

INCH-POUND

MIL-PRF-26539E  
07 October 1997  
SUPERSEDING  
MIL-P-26539D  
28 August 1989

## PERFORMANCE SPECIFICATION

## PROPELLANTS, DINITROGEN TETROXIDE

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 five types and two grades of dinitrogen tetroxide ( $N_2O_4$ ) propellants.

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

## Types

NTO - Nominal 99.5%  $N_2O_4$  purity with red-brown color.  
MON-1 - Nominal 99%  $N_2O_4$  and 1% NO with green color.  
MON-3 - Nominal 97%  $N_2O_4$  and 3% NO with green color.  
MON-10 - Nominal 90%  $N_2O_4$  and 10% NO with green color.  
MON-25 - Nominal 75%  $N_2O_4$  and 25% NO with green color.

## Grades

Standard - no iron requirement.  
Low-iron - maximum 0.5 parts per million iron.

## 2. APPLICABLE DOCUMENTS

2.1 General. The documents listed in this section are specified in Sections 3 and 4 of this specification. This section does not include documents 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 documents cited in sections 3 and 4 of this specification, whether or not they are listed.

2.2 Government documents.

Beneficial comments (recommendations, additions, deletions) and any pertinent data which may be of use in improving this document should be addressed to: Code (68) SA-ALC/SFSP, 1014 Billy Mitchell Blvd/STE 1, Kelly AFB TX 78241-5603, by using the standardization Document Improvement Proposal (DD Form 1426) appearing at the end of this document or by letter.

AMSC N/A

FSC 9135

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2.2.1 Specifications, standards, and handbooks. The following specifications form a part of this document to the extent specified herein. Unless otherwise specified, the issues of these documents are those listed in the issue of the Department of Defense Index of Specifications and Standards (DoDISS) and supplement thereto, cited in the solicitation (see 6.2).

## SPECIFICATIONS

## DEPARTMENT OF DEFENSE

MIL-PRF-25508	- Propellant, Oxygen
MIL-PRF-27401	- Propellant, Pressurizing Agent, Nitrogen
MIL-PRF-27407	- Propellant Pressurizing Agent, Helium
MIL-T-27730	- Tape, Antiseize, Tetrafluoroethylene with Dispenser

(Unless otherwise indicated, copies of the above specifications are available from the Standardization Document Order Desk, 700 Robbins Avenue, Building 4D, Philadelphia PA 19111-5094).

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 the documents which are DoD adopted are those listed in the issue of the DoDISS cited in the solicitation. Unless otherwise specified, the issues of documents not listed in the DoDISS are the issues of the documents cited in the solicitation (see 6.2).

## AMERICAN CHEMICAL SOCIETY (ACS)

## ACS Reagent Chemical Standards

(Application for copies should be addressed to the American Chemical Society, 1 River Rd, Niskayuna NY 12309.)

## AMERICAN SOCIETY FOR TESTING AND MATERIALS (ASTM)

ASTM E 29 - Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

(Application for copies should be addressed to 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, 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.

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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 for Using Significant Digits in Test Data to Determine Conformance with Specifications.

3.3 Filter. A filter with a 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.

TABLE I. Chemical composition and physical properties.

Composition	NTO (Red-Brown)	MON-1 (Green)	MON-3 (Green)	MON-10 (Green)	MON-25 (Green)	Test Para.
N <sub>2</sub> O <sub>4</sub> assay % wt, MIN	99.5	---	---	---	---	4.3.3
NO content % wt, MAX		1.0	3.0	11.0	26.0	4.3.2
% wt, MIN	<u>1</u> /	0.6	2.5	10.0	25.0	
N <sub>2</sub> O <sub>4</sub> + NO % wt, MIN	---	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	4.3.4
Chloride content % wt, MAX	0.040 <u>2</u> /	0.040	0.040	0.040	0.040	4.3.5
Nonvolatile residue <u>3</u> / mg/L, MAX	---	10.0	10.0	10.0	10.0	4.3.6
Iron content <u>3</u> / ppm wt, MAX	---	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	4.3.8

1/ The NO content shall be limited to that which does not change the specified red-brown color of the propellant (3.4).

2/ This test need not be performed on NTO propellant if the material was manufactured by the ammonia-oxidation process.

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3/ This requirement applies to the low-iron grade of the propellant only.

#### 4. VERIFICATION

4.1 Classification of inspections. The inspections shall be classified as quality conformance inspections.

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

a. Individual tests . . . . . 4.2.1

b. Sampling tests . . . . . 4.2.2

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

Examination of product . . . . . 4.3.1

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 content . . . . . 4.3.2

b. Dinitrogen tetroxide assay . . . . . 4.3.3

c. Water equivalent . . . . . 4.3.4

d. Chloride content . . . . . 4.3.5

e. Nonvolatile residue . . . . . 4.3.6

f. Iron content . . . . . 4.3.7

g. Particulate . . . . . 4.3.8

##### 4.2.2.1 Sampling plan.

4.2.2.1.1 Lot. A lot shall consist of one of the following:

a. The propellant produced in not more than 24 consecutive hours from a continuous process which is used to fill shipping containers directly from the process output. A continuous process shall be the production of product by continuous input of raw materials and output of finished product by one manufacturer in one plant with no change in manufacturing conditions or materials.

b. The propellant from individual runs of a batch process which is used to fill shipping containers directly from the process output. A batch process shall be the production of product by runs from single additions of raw materials which are reacted and purified forming the product.

c. The propellant from either or both the continuous and batch processes which is held in a single storage tank and subsequently withdrawn to fill

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shipping containers. The product shall be homogeneous at the time of withdrawal and shall not be added to while being withdrawn. After each addition to the storage tank, the contents shall constitute a separate lot.

4.2.2.1.2 Sample. A sample shall consist of not less than 800 milliliters (mL) of propellant. Two 400 mL samples may be taken for the tests specified in 4.2.2. One sample may be used for tests a through f and the other for test g. In the case of cylinder sampling, the sample(s) shall be taken from the same cylinder. Unless otherwise specified, quality conformance tests shall be performed on each sample of the propellant taken directly from the shipping containers. When required, samples shall be forwarded to a laboratory designated by the procuring activity for subjection to the quality conformance tests specified herein.

4.2.2.1.2.1 Sampler. The sampler shall be capable of accepting a 400 mL or 800 mL sample 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.

4.2.2.1.3 Cylinders, standard grade. The number of cylinders selected for sampling from each lot shall be according to Table II. The first and last containers to be filled within a given lot shall be sampled. Other samples may be selected at random. Each selected cylinder shall be thoroughly agitated immediately before sampling. The propellant from each container sampled shall constitute a separate sample.

TABLE II. Sampling for test.

Number of containers in lot	Number of containers to be sampled
1	1
2-8	2
9-27	3
28-64	4

4.2.2.1.4 Cylinders, low-iron grade. Each cylinder of low-iron grade material shall constitute a separate lot and shall be sampled.

4.2.2.1.5 Portable Tanks, Cargo Tanks, and Tank Cars. A sample shall be taken from each portable tank, cargo tank, or tank car.

4.2.2.1.6 Other containers. Unless otherwise specified, other containers of 100 gallons or less water capacity shall be sampled according to 4.2.2.1.3 or 4.2.2.1.4. Containers greater than 100 gallons water capacity shall be sampled according to 4.2.2.1.5

4.2.2.1.7 Method of taking sample. Connect a ... inch stainless steel tube approximately 1½ feet in length to the container s (cylinder or tank) dip-tube valve. Fit one end of the tube with a 1 inch to 1½ inch pipe-thread bushing for attaching to the dip-tube valve and fit the other end to a ... inch tee. Fit one leg of the tee with a ... inch needle valve for purging and the other leg for connecting to the sampler inlet valve. Attach approximately 5 feet of polyethylene tubing to the purging valve to direct the propellant fumes away from the sampling area or purge directly into an evacuated waste

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tank. Apply thread tape conforming to MIL-T-27730 to all thread connections. Wrap the tape under tension starting three threads back from the end and in the direction with the male pipe thread helix toward thread run-out. Wrap once plus an overlap of  $\frac{1}{8}$  inch at thread run-out end. Connect the evacuated sampler to the tee at an inclined  $45^\circ$  angle with the inlet valve down. Open the dip-tube valve on the purging valve. Purge until approximately 2,000 mL of propellant have been removed to clear the dip-tube. Then close the purging valve and open the sampler inlet valve. Open the outlet valve and continue sampling until liquid propellant appears. Close the sampler outlet, inlet, and dip-tube valves. Open the purging valve to clear the sample line and disconnect the sampler.

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 lot 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 paragraph 4.3.2.1 or by the alternate procedure described in paragraph 4.3.2.2. In the event of dispute, the procedure specified in paragraph 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 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 ( $O_2$ ). Connect a length of 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 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  $32^\circ\text{F}$  ( $0^\circ\text{C}$ ). After the sample has been allowed to cool for 10 minutes permit  $O_2$  to flow into the

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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<sub>2</sub> 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.

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 = O<sub>2</sub> 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 O<sub>2</sub> in grams.

4.3.2.1.4 Reagents and equipment. The following reagents and equipment or their equivalent shall apply as test conditions of 4.3.2.1:

a. Reagents

(1) Nitrogen, MIL-PRF-27401, Type I

(2) Oxygen, MIL-PRF-25508, Type I

b. Equipment

(1) Valve, needle, 1/8 inch NPT male inlet x ... inch Swagelok outlet, stainless steel.

(2) Bomb, sample, 2 inch diameter with 1/8 inch NPT female, 302 stainless steel, 24 gauge.

(3) Stand, ring.

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- (4) Tubing, polyethylene, length as required.
- (5) Rotameter, glass-ball, with 0 to 1.0 liter per minute capability.
- (6) Tubing, stainless steel, 1/16 inch diameter.
- (7) Bath, ice.
- (8) Balance, analytical, plus or minus 0.1 mg sensitivity, 0.1 mg accuracy.

4.3.2.2 Alternate procedure.

4.3.2.2.1 Preparation. Clamp the sampler specified in paragraph 4.3.2.1.2.1 to a stand as shown in Figure 1. Attach a 1/16 in 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 is available for purging excess  $N_2O_4$  from the 1/16 inch ID polytetrafluoroethylene tubing. The flow-through spectrophotometric cell depicted shall conform to the following:

- a.  $2.00 \pm 0.02$  mm sample path length.
- b. Coolant jacket for sample temperature control.
- c. Constructed of material compatible with  $N_2O_4$ .
- d. Constructed to fit instrument cell compartment.

Figures 2 and 3 show suggested designs. Maintain the temperature of the flow-through cell at  $32 \pm 1.8^\circ F$  ( $0 \pm 1^\circ C$ ) 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  $N_2O_4$  cylinder slightly and control the sample flow with the cell 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  $N_2O_4$ .



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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 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 to make 100 mL of a 4M stock solution.

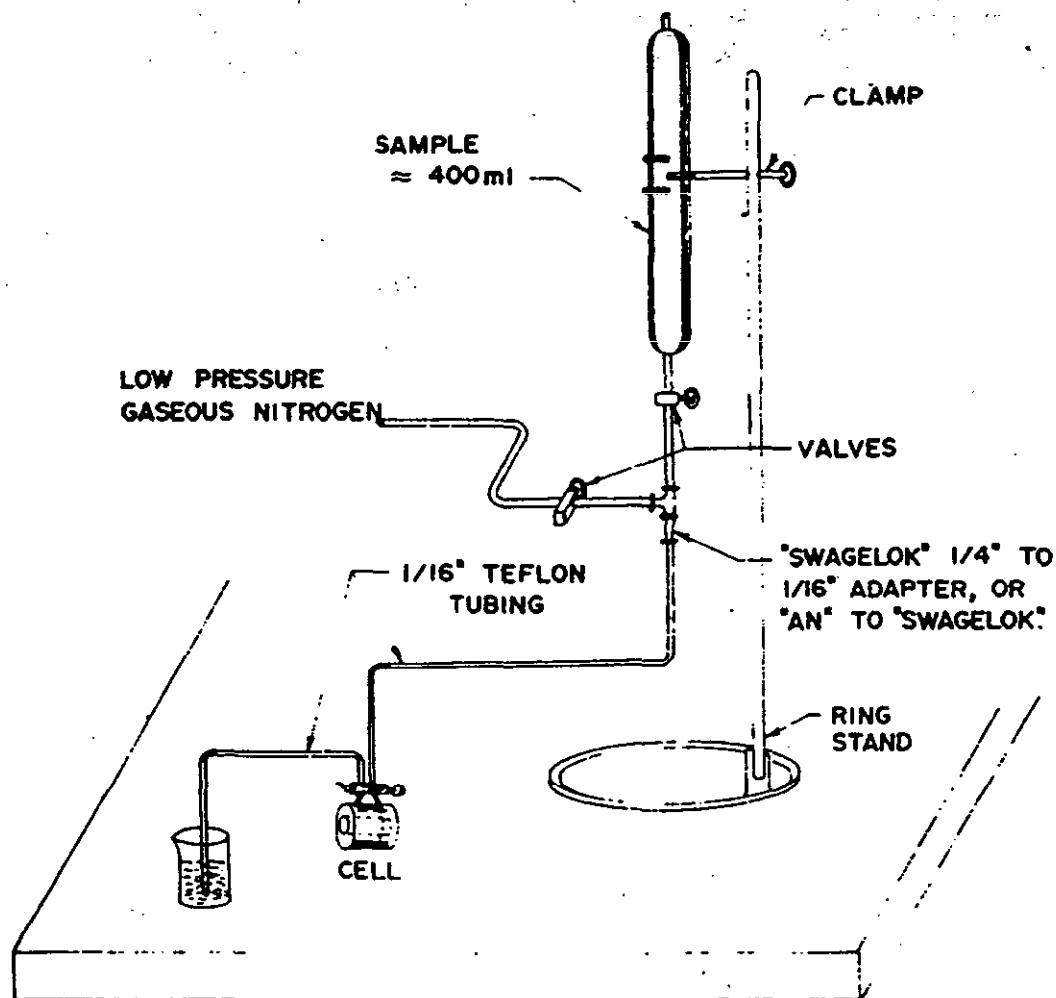
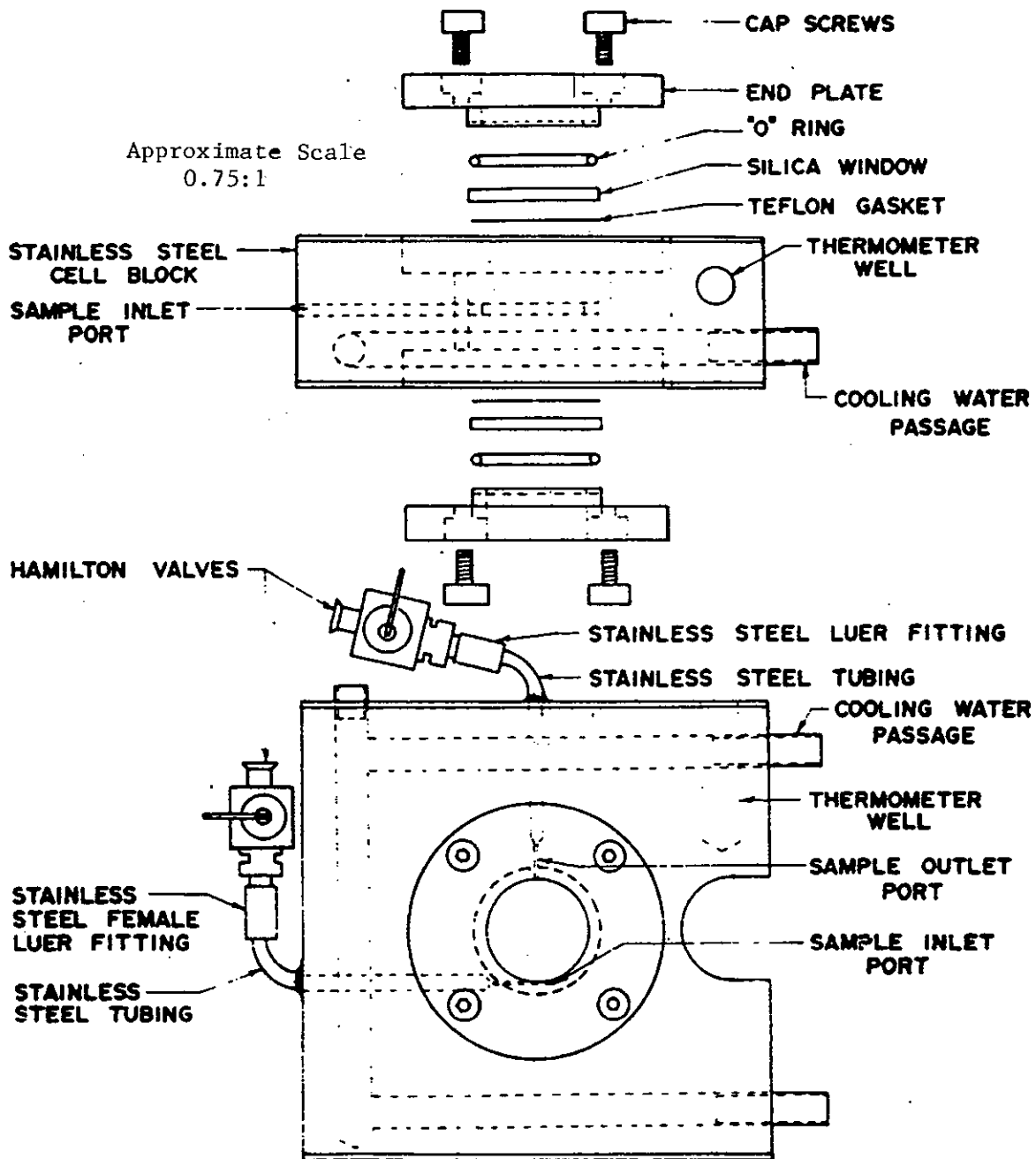


FIGURE 1. Nitric Oxide Sampler Apparatus

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FIGURE 2. *Stainless Steel Absorption Cell*

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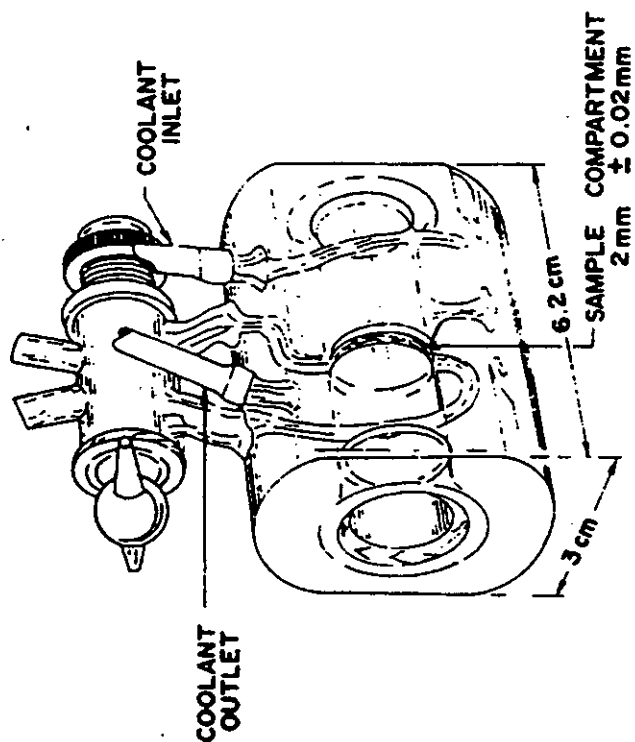
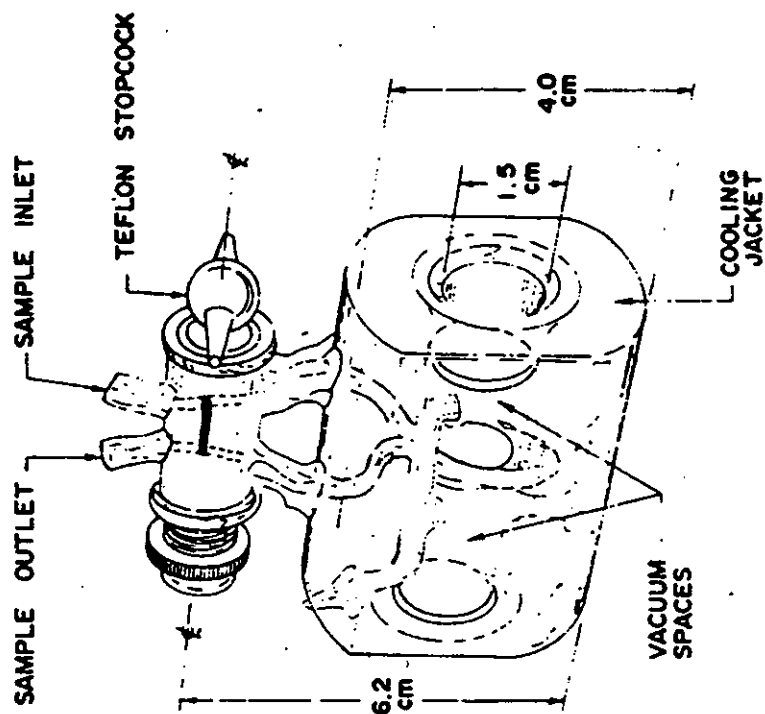


FIGURE 3. Glass Absorption Cell

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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  $\text{Ni}^{2+}$  solution in a 50 mL beaker. Add 4.00 mL of the 4M  $\text{NaN}_3$  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  $\text{Ni}^{2+}$  solution with 4.0 mL of the 4M  $\text{NaN}_3$  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.

4.3.2.2.4 Reagents and equipment. The following reagents and equipment shall apply as test conditions of 4.3.2.2.

## a. Reagents

- (1)  $\text{N}_2\text{O}_4$ , pure or conforming to NTO of this specification.
- (2) Nitrogen gas, conforming to MIL-PRF-27401.
- (3) Distilled water.
- (4) Nickel(ous) nitrate hexahydrate, ACS reagent grade, or equivalent.
- (5) Sodium azide, practical, Eastman catalog number P2352, or equivalent
- (6) Sodium hydroxide, flakes, technical grade.
- (7) Ethylene glycol, technical grade.
- (8) Oxygen, conforming to MIL-PRF-25508, Type I.

## b. Equipment

- (1) Special  $\text{N}_2\text{O}_4$  absorption cell 2 mm  $\pm$  0.02 mm.
- (2) 5.00 mm cell, silica, Pyrex, or Corex.
- (3) Ice bath.
- (4) Circulating pump.
- (5) Scrubber, 400 or 600 mL beaker, glass or plastic.
- (6) 1/16 inch polytetrafluoroethylene tubing, 12 inches.
- (7) Ring stand, heavy duty, with clamp.
- (8) Tubing, polyvinyl or rubber.

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- (9) Fitting, ... inch T , AN or Swagelok.
- (10) Fitting, ... inch to 1/16 inch adaptor, AN to Swagelok.
- (11) Buret, 10 mL, micro (0.02 mL graduations).
- (12) Valve, gas, ... inch, AN or Swagelok.
- (13) Spectrophotometer, capable of furnishing narrow band energy at 700 nm and capable of accepting the special cell.

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 oxides of nitrogen shall be assayed without further chemical treatment. Proceed to paragraph 4.3.3.1.2 and then to 4.3.3.2 and 4.3.4.

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 paragraph 4.3.2.1. Proceed to paragraph 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 paragraph 4.3.2.1 before proceeding to paragraph 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 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.

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. 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

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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 bromothymol blue indicator and titrate with 0.5 N NaOH solution to the end point. Run a reagent blank in the same manner as the sample.

4.3.3.3 Calculation. The wt%  $N_2O_4$  shall be calculated by one of the following formulas:

NTO

$$N_2O_4, \text{ percent by weight} = \frac{(a - b)N \times 4.6008}{W}$$

where:

a = mL NaOH for sample

b = mL NaOH for blank

N = normality of NaOH

W = grams of  $N_2O_4$  in ampoule

MON composition

$$N_2O_4, \text{ percent by weight} = 1.534 \times (A - B)$$

where:

$$A = \frac{(a - b)N \times (3.00 + 0.016 \times \%NO)}{W}$$

(see NTO for a, b, N definitions)

W = grams of oxidized  $N_2O_4$  in ampoule

B = percent by weight NO

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

## a. Reagents

(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 0.5N HCl or acid phthalate to the bromothymol blue end point. Quantitatively transfer 30 - 50 mL of the standard acid into a beaker from a 100 mL buret. Titrate the acid with the 0.5N NaOH using the same buret after cleaning. Store the 0.5N NaOH in a

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polyethylene container and ensure the exclusion of carbon dioxide during storage.

- (2) Distilled water.
- (3) Bromothymol blue indicator solution: 0.1 grams in 16 mL of 0.01N NaOH and 234 mL of distilled water.
- (4) Hydrogen peroxide, ACS, or equivalent, reagent grade, 30% wt.
- (5) Standard acid solution, 0.5N: 0.5N HCl standardized with primary standard grade diphenyl guanidine to the bromothymol blue end point, or a certified standard grade HCl or acid phthalate.
- (6) Diphenyl guanidine: Primary standard grade, F G Smith and Company, or equivalent.

b. Equipment

- (1) Buret, 100 mL, 0.2 mL graduations.
- (2) Flask iodine, 500 mL, heavy wall with 24/40 stopper.
- (3) Ampoule glass, 1 mL capacity.
- (4) Flasks, volumetric, 1000 mL capacity.
- (5) Ice bath.
- (6) Low temperature bath, crushed dry-ice or equivalent.
- (7) Glass rod.
- (8) Glass air condenser, 24/40 ground glass end with drip tip.
- (9) Beaker, 200 to 400 mL, as available.

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 paragraph 4.3.4.1 shall be the referee method.

4.3.4.1 Gas chromatographic method.

4.3.4.1.1 Analytical apparatus. Assemble the analytical apparatus as shown in figure 4. Connect one side of a 2  $\mu$ L stainless steel liquid inlet sampling valve to a 3 groove 6 port switching valve. Connect the other side of the same 2  $\mu$ L valve to a 12 inch x 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 550 and 600°C. Connect the other end of the copper-packed reactor to the separation column of the gas chromatograph through 1/16<sup>th</sup> inch stainless steel tubing. This is the sample inlet for the

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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  $\mu\text{L}$ ) connected to the switching valve. This is used for calibration of the chromatograph.

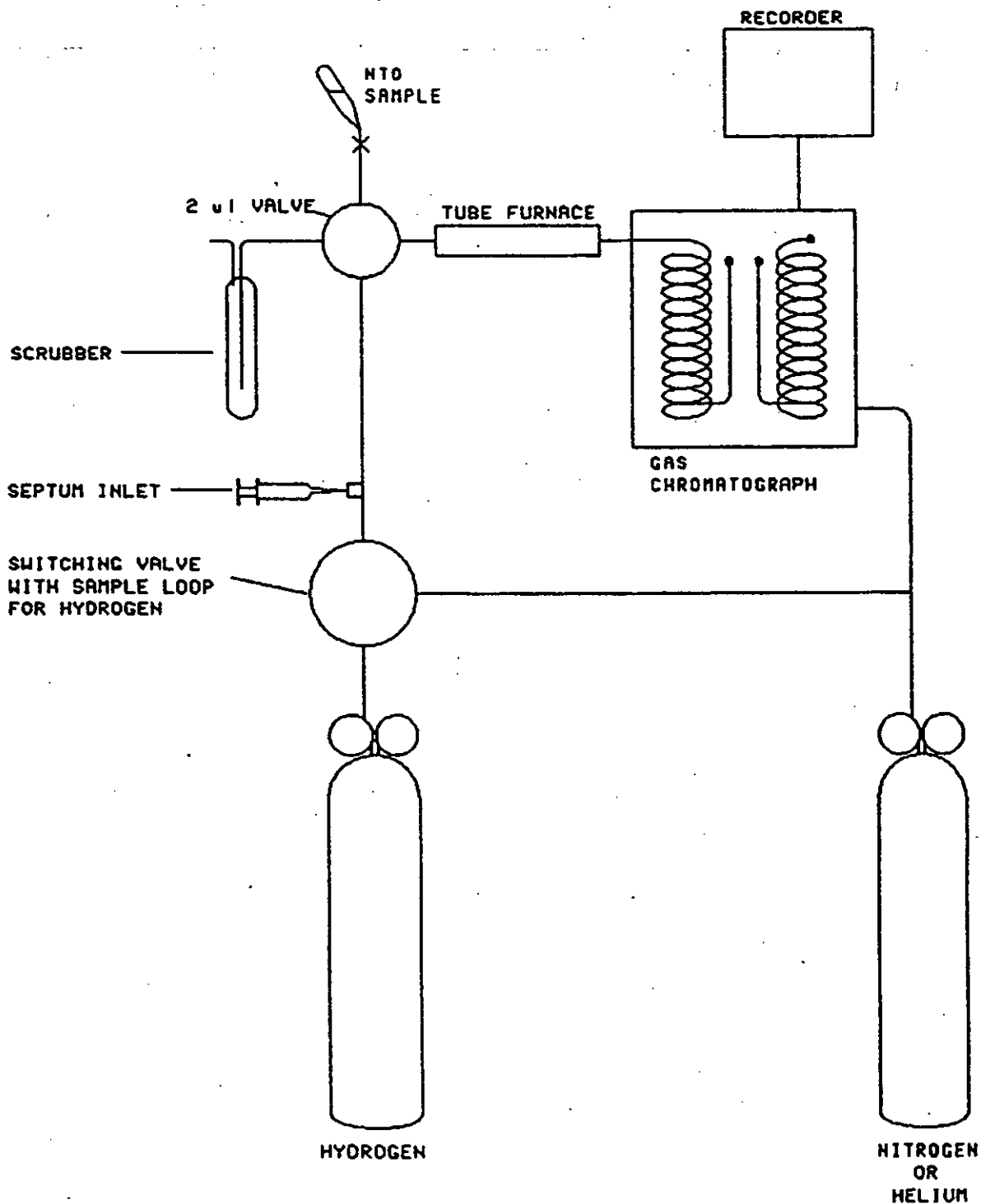


FIGURE 4. Water Equivalent Apparatus, Schematic



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The column of the gas chromatograph should be of sufficient length of 1/8 inch tubing and contain a support material to adequately resolve water when nitrogen is used as the carrier gas. 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 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 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 1/16 inch OD tubing of the shortest length possible and filling voids in furnace connections with copper wool.

**4.3.4.1.2 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 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 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 2 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.

**4.3.4.1.3 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 (4.3.4.1.4). 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.

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4.3.4.1.4 Calibration. A calibration curve shall be prepared as follows: Using a pressure-lok gas syringe having a 0 - 50  $\mu\text{L}$  range, inject a 5  $\mu\text{L}$  sample of hydrogen (at ambient pressure) into the partially oxidized copper reactor and record the peak height and area for the resultant water peak. Repeat this using 10  $\mu\text{L}$ , 25  $\mu\text{L}$  and 50  $\mu\text{L}$  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  $\mu\text{L}$  of hydrogen for each sample to  $\mu\text{g}$  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 =  $\mu\text{L}$  of each sample.

P = ambient barometric pressure in mm Hg

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

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.

4.3.4.1.5 Reagents and equipment. The following reagents and equipment shall apply as test conditions of 4.3.4.1.

a. Reagents

(1) Hydrogen, cylinder with regulator: Prepurified grade gas, 99.95%, 20 ppm  $\text{O}_2$  maximum.

(2) Carrier gas: Nitrogen conforming to MIL-PRF-27401, or helium conforming to MIL-PRF-27407.

(3) Copper, 20 - 40 mesh: Pure, ACS reagent grade chips or filings, Cuprin, or equivalent, size may be optimized for the particular system to obtain 5 - 6 injections per regeneration.

(4) Copper turnings: Pure, ACS reagent grade, or equivalent. Copper wool or copper pot and pan scrubber is sufficient.

(5) Gas chromatographic column: Acceptable columns and conditions follows:

(a) 6 to 10 ft of 5% polyethylene glycol on Teflon 40 - 60 mesh, at 158 $^{\circ}\text{F}$  (70 $^{\circ}\text{C}$ ) and 25 to 30 cc/min flow rate.

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(b) 6 to 10 ft of polystyrene-polyvinyl bead absorbent, Porapak QS, or equivalent, at 212°F (100°C) and 25 to 30 cc/min flow rate.

(c) Polyhalocarbon supports, Kel F, or equivalent, with polyesters or polyglycols are satisfactory.

(d) Diatomaceous earth supports or other water absorbing supports shall not be used as support materials.

(e) Column shall be aluminum or stainless steel, 1/8 inch OD.

b. Equipment

(1) Tubing: Stainless steel 1/8 and 1/16 inch OD as required in figure 4.

(2) Switching valve: H<sub>2</sub> - N<sub>2</sub> supply, Carle No 2821, or equivalent.

(3) 2 µL liquid injection valve: Internal construction of stainless steel with polytetrafluoroethylene seals, Carle No 2015 or equivalent.

(4) N<sub>2</sub>O<sub>4</sub> scrubber: N<sub>2</sub>O<sub>4</sub> disposal shall be accomplished in accordance with applicable local anti-pollution laws.

(5) Gas chromatograph: A chromatograph with a thermal conductivity detector.

(6) Recorder: A potentiometric recorder with a 1 millivolt span and a 1 sec FS response.

(7) Tube furnace: 10 to 12 inches long with a to 1... inch bore. Switch settings (voltage) shall be determined with a pyrometer so that it shall operate between 1022 to 1112°F (550 to 600°C), 500 to 1000 watts is adequate.

(8) Precision gas syringe: 0 - 50 µL capacity, graduated in 0.5 µL. Precision Sampling Corporation, No 050024 with needle, or equivalent.

(9) Reactor tubing: Vycor glass, 12 inch x 3/8 inch Corning No 743180, or equivalent.

(10) Alternate calibration sample loops: Stainless steel sample loop switching valve 1/16 inch diameter, 10 to 100 µL in volume.

4.3.4.2 Near infrared absorption method.

4.3.4.2.1 Preparation. Set the conditions of a Lambda 9 spectrophotometer as specified in Table III. These are suggested parameters and they may be varied by the analyst to optimize the procedure. Set the temperature of a circulating low temperature bath to -6 - 1°C (21.2 - 1.8°F). Attach the cell to the cooling bath and start the circulation. Purge the sample compartment with nitrogen so that the cells do not become coated with

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moisture. Throughout the procedure, minimize the exposure of the oxidized  $N_2O_4$  to the atmosphere.

Table III. Conditions for Lambda 9 spectrophotometer.

<u>Method</u>	<u>Scan/Manual</u>
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 /

4.3.4.2.2 Procedure. Transfer some of the oxidized  $N_2O_4$  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  $HNO_3$  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.

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

NTO composition

$$\text{Water Equivalent (wt\%)} = \frac{A_{HNO_3}}{hbf} + \frac{A_{H_2O}}{ab}$$

MON composition

$$\text{Water Equivalent (wt\%)} = \left( \frac{A_{HNO_3}}{hbf} + \frac{A_{H_2O}}{ab} \right) \left[ \frac{100 + C(\%NO)}{100} \right]$$

where:

$A_{HNO_3}$  = Absorption of  $HNO_3$

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$A_{H_2O}$  = 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

4.3.4.2.4 Reagents and equipment. The following reagents and equipment shall apply as test conditions of 4.3.4.2.

- a. Nitrogen conforming to MIL-PRF-27401, Type I
- b. Circulating low temperature bath.
- c. Two 1 cm cells with cooling jackets
- d. Syringe, 2 mL
- e. Erlenmeyer flask, 50 mL
- f. Spectrophotometer, Lambda 9, or equivalent

4.3.5 Chloride content. The chloride content of  $N_2O_4$  is determined by one of the following methods. In the event of a dispute the procedure specified in paragraph 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/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.

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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 completed, 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/lmin 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:

M = molarity of AgNO<sub>3</sub> titrant (moles/liter).

W = sample weight in mg.

4.3.5.1.4 Calibration. The AgNO<sub>3</sub> molarity (M) is obtained by titrating, in triplicate, a standard sodium chloride solution by the procedure in 4.3.5.1.2.

4.3.5.1.5 Reagents and equipment. The following reagents and equipment shall apply as test conditions of 4.3.5.1.

a. Reagents

(1) Sodium chloride: ACS reagent grade, or equivalent, dried for one hour at 212°F (100°C).

(2) Standard sodium chloride solution, 1 mL = 1.00 mg Cl<sup>-</sup>: Weigh 1.648 g dry sodium chloride into a one liter volumetric flask. Dilute to the mark with distilled water. Transfer the well mixed solution to a clean polyethylene bottle for storage.

(3) NaOH solution, 1M: Dissolve 40 g ACS reagent grade, or equivalent, sodium hydroxide in distilled water. Dilute to 1000 mL.

(4) HNO<sub>3</sub> solution, 1:1: Mix 500 mL ACS reagent grade, or equivalent, nitric acid with 500 mL distilled water.

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(5)  $\text{AgNO}_3$ , 0.05M: Dissolve 8.494 g ACS reagent grade, or equivalent, silver nitrate in distilled water to which has been added 10 mL of 1:1  $\text{HNO}_3$  solution. Dilute to 1000 mL. Store the well mixed solution in a light-proof bottle.

(6) Urea: ACS reagent grade, or equivalent, crystals.

b. Equipment

(1) Balance, analytical, 0.1 g sensitivity.

(2) Chloride ion selective electrode: Orion No 941700, or equivalent.

(3) Silver/sulfide ion selective electrode: Orion No 941600, or equivalent.

(4) Double junction reference electrode: Orion No 900200, or equivalent.

(5) Millivolt meter, high impedance pH meter with recorder output: Orion Model 701A, or equivalent.

(6) Recorder, 1, 10, 100 mV full scale: Beckman Model 1005, or equivalent.

(7) Syringe pump, 50 mL syringe, delivery rate 0.1 to 1.0 mL/min: Sage Model 341-A or equivalent, with syringe.

(8) Magnetic stirrer.

(9) Polytetrafluoroethylene tubing and coated stirring bars.

(10) Glassware, assorted: Pyrex, or equivalent.

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  $\text{N}_2\text{O}_4$  through 40 to 50 mL of chloride-free distilled water contained in each of two 250 mL Fleming absorbers, connected in series with polyvinyl tubing. The sample must be scaled to contain less than 0.050 mg  $\text{Cl}^-$ . 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 to each of the 250 mL beakers and neutralize each with concentrated ammonia to the yellow end-point. Adjust the volume in the sample beaker to contain one gram of  $\text{N}_2\text{O}_4$  per milliliter of solution by evaporating on a hot plate. Into three other 25 mL volumetric flasks add 0.010 mg  $\text{Cl}^-$ , 0.020 mg  $\text{Cl}^-$ , and 0.040 mg  $\text{Cl}^-$  of the dilute standard  $\text{Cl}^-$  solution, using a 5 mL microburet. Add chloride free distilled water to all flasks so that they contain about 20 mL of liquid. Add exactly 2.0 mL of the iron (III) ammonium sulfate reagent to the flasks and mix. Add exactly 1.0 mL of the saturated mercury (II) thiocyanate reagent, 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

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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<sup>-</sup> 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 (ie 1/1 to 5/1)

4.3.5.2.3 Reagents and equipment. The following reagents and equipment shall apply as test conditions of 4.3.5.2.

a. Reagents

(1) Chloride free distilled water: The water is considered chloride free if a 100 mL sample, treated with silver nitrate, shows no turbidity during a 24 hour period, when stored in darkness.

(2) 2,4-dinitrophenol indicator, 0.1% wt in alcohol and water.

(3) Ammonia, ACS reagent grade, 28% NH<sub>3</sub>.

(4) Nitric acid: ACS reagent grade, 70% HNO<sub>3</sub>.

(5) Iron (III) ammonium sulfate, 0.25M: Weigh 60.275 g of iron (III) ammonium sulfate dodecahydrate, FeNH<sub>4</sub>(SO<sub>4</sub>)<sub>2</sub>•12H<sub>2</sub>O, ACS reagent grade, and make up to 500 mL volume with 9M nitric acid. Filter or decant after 24 hours.

(6) Saturated mercury (II) thiocyanate: Dissolve 100 mg ACS reagent grade Hg(SCN)<sub>2</sub> in 100 mL 95% ethanol. Allow to stand, decant, and store in darkness.

(7) Stock standard chloride solution: Dissolve 1.649 g of dry primary standard grade sodium chloride in chloride free distilled water, and dilute to the mark in a 500 mL volumetric flask (1 mL = 2.0 mg Cl<sup>-</sup>).

(8) Dilute standard Cl<sup>-</sup> solution: Dilute 1.00 mL of the stock standard chloride solution to the mark in a 200 mL volumetric flask with chloride free distilled water (1 mL = 0.010 mg Cl<sup>-</sup>).

b. Equipment

(1) Chloride free glassware: All glassware used must be washed with nitric acid and rinsed with chloride free distilled water.

(2) Volumetric flasks, 25 mL, 100 mL, 200 mL, 500 mL.

(3) Volumetric pipette, as required.



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- (4) Beakers, 250 mL
- (5) Analytical balance, 0 - 100 g, 0.1 mg sensitivity.
- (6) 5.00 cm spectrophotometer cells.
- (7) Spectrophotometer; capable of furnishing narrow band light between 400 to 500 nm, and capable of accepting 5.0 cm cells.
- (8) Oven, variable temperature, to 230°F (110°C).
- (9) Ringstand and clamps, as required.
- (10) Microburet, 5.00 mL capacity.
- (11) Hot plate.
- (12) Fleming gas absorbers, 250 mL size.

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 105 - 5°C (220 - 10°F). 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  $N_2O_4$  to each dish. Using the hot plate, evaporate the sample to near 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.

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

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

where:

$W_S$  = Weight of sample dish after drying (mg)

$W_E$  = Weight of empty dish (mg)

$V_S$  = Volume of sample used (liters)

4.3.6.3 Reagents and equipment. The following reagents and equipment shall apply as test conditions of 4.3.6.

- a. Platinum evaporating dishes.
- b. Hot plate; porcelain topped.
- c. Graduated cylinder; 50 mL.

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- d. Oven, 230°F/(110°C).
- e. Analytical balance; 0.01 mg sensitivity.
- f. Watch glasses.

4.3.7 Iron content. The iron content of the low-iron propellant is determined as follows:

4.3.7.1 Procedure. Transfer 20 to 50 mL of the low-iron grade 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 at an iron wavelength closest to 2480 m on a suitable atomic absorption spectrophotometer 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 low-iron grade, MON type propellant shall be calculated as follows:

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

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)

I = Iron concentration (ppm by wt)

4.3.7.3 Calibration. Prepare 1 ppm Fe, 2 ppm Fe, 5 ppm Fe, 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

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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 m $\mu$ , 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.

4.3.7.4 Reagents and equipment. The following reagents and equipment shall apply as test conditions of 4.3.7.

a. Reagents

- (1) Sulfuric acid, reagent grade.
- (2) Hydrochloric acid, reagent grade.
- (3) Iron wire, reagent grade.
- (4) Iron standard solution, 1000 ppm: Use a commercial iron standard or prepare the standard by the following method: Weigh 1.000 g of reagent grade iron wire accurately. Transfer to a 1000 mL volumetric flask and add 15 mL of concentrated HCl solution. Heat if necessary to completely dissolve the iron wire. Dilute to the mark with distilled water.

- (5) Distilled water.

b. Equipment

- (1) Volumetric flasks, 10, 25, 1000 mL, as required.
- (2) Beaker, 50 mL.
- (3) Cylinder, graduated, 10 mL.
- (4) Balance, triple beam, 5 lb, capacity.
- (5) Balance, macro, 200 g capacity, Mettler, or equivalent.
- (6) Hot plate, controllable heat settings.
- (7) Plastic bottles, screw-cap, 8 oz, as required.
- (8) Atomic absorption spectrophotometer, with an Fe hollow cathode lamp.

4.3.8 Particulate. The particulate matter of N<sub>2</sub>O<sub>4</sub> is determined as follows:

4.3.8.1 Preparation of the membrane filter. Using forceps place a 47-mm membrane filter of nominal pore size (10  $\mu$ m) in a clean petri dish. Place the petri dish, with its lid slightly ajar, in an oven at 90 - 5°C (194 - 9°F) and leave it for 30 minutes. Remove the petri dish from the oven and place it near the balance. The petri dish cover should be ajar but still protecting the membrane filter from contamination from the atmosphere. Allow 30 minutes

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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. When possible, 400 - 500 mL (1 pt) of sample should be passed through the filter assembly during sampling. 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 400 to 500 mL of sample through the filter holder. Follow with clean, dry nitrogen gas to purge remaining  $N_2O_4$ . 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.

4.3.8.5 Equipment. The following equipment shall apply as test conditions of 4.3.8:

- a. Analytical balance, single or double pan, the precision standard deviation of which must be 0.07 mg or better.
- b. Oven, of the static type (without fan-assisted air circulation), controlling to 90 - 5°C (194 - 9°F).
- c. Petri dishes, approximately 50 mm in diameter with removable glass supports for membrane filters.
- d. Forceps, flat-bladed without serrations, non-pointed tips.
- e. Membrane filters, 47-mm diameter, polytetrafluoroethylene, filter disc with rating of 10 - 3  $\mu$ m.
- f. High pressure filter holder, 47 mm.
- g. Clean, dry nitrogen, water vapor - 26 ppm by vol max.
- h. Air ionizer for the balance case.

## 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 personnel, these personnel need to contact the responsible packaging activity to ascertain requisite packaging requirements. Packaging requirements are maintained by the

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Inventory Control Point's packaging activity within the Military Department or Defense Agency, or within the Military Department's System Command. 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

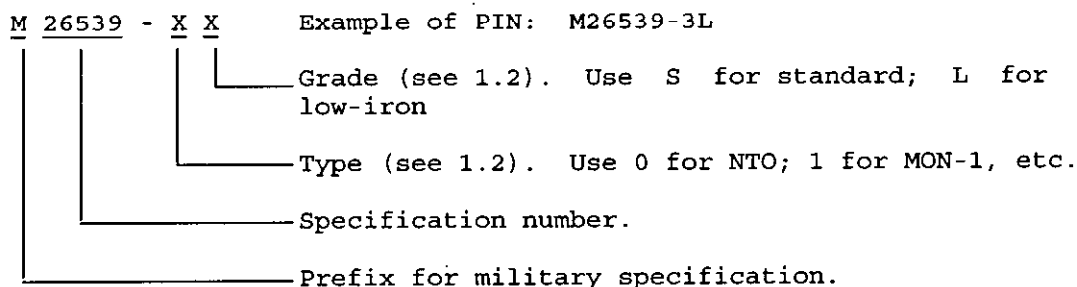
(This section contains information of a general or explanatory nature that may be helpful but is not mandatory.)

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 the specification.
- b. Type and grade of the propellant required (see 1.2).
- c. Issue of DoDISS to be cited in the solicitation, and, if required, the specific issue of individual documents referenced (see 2.2.1 and 2.3).
- d. Method of shipment, type and capacity of containers.
- e. Quantity by weight.
- f. Packaging requirements (see 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.

6.5 Subject term (key word listing).

Dinitrogen tetroxide

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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.

Custodians  
Navy - AS  
Air Force - 68

Review Activities  
Air Force - 19

Preparing Activity  
Air Force - 68

Civil Agency Interest  
NASA

(Project 9135-0137)

## STANDARDIZATION DOCUMENT IMPROVEMENT PROPOSAL

## INSTRUCTIONS

1. The preparing activity must complete blocks 1, 2, 3, and 8. In block 1, both the document number and revision letter should be given.
2. The submitter of this form must complete blocks 4, 5, 6, and 7.
3. The preparing activity must provide a reply within 30 days from receipt of the form.

NOTE: This form may not be used to request copies of documents, nor to request waivers, or clarification of requirements on current contracts. Comments submitted on this form do not constitute or imply authorization to waive any portion of the referenced document(s) or to amend contractual requirements.

## I RECOMMEND A CHANGE:

1. DOCUMENT NUMBER  
MIL-PRF-26539E

2. DOCUMENT DATE (YYMMDD)  
97/10/07

## 3. DOCUMENT TITLE

Propellants, Dinitrogen Tetroxide

## 4. NATURE OF CHANGE (Identify paragraph number and include proposed rewrite, if possible. Attach extra sheets as needed.)

## 5. REASON FOR RECOMMENDATION

## 6. SUBMITTER

a. NAME (Last, First, Middle Initial)

b. ORGANIZATION

c. ADDRESS (Include Zip Code)

d. TELEPHONE (Include Area Code)

e. DATE SUBMITTED  
(YYMMDD)

(1) Commercial  
(2) AUTOVON  
(If applicable)

## 8. PREPARING ACTIVITY

a. NAME

SA-ALC/SFSP

b. TELEPHONE (Include Area Code)

(1) Commercial

(210) 925-7847

(2) AUTOVON

945-7847

c. ADDRESS (Include Zip Code)

1014 Billy Mitchell Blvd, STE 1  
Kelly AFB, TX 78241-5603

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5203 Leesburg Pike, Suite 1403, Falls Church, VA 22041-3466  
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