5.1.2	Procedure	17
4.3.5.1.3	Calculation	17
4.3.5.1.4	Calibration	18
4.3.5.2	Colorimetric method	18
4.3.5.2.1	Procedure	18
4.3.5.2.2	Calculation	18
4.3.6	Nonvolatile residue	18
4.3.6.1	Procedure	18
4.3.6.2	Calculation	19
4.3.7	Iron content	19
4.3.7.1	Procedure	19
4.3.7.2	Calculation	19
4.3.7.3	Calibration	20
4.3.8	Particulate	20
4.3.8.1	Preparation of the membrane filter	20
4.3.8.2	Sampling	20
4.3.8.3	Procedure	20
4.3.8.4	Calculation	20
4.4	Leakage	20
5	PACKAGING	20
5.1	Packaging	20
6	NOTES	21
6.1	Intended use	21
6.2	Acquisition requirements	21
6.3	Part or identifying number (PIN)	21
6.4	Definitions	21
6.4.1	Particulate	21
6.4.2	Single-phase liquid	21
6.5	Subject term (key word) listing	22
6.6	Changes from previous issue	22
TABLE		
I	Chemical composition and physical properties	3
II	Conditions for the spectrophotometer	13
FIGURE		
1.	Nitric oxide sampler apparatus	8
2.	Stainless steel absorption cell	9
3.	Glass absorption cell	10
4.	Water equivalent apparatus, schematic	15

MIL-PRF-26539F

This specification is approved for use by all Departments and Agencies of the Department of Defense.

1. SCOPE

1.1 Scope. This specification covers the requirements for all types of dinitrogen tetroxide (N₂O₄) propellants.

1.2 Classification. Dinitrogen tetroxide propellants will be of the following designated types as specified (6.2).

Types

NTO	- Nominal 99.5% N ₂ O ₄ purity with red-brown color.
MON-1	- Nominal 99% N ₂ O ₄ and 1% NO with green color.
MON-3	- Nominal 97% N ₂ O ₄ and 3% NO with green color.
MON-10	- Nominal 90% N ₂ O ₄ and 10% NO with green color.
MON-15	- Nominal 85% N ₂ O ₄ and 15% NO with green color.
MON-25	- Nominal 75% N ₂ O ₄ and 25% NO with green color.

All MON types must meet a maximum limit of 0.5 parts per million iron.

2. APPLICABLE DOCUMENTS

2.1 General. The documents listed in this section are specified in sections 3, 4, or 5 of this specification. This section does not include documents cited in other sections of this specification or recommended for additional information or as examples. While every effort has been made to ensure the completeness of this list, document users are cautioned that they must meet all specified requirements of documents cited in sections 3, 4, or 5 of this specification, whether or not they are listed.

2.2 Government documents.

2.2.1 Specifications, standards, and handbooks. The following specifications, standards and handbooks form a part of this document to the extent specified herein. Unless otherwise specified, the issues of these documents are those cited in the solicitation or contract.

COMMERCIAL ITEM DESCRIPTIONS

A-A-58092	Tape, Antiseize, Polytetrafluoroethylene
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DEPARTMENT OF DEFENSE SPECIFICATIONS

MIL-PRF-25508	Propellant, Oxygen
MIL-PRF-27401	Propellant, Pressurizing Agent, Nitrogen
MIL-PRF-27407	Propellant, Pressurizing Agent, Helium

(Copies of these documents are available online at <http://assist.daps.dla.mil> or from the Standardization Document Order Desk, 700 Robbins Avenue, Bldg 4D, Philadelphia PA 19111-5094.)

MIL-PRF-26539F

2.3 Non-government publications. The following documents form a part of this document to the extent specified herein. Unless otherwise specified, the issues of these documents are those cited in the solicitation or contract.

AMERICAN CHEMICAL SOCIETY (ACS)

ACS Reagent Chemical Standards

(Copies of these documents are available online at <http://pubs.acs.org> or the American Chemical Society, 1155 Sixteenth Street, NW, Washington, DC 20036.)

AMERICAN SOCIETY FOR TESTING AND MATERIALS, INC. (ASTM)

ASTM E 29

Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications (DoD Adopted)

(Copies of these documents are available online at <http://www.astm.org> or the American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken PA 19428-2959)

2.4 Order of precedence. In the event of a conflict between the text of this document and the references cited herein (except for related specification sheets), the text of this document takes precedence. Nothing in this document, however, supersedes applicable laws and regulations unless a specific exemption has been obtained.

3. REQUIREMENTS

3.1 Chemical composition and physical properties. The chemical composition and physical properties of the propellants shall conform to Table I.

3.2 Limiting values. The following applies to all specified limits in this specification: For purposes of determining conformance with these requirements, an observed value or a calculated value shall be rounded off "to the nearest unit" in the last right-hand digit used in expressing the specification limit according to the rounding-off method of ASTM Practice E 29, Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications.

3.3 Filter. A filter with a rating of at least 10 micrometer nominal and 40 micrometer absolute rating shall be installed between the manufacturer's plant and the container to be filled for delivery.

3.4 Qualitative. The propellant shall be a clear, single-phased liquid when examined visually by transmitted light according to 4.3.1. Type NTO shall be red-brown in color; type MON compositions shall be green in color.

MIL-PRF-26539F

TABLE I. Chemical composition and physical properties.

Composition	NTO (Red-Brown)	MON-1 (Green)	MON-3 (Green)	MON-10 (Green)	MON-15 (Green)	MON-25 (Green)	Test Paragraph
N ₂ O ₄ assay % wt, MIN	99.5	----	----	----	----	----	4.3.3
NO content %wt, MAX %wt, MIN	\1	1.0 0.6	3.0 2.5	11.0 10.0	16.0 15.0	26.0 25.0	4.3.2
N ₂ O ₄ + NO %wt, MIN	----	99.5	99.5	99.5	99.5	99.5	4.3.3
Water equivalent %wt, MAX	0.17	0.17	0.17	0.17	0.17	0.17	4.3.4
Chloride content %wt, MAX ^{\2}	0.040	0.040	0.040	0.040	0.040	0.040	4.3.5
Nonvolatile residue mg/L, MAX	----	10.0	10.0	10.0	10.0	10.0	4.3.6
Iron content ppm wt, MAX	----	0.5	0.5	0.5	0.5	0.5	4.3.7
Particulate mg/L, MAX	10.0	10.0	10.0	10.0	10.0	10.0	4.3.8
<p>NOTES</p> <p>\1. The NO content shall be limited to that which does not change the specified red-brown color of the propellant (3.4)</p> <p>\2. The chloride test need not be performed on any propellant type if the material was manufactured by the ammonia oxidation process</p>							

3.5 Leakage. Shipping containers shall not leak when tested according to 4.4.

MIL-PRF-26539F

4. VERIFICATION

4.1 Classification of inspections. The inspections shall be classified as quality conformance inspections (see 4.2).

4.2 Quality conformance inspection. The quality conformance inspection shall consist of the following:

a. Individual tests4.2.1

b. Sampling tests4.2.2

4.2.1 Individual tests. The propellant shall be subjected to the following test as described under 4.3 and 4.4.

Examination of product4.3.1

Leak Test.....4.4

4.2.2 Sampling tests. The propellant shall be selected according to 4.2.2.1 and subjected (as appropriate to the designated type) to the following tests as described under 4.3:

a. Nitric oxide content4.3.2

b. Dinitrogen tetroxide assay4.3.3

c. Water equivalent4.3.4

d. Chloride content4.3.5

e. Nonvolatile residue4.3.6

f. Iron content4.3.7

g. Particulate4.3.8

4.2.2.1 Sampling plan.

4.2.2.1.1 Sample. A sample shall consist of not less than 800 milliliters (mL) of propellant for all tests specified in 4.2.2. Unless otherwise specified, quality conformance tests shall be performed on each sample of the propellant taken directly from the shipping containers (other than the container loading filter specified in paragraph 3.3, product sampled shall not be exposed to additional filtration prior to sample analysis). When required, samples shall be forwarded to a laboratory designated by the procuring activity for subjection to the quality conformance tests specified herein.

4.2.2.1.1.1 Sampler. The sampler(s) shall be capable of accepting a minimum of 400 mL of product and constructed of 300 series stainless steel. The top and bottom valves and any outlets or welds shall also be of 300 series stainless steel. Samplers shall be precleaned in a manner such as to preclude contamination of propellant samples.

MIL-PRF-26539F

4.2.2.1.2. Cylinders, portable tanks, cargo tanks, tank cars and other containers. A sample shall be taken from each individual shipping container.

4.2.2.1.3 Method of taking sample. Samples taken from the shipping container shall be representative of the entire contents of the container. The container's dip tube must be completely purged of product prior to taking the sample (approximately 2.0 liters).

4.2.3 Rejection. When any sample of the propellant tested in accordance with 4.3 fails to conform to the requirements specified herein, the entire contents of the shipping container represented by the sample shall be rejected.

4.3 Test methods.

4.3.1 Examination of product. The sample (4.2.2.1.2) shall be examined with transmitted light to satisfy the qualitative requirements. Place 100 mL of sample in a clean, clear glass container (graduated cylinder or large test tube), cool in an ice-bath for 10 minutes, wipe dry, and examine visually by transmitted light from a light bulb or sunlight. The presence of visible sediment in the sample shall be cause for rejection.

4.3.2 Nitric oxide (NO) content. The NO content of MON type samples shall be determined by the procedure specified in 4.3.2.1 or by the alternate procedure described in 4.3.2.2. In the event of dispute, the procedure specified in 4.3.2.1 shall be used as the referee method.

4.3.2.1 Nitric oxide assay. The NO content of the sample shall be determined by the following method.

4.3.2.1.1 Tared sample. Evacuate and weigh to the nearest 0.001 gram (g) a sample bomb of approximately 60 mL capacity, fitted with a needle valve. Support the sampler in a vertical position on a ring stand in a hood. Connect the sample bomb to the sampler and provide for evacuating the connecting line. Evacuate the connecting line, then, open the sample bomb and sampler valves. Transfer 40 to 60 g of the sample. Close all valves and then evacuate the connecting line. Disconnect the sample bomb and flush the exposed opening of the valve with nitrogen gas conforming to MIL-PRF-27401, until residual N_2O_4 disappears. Accurately reweigh the sample bomb to the nearest 0.001 g, obtaining the sample weight by difference. If sample weight is below 40 g, another sample shall be taken.

4.3.2.1.2 Procedure. Attach a rotameter with stainless steel tubing to the reducing valve of a cylinder of oxygen (O_2) gas conforming to MIL-PRF-25508. Connect a length of $\frac{1}{16}$ inch stainless steel tubing to the exit end of the rotameter. Open the cylinder valve and purge residual air from the connecting lines and rotameter. Immediately attach the sample bomb to the other end of the $\frac{1}{16}$ inch tubing and, using the reducing valve, adjust the oxygen pressure to 30 pounds per square inch (psi). Close the cylinder valve. Place the sample bomb in an ice bath and maintain the temperature at approximately 32°F (0°C). After the sample has been allowed to cool for 10 minutes, permit O_2 to flow into the sample bomb by first opening the cylinder valve and then the bomb valve. Occasionally shake the bomb to hasten absorption and oxidation. Lack of O_2 flow through the rotameter indicates completion of reaction. Allow the sample bomb to remain in the ice bath for 15 minutes, with valves open after reaction has been completed. Disconnect the sample bomb, remove from the bath, warm to ambient temperature and wipe dry. Place on a balance and record the weight to the nearest 0.001 g.

MIL-PRF-26539F

4.3.2.1.3 Calculation. The percent NO shall be calculated by the following formulas:

$$x = B - A$$

$$y = C - B$$

$$\text{NO, percent by wt} = \frac{\left[y - 0.003857 \left(z - \frac{x + y}{1.49} \right) \right] 187.5}{x} - 0.15$$

where:

x = sample weight in grams.

y = O₂ weight in grams.

z = volume of sample bomb in mL. Determined by difference in weight from evacuated and water filled.

A = weight of empty sample bomb in grams.

B = weight of sample bomb plus sample in grams.

C = weight of sample bomb plus sample and O₂ in grams.

4.3.2.2 Alternate procedure.

4.3.2.2.1 Preparation. Clamp the sampler specified in 4.3.2.1 to a stand as shown in Figure 1. Attach a ¹/₁₆ inch ID length of polytetrafluoroethylene tubing to the outlet valve. Place another length of ¹/₁₆ inch ID polytetrafluoroethylene tubing in a beaker containing a strong NaOH solution. Set this apparatus up in a fume hood in which low pressure gaseous nitrogen, conforming to MIL-PRF-27401, is available for purging excess N₂O₄ from the ¹/₁₆ inch ID polytetrafluoroethylene tubing. The flow-through spectrophotometric cell depicted shall conform to the following:

- 2.00 ± 0.02 mm sample path length.
- Coolant jacket for sample temperature control.
- Constructed of material compatible with N₂O₄.
- Constructed to fit instrument cell compartment.

Figure 2 and 3 show suggested designs. Maintain the temperature of the flow-through cell at 32 ± 1.8°F (0 ± 1°C) by connecting the cell to a circulating ice-water glycol (20:1) bath located at the apparatus in the fume hood and/or at the spectrophotometer. Maintain a purge of low pressure gaseous nitrogen, conforming to MIL-PRF-27401, in the spectrophotometer cell compartment or on the cell assembly to prevent condensation of moisture on the cell windows when the cell is in the spectrophotometer.

4.3.2.2.2 Procedure. Clamp a cylinder containing red-brown dinitrogen tetroxide (NTO) in the apparatus according to Figure 1. Connect the spectrophotometric cell to the cylinder by means of ¹/₁₆ inch ID polytetrafluoroethylene tubing. Purge the cell with dry nitrogen for several minutes. Close the inlet and outlet valves. Connect the cold bath to the cell and precool by pumping coolant for several minutes. Open the lower valve on the N₂O₄ cylinder slightly and control the sample flow with the cell

MIL-PRF-26539F

valves. Pass several cell volumes (at least 10 mL) of sample through the cell. Make sure the cell is free of bubbles, then close the cell outlet and inlet valves and the N_2O_4 cylinder valve, in that order. If possible, purge the cell with dry nitrogen before cooling, using several cell volumes of sample, and then checking for the absence of bubbles. Place the cell in the spectrophotometer cell compartment and connect to an ice-water-glycol bath through suitable tubing. Allow the coolant to circulate for approximately 5 minutes. Set the absorbance to zero (100%T) at a wave length of 700 nm. Remove the cell to the apparatus (Figure 1) in the hood and expel the N_2O_4 into the scrubber with a low pressure stream of nitrogen. Repeat the above procedure substituting the sampler. The temperature of the sampler should be $77 \pm 3.6^\circ\text{F}$ ($25 \pm 2^\circ\text{C}$). Measure the absorbance of the sample at $32 \pm 1.8^\circ\text{F}$ ($0 \pm 1^\circ\text{C}$) and at a wave length of 700 nm. Determine the NO percent by weight from a calibration curve prepared according to 4.3.2.2.3.

4.3.2.2.3 Calibration curve. A calibration curve shall be prepared as follows: Weigh accurately 58.164 g of ACS reagent grade or equivalent nickel nitrate hexahydrate $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$, to make 100 mL of a 2.0M stock solution. In a similar manner weigh out 26.008 g of sodium azide (NaN_3) to make 100 mL of a 4M stock solution. Filter or decant the latter after allowing it to stand overnight. Standard A, equivalent to 0.5 wt% NO, is prepared by placing exactly 1.00 mL of the 2M Ni^{2+} solution in a 50 mL beaker. Add 4.00 mL of the 4M NaN_3 solution and 15.0 mL distilled water and mix. Standard B, equivalent to 0.86 wt% NO, is prepared by mixing 1.00 mL of the 2M Ni^{2+} solution with 4.0 mL of the 4M NaN_3 solution, and 8.34 mL of distilled water in a second 50 mL beaker. Fill a 5.0 mm absorption cell with distilled water as a blank. Set the spectrophotometer at 700 nm. Set the blank at 100%T (0 absorbance). Determine the absorbance of standards A and B in the same 5.0 mm cell at 700 nm. Plot the absorbance of Standards A and B versus the equivalent wt% NO (x-axis) and draw a straight line through the origin (0 wt% NO). The mixed synthetic standard solutions are stable for 48 hours. The sodium azide stock solution is stable for 30 days in the dark. The nickel nitrate stock solution is stable indefinitely.

MIL-PRF-26539F

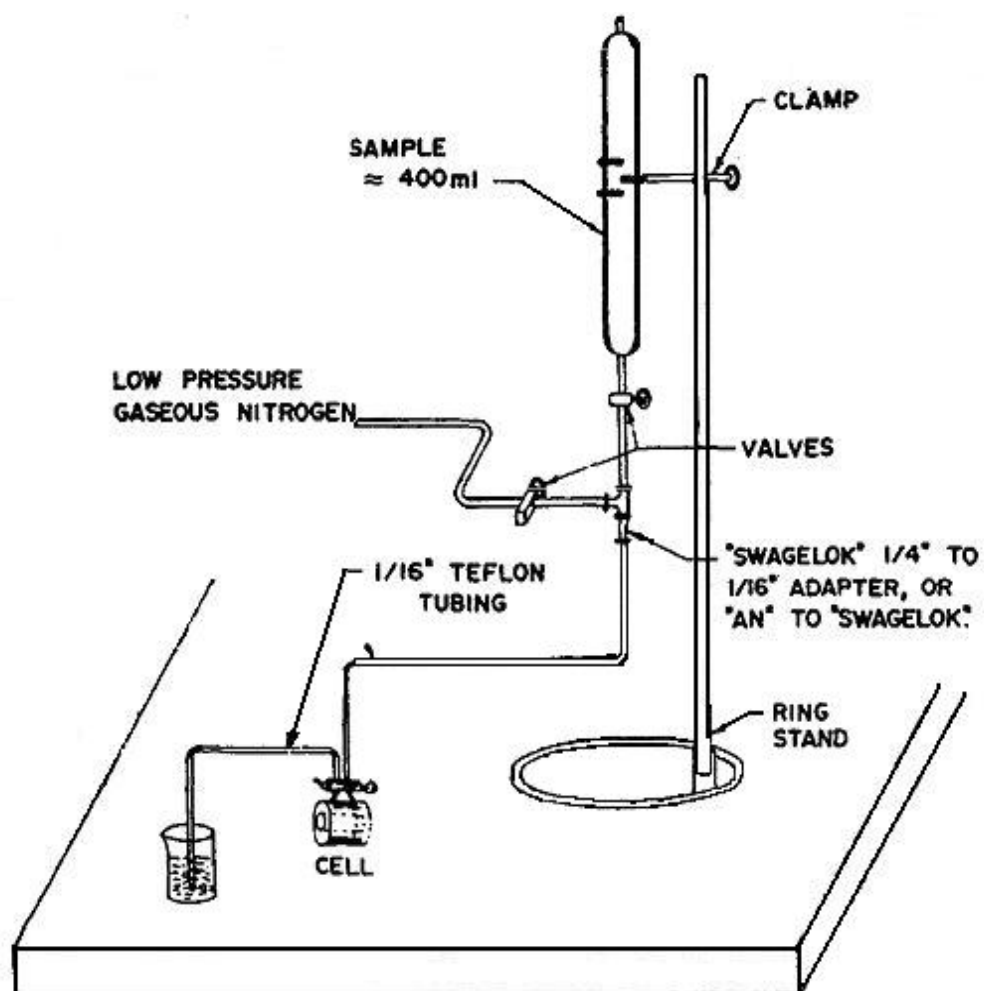


FIGURE 1. Nitric oxide sampler apparatus.

MIL-PRF-26539F

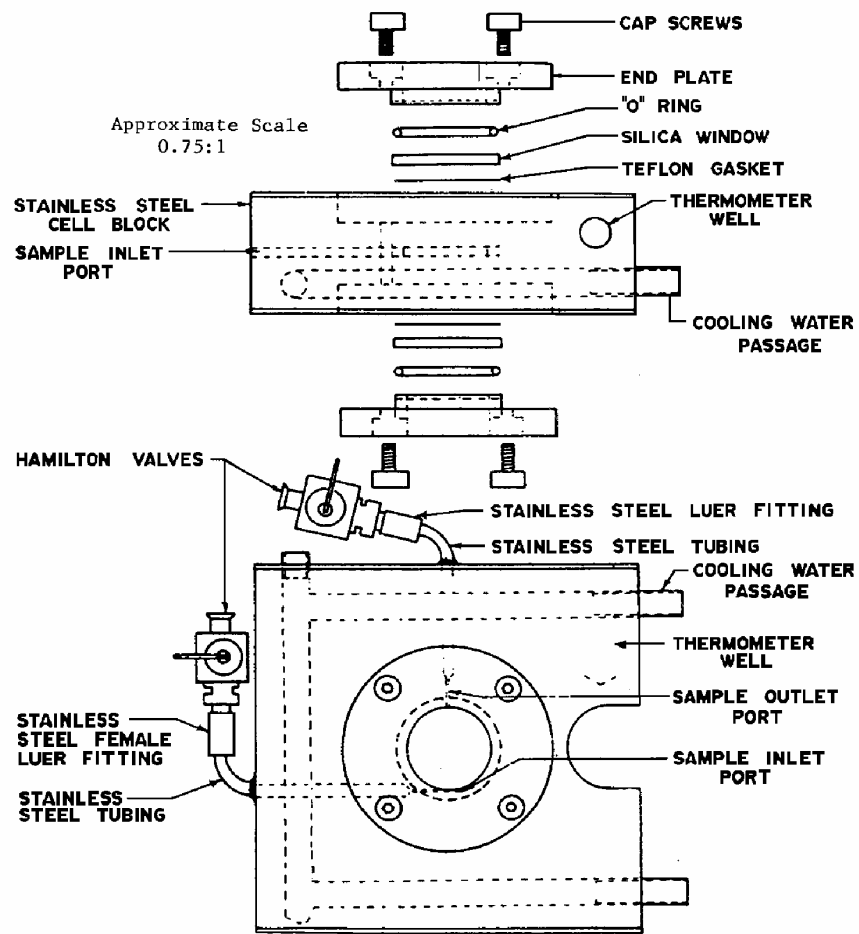


FIGURE 2. Stainless steel absorption cell.

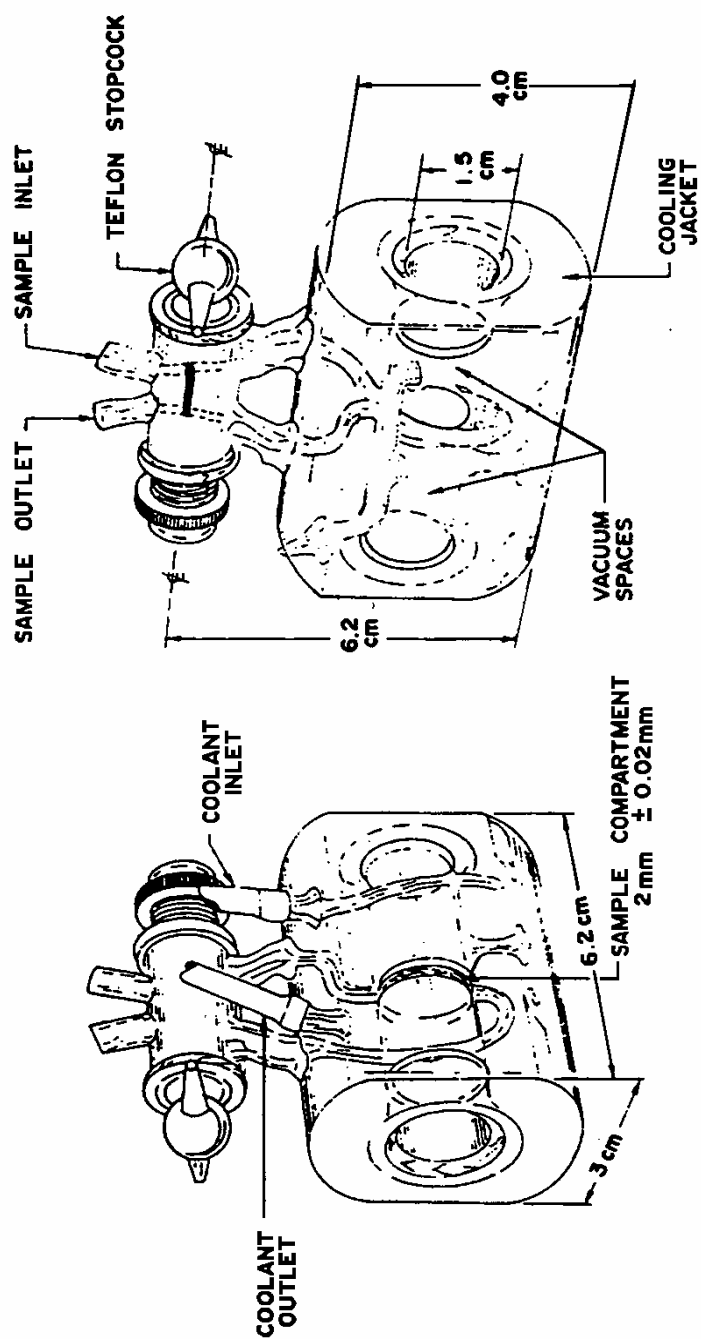


FIGURE 3. Glass absorption cell.

MIL-PRF-26539F

4.3.3 Dinitrogen tetroxide assay. The N_2O_4 content of the sample shall be determined by the following procedure.

4.3.3.1 Preparation of sample.

4.3.3.1.1 Oxidation state. Prior to the weighing and sealing of the assay sample, comply with one of the following requirements.

4.3.3.1.1.1 NTO composition. NTO shall be assayed without further chemical treatment. Proceed to 4.3.3.1.2 and then to 4.3.3.2.

4.3.3.1.1.2 MON composition. The N_2O_4 assay of MON material shall be performed without further chemical treatment on the oxidized sample specified in 4.3.2.1. Proceed to 4.3.3.1.2 and to 4.3.3.2. If the NO content of the MON material was determined by the alternate method (spectrophotometric), then, a 10 – 15 mL sample shall be oxidized as specified in 4.3.2.1 before proceeding to 4.3.3.1.2 and 4.3.3.2 below.

4.3.3.1.2 Sample sealing. Cool the sample to approximately 32°F (0°C) with crushed ice. Introduce the cooled sample into a clean, weighed (2 mL) glass ampoule directly from the sampler through a $\frac{1}{16}$ inch stainless steel tube. Insert the ampoule tip into an adequate size polyvinylchloride tube, approximately 6 inches long. Freeze the contents of the ampoule by placing in a tray of crushed dry-ice or by some other appropriate method. Lift the ampoule containing frozen N_2O_4 and wrap it with a piece of soft paper, and remove the polyvinylchloride tube. Seal the ampoule in the hot flame of a CH_4/O_2 or H_2/O_2 torch by rotating at an angle. Test for leakage. Wash, dry, and weigh the ampoule. Sample sizes should average approximately 1.3 g when 0.5N alkali is used in 4.3.3.2. (Alternate procedures may be used provided sample integrity is not compromised).

4.3.3.2 Procedure. Place the sealed ampoule into a heavy-walled glass stoppered Pyrex bottle, or iodine flask, containing 100 mL of water plus 20 mL of 30% hydrogen peroxide. Chill contents in ice water or some other appropriate method. Lubricate the stopper with stopcock grease and insert it into the ground glass neck of the bottle and/or flask. Break the sealed ampoule by shaking vigorously, keeping the stopper firmly in place. Continue shaking until all brown fumes disappear. Return the bottle or flask to the ice water to keep the contents cool. Shake the bottle from time to time over a 15 minute period. Remove the stopper, rinse it off with distilled water into the contents of the bottle or flask, and replace it with an air condenser. Remove this assembly from the ice water and place on a steam bath or hot plate at moderate heat setting (approximately 250°F/120°C) for 45 minutes. Allow the contents to cool to ambient temperature. Rinse the air condenser carefully and remove it. Pulverize the broken glass of the ampoule with the flat end of a heavy glass rod. Rinse the rod with distilled water into the bottle or flask. Add 3 – 5 drops of methyl red indicator and titrate with 0.5 N NaOH solution to the end point. Run a reagent blank in the same manner as the sample.

MIL-PRF-26539F

4.3.3.3 Calculation. The wt % N_2O_4 shall be calculated by the following formula:

NTO

$$\text{N}_2\text{O}_4, \text{ percent by weight} = \frac{(a - b)N \times 4.6008}{W}$$

where:

a = mL NaOH for sample.

b = mL NaOH for blank.

N = normality of NaOH.

W = grams of N_2O_4 in ampoule.

4.3.3.4 Reagents The following reagents shall apply as test conditions of 4.3.3.

(1) Sodium hydroxide solution, 0.5N: Dissolve 20 g of ACS, or equivalent, reagent grade, low carbonate, NaOH in distilled water in a 1000 mL volumetric flask. Allow to cool and dilute to the mark with distilled water. Standardize this solution with standard potassium acid phthalate (KHP) to the phenolphthalein end point. Store the 0.5N NaOH in a polyethylene container and ensure the exclusion of carbon dioxide during storage.

(2) Distilled water.

(3) Potassium acid phthalate (Primary Standard Grade): Dry at 105 °C for 2 hours. Weigh to ± 0.1 mg and dissolve in distilled water.

(4) Phenolphthalein indicator solution: 1 g in 100 ml of anhydrous denatured ethyl alcohol

(5) Hydrogen peroxide, ACS, or equivalent, reagent grade, 30% wt.

(6) Methyl Red indicator solution: 0.1g in 100 ml of distilled water.

4.3.4 Water equivalent. The water equivalent of the sample shall be determined by one of the following procedures. In the event of dispute, the procedure specified in 4.3.4.1 shall be the referee method.

4.3.4.1 Near infrared absorption method.

4.3.4.1.1 Preparation. Optimize the conditions of the spectrophotometer. Table II shows suggested parameters for initial setup. These parameters will vary depending on model of spectrophotometer. Set the temperature of a circulating low temperature bath to $21.2 \pm 1.8^\circ\text{F}$ ($-6 \pm 1^\circ\text{C}$). Attach the cell to the cooling bath and start the circulation. Purge the sample compartment with nitrogen gas conforming to MIL-PRF-27401 so that the cells do not become coated with moisture. Throughout the procedure, minimize the exposure of the oxidized N_2O_4 to the atmosphere.

MIL-PRF-26539F

TABLE II. Conditions for the spectrophotometer.

Method	Scan/Manual
01 Ord/Absc Mode	Abs/WL
02 Slit/Gain/Sens	2.00 nm/ /2
03 Scan Speed	240 nm/min
04 Response	0.5 S
05 Lamp/Det	319.2 / 860.8 nm
06 Cycles/Time	1 / 0.05 min
07 Peak Threshold	0.01 A
08 Recorder	SERIAL / DASH 1
09 Ord Min/Max	.0000 / 0.500
10 Absc Min/Max	1300.0 / 1650.0
11 Abscissa Format	20 nm/cm
12 Printer	/ SCALE /

4.3.4.1.2 Procedure. Transfer some of the oxidized N₂O₄ to a small cooled Erlenmeyer flask. Load the cell from the flask, using a cooled 2 mL syringe, then, place the loaded cell in sample beam of the spectrophotometer. Place an empty cell in the reference beam. Set the spectrophotometer to 1300 nm, then, zero the instrument. Push the RUN/STOP button to start the scan. The absorption of the HNO₃ band pass has to be measured from the baseline which is found by connecting the minimal points at 1430 nm and 1615 nm. The band pass of atmospherical (free) water can be found by entering 1404 PEAK FIND. Record the absorbance.

4.3.4.1.3 Calculations. The wt % water equivalent shall be calculated by one of the following formulas:

NTO composition

$$\text{Water Equivalent (wt\%)} = \frac{A_{\text{HNO}_3}}{\text{hbf}} + \frac{A_{\text{H}_2\text{O}}}{\text{ab}}$$

MON composition

$$\text{Water Equivalent (wt \%)} = \left(\frac{A_{\text{HNO}_3}}{\text{hbf}} + \frac{A_{\text{H}_2\text{O}}}{\text{ab}} \right) \left[\frac{100 + C(\% \text{NO})}{100} \right]$$

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where:

A_{HNO_3} = absorption of HNO_3 .

$A_{\text{H}_2\text{O}}$ = absorption of free water.

h = absorption coefficient of HNO_3 = 0.178.

b = thickness of sample (cm).

f = factor for conversion of HNO_3 to H_2O = 7.

a = absorption coefficient of free water = 0.55.

C = calculation coefficient (NO to N_2O_4) = 0.534.

4.3.4.2 Gas chromatographic method.

4.3.4.2.1 Analytical apparatus. Assemble the analytical apparatus as shown in Figure 4. Connect one side of a 2 μL stainless steel liquid inlet sampling valve to a multi-port, multifunctional switching valve. Connect the other side of the same 2 μL valve to a 12 inch x $\frac{3}{8}$ inch Vycor glass tube filled with copper filings and loosely plugged with copper turnings or quartz wool at each end. The copper filings should be of sufficient surface area to reduce 5 or 6 injections of N_2O_4 without peak deterioration but large enough in size to not restrict gas flow. These may be produced by a rough file on copper metal. Place the copper packed reactor in a split tube furnace capable of maintaining a constant temperature between 1022 and 1112°F (550 and 600 °C). Connect the other end of the copper-packed reactor to the separation column of the gas chromatograph through $\frac{1}{16}$ inch stainless steel tubing. This is the sample inlet for the separation. The distance between the copper reactor and gas chromatograph must be 2 inches or less and insulated with glass wool with an aluminum foil over-wrap. Do not heat interconnecting lines; insulation may be used where necessary. The inlet system should also contain a septum inlet or sample loop or loops of known volume (in the range of 10 to 100 μL) connected to the switching valve. This is used for calibration of the chromatograph. The column of the gas chromatograph should be of sufficient length of $\frac{1}{8}$ inch tubing and contain a support material to adequately resolve water when nitrogen is used as the carrier gas (diatomaceous earth supports or other water absorbing supports shall not be used as support materials). The detector should have a minimum sensitivity of 0.25 millivolt per microgram of water. The reference and sample flow rates should be matched within 5 percent. Optimize the column and detector temperatures to produce sharp peaks with adequate resolution. To regenerate the reactor, engage the switching valve to the hydrogen gas source (prepurified grade, 99.95%, 20ppm O_2 maximum) and isolate the chromatograph. When the copper reactor is disconnected from the chromatograph for isolation, turn off the detector to prevent air contact. Regeneration is accomplished by alternating small amounts of hydrogen with the carrier gas flow (nitrogen conforming to MIL-PRF-27401 or helium conforming to MIL-PRF-27407) into the apparatus until no more water can be detected at the outlet or when black copper oxide has returned to bright metallic copper. Dead volume must be kept to a minimum throughout the system by using $\frac{1}{16}$ inch OD tubing of the shortest length possible and filling voids in furnace connections with copper wool.

MIL-PRF-26539F

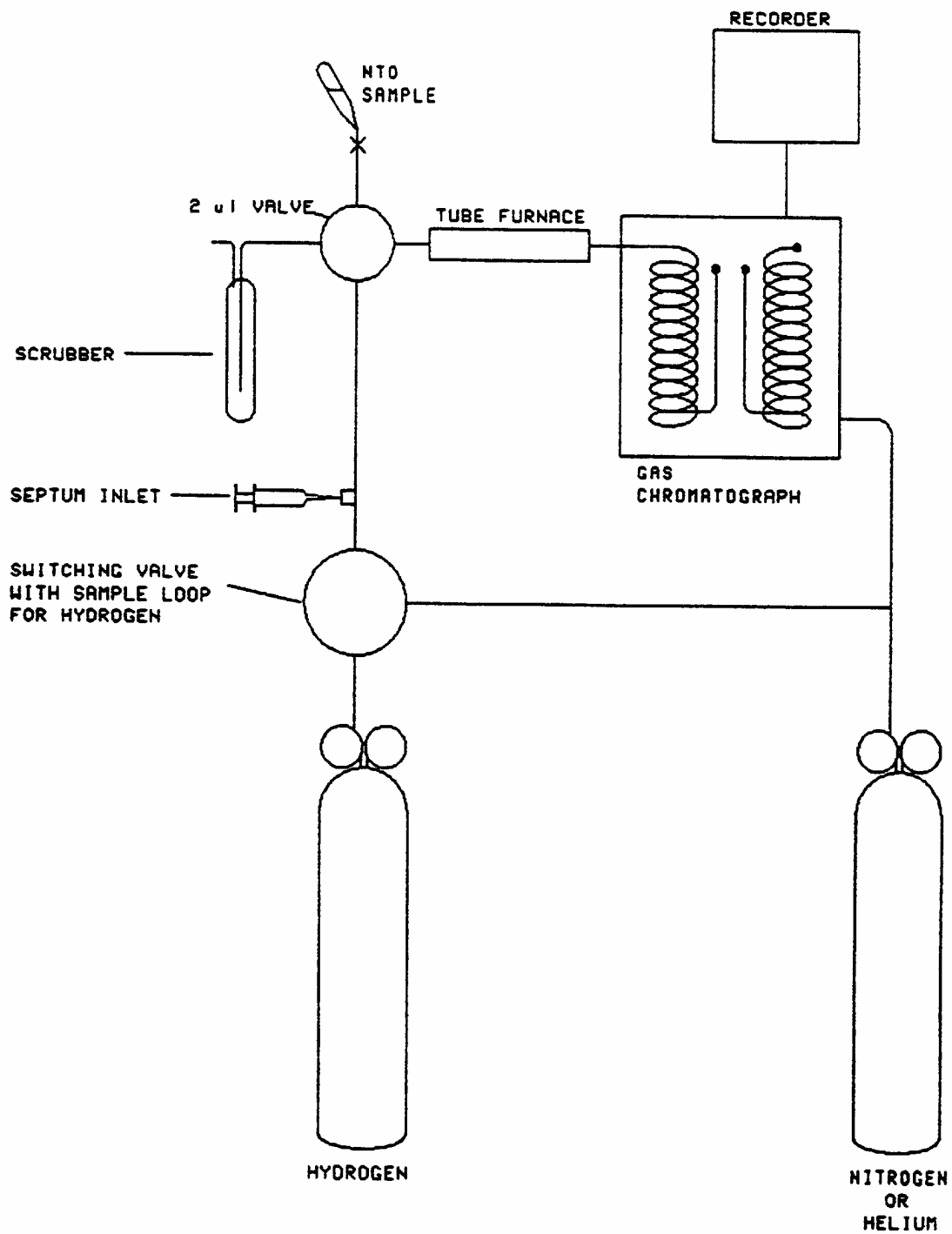


FIGURE 4. Water equivalent apparatus, schematic.

MIL-PRF-26539F

4.3.4.2.2 Procedure. The NTO sample specified in 4.3.3.1.1 shall be connected to the 2 μL liquid valve shown in Figure 4 by means of a $\frac{1}{8}$ inch stainless steel tube. The MON material shall be oxidized according to 4.3.2.1 prior to connecting it to the 2 μL valve. Excess oxygen in the vessel head space shall be released into the NTO scrubber and the vessel pressurized to 30 – 60 psi with dry nitrogen or helium. The apparatus specified in Figure 4 shall be in operational mode ready to analyze a 2 μL aliquot. When the vessel containing the oxidized NTO is connected to the $\frac{1}{16}$ inch line leading to the 2 μL valve, the vessel should at no time be held directly vertical with the valve downward. Connect and clamp the vessel at a slight angle from vertical. It should also not be agitated prior to connection. These precautions are necessary to prevent any particulate from entering and plugging the 2 μL valve. Allow the NTO to flow through the 2 μL sample valve to the NTO scrubber. When a steady stream of liquid flows introduce the aliquot and stop the NTO flow. Reject the first run after regeneration as it will be high due to removal of dead volume hydrogen. If a manual valve is used switching must be rapid and consistent with a low NTO flow to avoid valve leakage. Repeat the analysis two more times. Determine the areas or peak heights. When the peak heights or areas of subsequent injections after the first rejected injection begin to decrease regenerate the copper in the reaction tube. Repeatability should be within 0.02% water equivalents. If repeated injections are out of this range a dead volume check should be performed by checking all connections for proper filling of copper wool and the injection valve should be evaluated for leaking.

4.3.4.2.3 Calculation. The water equivalent shall be calculated as follows:

Average the peak heights or areas and determine the micrograms (μg) of water from a previously prepared calibration graph (4.3.4.2.4). Calculate the water equivalent content using the following formula.

$$\text{Water equivalent, percent by weight} = \frac{\mu\text{g H}_2\text{O}}{29}$$

The peak heights or areas of the duplicates must be reproducible within 2 percent. If they are not, premature sample vaporization and/or a contaminated valve may be responsible for variations.

4.3.4.2.4 Calibration. A calibration curve shall be prepared as follows: Using a pressure-lok gas syringe having a 0 – 50 μL range, inject a 5 μL sample of hydrogen (at ambient temperature) into the partially oxidized copper reactor and record the peak height and the area for the resultant water peak. Repeat this using 10 μL , 25 μL , and 50 μL of hydrogen gas. Calibration may also be performed by using a sample loop of known volume connected to a switching valve. The volume may be determined by the difference in weight when filling the loop with a solvent of known density. Record peak heights and areas for each sample. The calculation to convert μL of hydrogen for each sample to μL of water is as follows:

$$\mu\text{g H}_2\text{O} = \frac{18(a \times P \times 273)}{22.4 \times 760 \times T} = \frac{0.2887(aP)}{T}$$

where:

a = μL of each sample.

P = ambient barometric pressure in mm Hg.

T = ambient temperature in $^{\circ}\text{K}$.

MIL-PRF-26539F

Construct a calibration graph of peak height or area versus $\mu\text{g H}_2\text{O}$ and draw a smooth line through the origin. A single point calibration may be used using one sample loop to confirm the calibration in subsequent analyses. This evaluates the detector or column deterioration while preventing the leaking of syringe ports or connections to sample loops deteriorated from multiple removal. The single point calibration should be performed before and after each set of samples.

4.3.5 Chloride content. The chloride content on N_2O_4 is determined by one of the following methods. In the event of a dispute the procedure specified in 4.3.5.1 shall be used as the referee method.

4.3.5.1 Silver nitrate titration method.

4.3.5.1.1 Sample preparation. Place a 250 mL beaker on a magnetic stirrer in a laboratory hood. Add to the beaker a polytetrafluoroethylene stirring bar and 150 mL 1M NaOH solution. Activate stirrer. Weigh a sampler containing NTO or oxidized (4.3.2.1) MON material to 0.1 gram. A sample vessel that holds approximately 100 mL is best for weighing accuracy. Attach a polytetrafluoroethylene tube to the sampler. Slowly add 6 to 8 mL (9 to 12 grams) of sample via the tube below the surface of the caustic. The rate should be low enough so that no red vapors form from breaking bubbles which will reduce the amount of sample introduced. Remove the tube and determine the sample weight by difference. Slowly add with stirring an amount of urea equal to one-half (0.5) the sample weight in grams. Care should be taken to prevent sample loss due to bubbling. Slowly add with stirring 1:1 HNO_3 until gas evolution ceases or the pH stabilizes between 2.5 to 3.0. The pH of the solution should be checked often while adding the acid to make sure that a pH less than 2.5 is not produced. Allow the solution to stand 15 minutes in preparation for titration.

4.3.5.1.2 Procedure. Fill a syringe pump, adjusted to deliver a constant volume of titrant per unit time (in the range of 0.5 to 0.7 mL/min) with 0.05M AgNO_3 solution. Connect the pump to the prepared sample with a polytetrafluoroethylene tube. Place a chloride or silver standard ion electrode and a double junction reference electrode in the sample solution. The electrode should be connected to a millivolt meter and recorder. With sample stirring, turn on meter, recorder, and pump. Chart speed should be approximately one inch per minute. Mark the point where the syringe pump delivery begins. As soon as the S shape curve is complete, turn off the pump and recorder. Determine the inflection point by drawing tangents to the curve, dropping a perpendicular from the upper to lower tangent, and constructing a perpendicular bisector. Measure the exact titrant delivery time, such as 5.75 minutes. Run a blank in the same manner. Delivery time of titrant in minutes multiplied by delivery rate in mL/min equals titrant volume in mL. Alternately the S shape may be generated by incremental additions of the silver nitrate solution with a 25 mL burette and detection of millivolts from the millivolt meter. The millivolts vs milliliters shall be plotted during silver nitrate addition to determine when the S curve is approaching. Increments should be 1 mL or less to the inflection point and 0.25 or less at the rise to the inflection point, and returning to 1 mL increments after the rise. An automatic titrator may also be substituted for the syringe pump provided the detection uses the same electrodes and the end point is identical to the plotted S curve. The silver nitrate may require dilution for automatic titrators.

4.3.5.1.3 Calculation. The percent by weight chloride is calculated as follows:

$$\text{Chloride, percent by weight} = \frac{(\text{mL AgNO}_3 - \text{mL blank}) \times M \times 35.45 \times 100}{W}$$

where:

MIL-PRF-26539F

M = molarity of AgNO₃ titrant (moles/liter).

W = sample weight in mg.

4.3.5.1.4 Calibration. The AgNO₃ molarity (M) is obtained by titrating, in triplicate, a standard sodium chloride solution by the procedure in 4.3.5.1.2.

4.3.5.2 Colorimetric method.

4.3.5.2.1 Procedure. Weigh the cylinder containing the oxidized sample prepared in 4.3.2.1 to the nearest 0.10 gram. Slowly bubble 1 to 50 g of N₂O₄ through 40 to 50 mL of chloride-free distilled water contained in each of two 250 mL gas scrubbers, connected in series with polyvinyl tubing. The sample must be scaled to contain less than 0.050 mg Cl⁻. Combine the two solutions in a 250 mL beaker. Prepare a reagent blank with 50 mL of chloride free distilled water in a second beaker. Reweigh the cylinder. Add 2 to 5 drops of 2,4-dinitrophenol (0.1% wt in alcohol and water) to each of the 250 mL beakers and neutralize each with concentrated ACS reagent grade ammonia to the yellow end-point. Adjust the volume in the sample beaker to contain one gram of N₂O₄ per milliliter of solution by evaporating on a hot plate. Into three other 25 mL volumetric flasks add 0.010 mg Cl⁻, 0.020 mg Cl⁻, and 0.040 mg Cl⁻ of the dilute standard Cl⁻ solution, using a microburet. Add chloride free distilled water to all flasks so that they contain about 20 mL of liquid. Add exactly 2.0 mL of a 0.25M iron (III) ammonium sulfate [FeNH₄(SO₄)₂•12H₂O] solution to the flasks and mix. Add exactly 1.0 mL of a saturated mercury (II) thiocyanate [Hg(SCN)₂] solution, make up to mark with chloride free distilled water and mix. Place all flasks in darkness for 15 to 30 minutes. Measure the absorbance of the sample and the standards in a 5.00 cm cell at 460 nm, after setting the blank in a 5.00 cm cell at zero absorbance (100%T). Plot the absorbance of the standards versus mg Cl⁻ and draw a curve through the origin.

4.3.5.2.2 Calculation. The weight percent chloride shall be calculated as follows:

$$\text{Chloride, percent by weight} = \frac{(\text{mg Cl}^- \text{ from curve}) \times F \times 100}{\text{mg N}_2\text{O}_4}$$

where:

F = aliquot factor (such as 1/1 to 5/1).

4.3.6 Nonvolatile residue. The nonvolatile residue of the propellant shall be determined by the following method.

4.3.6.1 Procedure. Thoroughly clean two platinum evaporating dishes per sample. Dry the dishes in an oven at 220 ± 10°F (105 ± 5°C). After drying, cover the dishes with a watch glass and allow them to cool next to the balance for 30 minutes. Weigh each dish to the nearest 0.01 milligram. Place a hot plate in an exhaust hood and place the weighed dishes on it. Transfer 50 mL of the N₂O₄ to each dish. Using the hot plate, evaporate the sample to dryness. Oven dry the dishes for one hour. Cover the dishes with a watch glass and allow to cool next to the balance for 30 minutes. Weigh each dish to the nearest 0.01 mg. Repeat oven drying until constant weight is attained.

MIL-PRF-26539F

4.3.6.2 Calculation. The mg/L nonvolatile residue shall be calculated by the following formula:

$$\text{NVR}(\text{mg/L}) = \frac{W_S - W_E}{V_S}$$

where:

W_S = weight of sample dish after drying (mg).

W_E = weight of empty dish (mg).

V_S = volume of sample used (liters).

4.3.7 Iron content. The iron content is determined as follows:

4.3.7.1 Procedure. Transfer 20 to 50 mL of the propellant to a 100 mL beaker. Use larger sample sizes when less iron is expected. Calculate the weight of sample by using the appropriate density. Place the beaker on a hot plate containing an asbestos pad or equivalent and set to the low heat range. Slowly evaporate the sample. Add 1 mL of concentrated H_2SO_4 when the sample evaporates to approximately 5 mL. Allow the sample to evaporate to a clear-straw colored liquid, then set it aside to cool to room temperature. Transfer the contents of the beaker to a 25 mL volumetric flask. Rinse the beaker with additional distilled water and transfer the rinse water to the 25 mL volumetric flask. Dilute the sample in the flask to the mark with distilled water. Stopper the flask and shake to ensure complete mixing. Determine the absorption of the sample in the volumetric flask on either an Inductively Coupled Plasma (ICP) or on a suitable atomic absorption spectrophotometer at an iron wavelength closest to 2480 Å after setting the zero absorption with distilled water. Prepare a series of iron standard solutions in the 1 to 10 ppm range in accordance with 4.3.7.3. Determine the absorption of the iron standards at the iron wavelength.

4.3.7.2 Calculation. The iron content of the MON type propellant shall be calculated as follows:

$$I = \frac{(A_{\text{MON}} - A_{\text{blk}})CVF_d}{A_0 W}$$

where:

A_{MON} = absorbance of MON type propellant sample.

A_{blk} = absorbance of blank solution prepared without sample.

A_0 = absorbance of nearest standard solution.

C = concentration of nearest standard solution.

V = volume of the undiluted sample solution (mL).

F_d = dilution factor, if used.

W = weight of N_2O_4 used (g).

MIL-PRF-26539F

I = iron concentration (ppm by wt).

4.3.7.3 Calibration. Prepare 1 ppm, 2 ppm, 5 ppm, and 10 ppm Fe standard solutions by the separate addition of 0.2 mL, 0.4 mL, 1.0 mL and 2 mL aliquots of the 1000 ppm Fe stock standard solution to each of four 200 mL volumetric flasks. To each flask are added 50 mL of distilled water and 2 mL of concentrated sulfuric acid. Dilute to the mark with distilled water. Transfer each of the four standard solutions to plastic screw-cap bottles. Determine the absorption of the four standards at 2480 Å, which is the same Fe line as for the sample, using distilled water to set the instrument at zero absorption. The standard iron solution having the absorption nearest to the sample is used to calculate the iron content of the sample.

4.3.8 Particulate. The particulate matter of N₂O₄ is determined as follows:

4.3.8.1 Preparation of the membrane filter. Using forceps place a 47 mm, polytetrafluoroethylene membrane filter of nominal pore size (10 µm) in a clean Petri dish. Place the Petri dish, with its lid slightly ajar, in an oven of the static type at 194 ± 9°F (90 ± 5°C) and leave it for 30 minutes. Remove the Petri dish from the oven and place it near an analytical balance (must have a minimum precision standard deviation of 0.07mg). The Petri dish cover should be ajar but still protecting the membrane filter from contamination from the atmosphere. Allow 30 minutes for the membrane filter to come to equilibrium with the ambient air temperature and humidity. Remove the membrane filter from the Petri dish with forceps, handling it by the edge only, and place it on the center of the weighing pan. Weigh and return it to the Petri dish.

4.3.8.2 Sampling. At minimum, a 400 mL aliquot of the sample should be passed through the filter assembly. The sample volume actually employed must be reported.

4.3.8.3 Procedure. Assemble the high pressure filter holder with the weighed membrane filter and position it so that the filter membrane is in a horizontal position. Pass a minimum of 400 mL of sample through the filter holder. Follow with dry nitrogen gas conforming to MIL-PRF-27401 to purge remaining N₂O₄. Carefully remove the membrane filter, and place it in a clean, covered Petri dish. Dry and reweigh the membrane filter taking care not to disturb the contaminant on its surface. The drying procedure described in 4.3.8.1 should be followed in detail.

4.3.8.4 Calculation. Subtract the initial weight of the test membrane filter, W₁, from the final weight, W₂. Divide the resulting weight by the volume of sample filtered and report the result as total contaminant, expressed in milligrams per liter to the nearest 0.01 mg/L. Also report the volume of sample used in the test.

4.4 Leakage. Each shipping container will be checked for leaks at all potential sources for leaks such as valves and fittings. Leaks shall be tested for by utilizing a toxic vapor detector with a lower detection limit for NO₂ of at least 1.0 ppm. The detector wand shall be placed ½ - 1 inch from each potential leak source for at least 3-5 seconds. Any positive reading on the toxic vapor detector constitutes a leak.

5. PACKAGING

5.1 Packaging. For acquisition purposes, the packaging requirements shall be as specified in the contract or order (see 6.2). When actual packaging of materiel is to be performed by DoD or in-house contractor personnel, these personnel need to contact the responsible packaging activity to ascertain packaging requirements. Packaging requirements are maintained by the Inventory Control Point's

MIL-PRF-26539F

packaging activities within the Military Service or Defense Agency, or within the military service's system commands. Packaging data retrieval is available from the managing Military Department's or Defense Agency's automated packaging files, CD-ROM products, or by contacting the responsible packaging activity.

6. NOTES

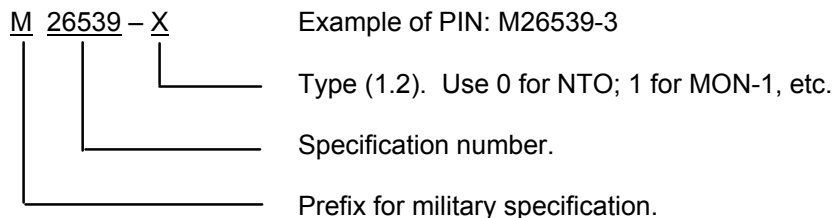
(This section contains information of a general or explanatory nature that may be helpful, but is not mandatory.)

6.1 Intended Use. The propellant described by this specification is intended for use as an oxidizer in rocket engines.

6.2 Acquisition requirements. Acquisition documents must specify the following:

- a. Title, number, and date of this specification.
- b. Type of propellant required (1.2).
- c. Method of shipment, type and capacity of containers.
- d. Quantity by weight.
- e. Packaging requirements (5.1).

6.3 Part or identifying number (PIN). The PINs to be used for dinitrogen tetroxide acquired to this specification are created as follows:



6.4 Definitions.

6.4.1 Particulate. The undissolved solids in a given product retained on a 10 micron filter membrane.

6.4.2 Single-phased liquid. A single-phased liquid is devoid of any visible foreign liquid but may contain solid material as permitted within this specification.

MIL-PRF-26539F

6.5 Subject term (key word) listing.

Dinitrogen tetroxide
Nitric oxide
Oxidizer
Propellant
Rocket engine

6.6 Changes from previous issue. Marginal notations are not used in this revision to identify changes with respect to the previous issue due to the extent of the changes.

CONCLUDING MATERIAL

Custodians:

Navy – AS
Air Force – 68
DLA – PS

Preparing activity:

Air Force – 68
(Project 9135-2005-003)

Review activities:

Air Force – 19

Note: The activities listed above were interested in this document as of the date of this document. Since organizations and responsibilities can change, you should verify the currency of the information using the ASSIST Online database at <http://assist.daps.dla.mil>.