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PROPELLANTS, RECOVERED NITROGEN TETROXIDE SOLUTION, SPECIFICATION FOR

LOGISTICS OPERATIONS DIRECTORATE

National Aeronautics and
Space Administration

John F. Kennedy Space Center

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TABLE OF CONTENTS

Section	Title	Page
1.	SCOPE	1
2.	APPLICABLE DOCUMENTS	1
2.1	Governmental	1
2.1.1	Specifications	1
2.1.2	Other Documents	2
2.2	Non-Governmental	2
3.	REQUIREMENTS	3
3.1	Chemical and Physical Properties	3
3.2	Limiting Values	3
3.3	Filter	3
3.4	Qualitative Requirements	4
4.	QUALITY ASSURANCE PROVISIONS	4
4.1	Responsibility for Inspection	4
4.2	Classification of Tests	4
4.3	Quality Conformance Tests	4
4.3.1	Individual Tests	4
4.3.2	Sampling Tests	4
4.3.2.1	Sampling Plan	5
4.4	Rejection	6
4.5	Test Methods	6
4.5.1	Examination of Product	6
4.5.2	NO Content	6
4.5.2.1	Tared Sample	6
4.5.2.2	Procedure	6
4.5.2.3	Calculation	7
4.5.2.4	Reagents and Equipment	7
4.5.3	Nitrogen Tetroxide Assay	8
4.5.3.1	Preparation of Sample	8
4.5.3.2	Calculation	9
4.5.3.3	Reagents and Equipment	10
4.5.4	Nitric Acid and Water Assay	11

TABLE OF CONTENTS (cont)

Section	Title	Page
4.5.4.1	Preparation	11
4.5.4.2	Procedure	11
4.5.4.3	Calculation	12
4.5.4.4	Reagents and Equipment	13
4.5.5	$NO + N_2O_4 + HNO_3 + H_2O$ + Assay	14
4.5.6	Chlorides	14
4.5.6.1	Silver Nitrate ($AgNO_3$) Titration Method	14
4.5.6.2	Colorimetric Method	16
4.5.7	Sodium	18
4.5.7.1	Procedure	19
4.5.7.2	Calculation	19
4.5.7.3	Standard Solution	19
4.5.7.4	Reagents and Equipment	19
4.5.8	Nonvolative Residue	19
4.5.8.1	Procedure	20
4.5.8.2	Calculation	20
4.5.8.3	Reagents and Equipment	20
4.5.9	Particulate	21
4.5.9.1	Preparation of Test Membrane Filter	21
4.5.9.2	Sampling	21
4.5.9.3	Procedure	21
4.5.9.4	Calculation	21
4.5.9.5	Equipment	21
4.5.10	Density Hygrometer Method	22
4.6	Preparation for Delivery Inspection	22
5.	PREPARATION FOR DELIVERY	22
5.1	Packaging	22
5.2	Preparation of Containers	22
5.3	Filling	23
5.4	Labeling and Marking	23
5.4.1	Identification Tag	23
5.4.2	Precautionary Label	23

TABLE OF CONTENTS (cont)

Section	Title	Page
6.	NOTES	23
6.1	Intended Use	23
6.2	Definitions	23
6.3	Pollution Control	23

ABBREVIATIONS AND ACRONYMS

$AgNo_3$	silver nitrate
ANSI	American National Standards Institute
ASTM	American Society for Testing and Materials
CCAS	Cape Canaveral Air Station
CFR	Code of Federal Regulations
CH_4	methane
cm	centimeter
DOT	Department of Transportation
g	gram
H	hydrogen
H_2O	water
HCL	hydrochloric acid
HNO_3	nitric acid
lb/gal	pound per gallon
IM	Installation Management and Operations Directorate
in	inch
JPC	Joint Propellants Contractor
kg/L	kilogram per liter
kPa	kilopascal
KSC	John F. Kennedy Space Center
L	liter
M	molarity
MIL	military
mg	milligram
min	minute
mL	milliliter
mm	millimeter
MON	mixed oxides of nitrogen
N	normality
Na	sodium
NaOH	sodium hydroxide
NH_3	ammonia
nm	nanometer
NO	nitric oxide
N_2O_4	nitrogen tetroxide
NPT	national pipe thread
O_2	oxygen
OS	oxidizer solution
psi	pound per square inch
S	second

ABBREVIATIONS AND ACRONYMS (cont)

STD	standard
SPEC	specification
USAF	United States Air Force
wt %	weight percent
μm	micrometer
°C	degree Celsius
°F	degree Fahrenheit

PROPELLANTS, RECOVERED NITROGEN TETROXIDE SOLUTION SPECIFICATION FOR

1. SCOPE

This specification covers the requirement for nitrogen tetroxide (N_2O_4) solution, also known as oxidizer solution (OS), recovered from propellant systems. N_2O_4 solution is actually a blend of N_2O_4, nitric acid (HNO_3), and water (H_2O). This specification provides a means of categorizing recovered propellants for either reclamation for alternate reuse or for reprocessing to original manufacturing purity.

2. APPLICABLE DOCUMENTS

The following documents form a part of this document to the extent specified herein. When this document is used for procurement, including solicitations, or is added to an existing contract, the specified revision levels, amendments, and approval dates of said documents shall be specified in an attachment to the Solicitation/Statement of Work/Contract. In the event of conflict between the documents referenced herein and the contents of this specification, the contents of this specification shall be considered a superseding requirement. The latest revision at the publication date of this specification shall apply, unless otherwise noted.

2.1 Governmental.

2.1.1 Specifications.

John F. Kennedy Space Center (KSC), NASA

KSC-C-123	Surface Cleanliness of Fluid Systems, Specification for
81K04331	Propellant Portable Container Marking, Specification for

Federal

49 CFR 170-190	Department of Transportation Rules and Regulations for the Transportation of Explosives and Other Dangerous Articles

Military

MIL-P-25508	Propellant, Oxygen
MIL-P-26539	Propellant, Nitrogen Tetroxide
MIL-P-27401	Propellant, Pressurizing Agent, Nitrogen

2.1.2 Other Documents.

KHB 8800.7	Hazardous Waste Management
OPLAN 19-14	

(Copies of specifications, standards, drawings, and publications required by suppliers in connection with specified procurement functions should be obtained from the procuring activity or as directed by the Contracting Officer.)

2.2 Non-Governmental.

American National Standards Institute (ANSI)

ANSI Z129.1	Hazardous Industrial Chemicals, Precautionary Labeling

(Application for copies should be addressed to the American National Standards Institute, 1430 Broadway, New York, NY 10018.)

American Society for Testing and Materials (ASTM)

ASTM D287	Test Method for API Gravity of Crude Petroleum and Petroleum Products (Hydrometer Method)
ASTM E29	Practice for Using Significant Digits in Test Data To Determine Conformance With Specifications

(Applications for copies should be addressed to the American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103.)

3. REQUIREMENTS

3.1 Chemical and Physical Properties. - The chemical and physical properties of the recovered propellants shall conform to the grades listed in table 1 when tested in accordance with the applicable test methods (4.5).

Table 1. Chemical Properties

Composition	N_2O_4 Solution	Test Paragraph
Nitric oxide (NO) (percent by weight)	Report	4.5.2
Nitrogen tetroxide (N_2O_4) (percent by weight)	Report	4.5.3
Nitric acid (HNO_3) (percent by weight)	Report	4.5.4
Water (H_2O) (percent by weight)	5 maximum	4.5.4
$NO+N_2O_4+HNO_3+H_2O$ (percent by weight)	99 minimum	4.5.5
Chloride (percent by weight)	0.04 maximum	4.5.6
Sodium (ppm by weight)	10 maximum	4.5.7
Nonvolatile residue (mg/L)	25 maximum	4.5.8
Particulate (mg/L)	10 maximum	4.5.9
Density (kg/L)	Report	4.5.10

3.2 Limiting Values. - The following statement 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 righthand place of figures used in expressing the limitation value, in accordance with the rounding-off method of ASTM E29.

3.3 Filter. - A filter with a 10-micrometer (μm) nominal and a 40-μm absolute rating shall be used whenever recovered propellant is transferred into bulk cylinders, portable tanks, or cargo tanks.

3.4 Qualitative Requirements. - The propellant shall be red-brown to emerald green (N_2O_4) homogenous liquid when examined visually by transmitted light. A red-brown color will indicate that the propellant has very low nitric oxide (NO) content. That portion of the analysis may be skipped and reported as zero. Any presence of particulates shall be noted on the analysis sheet. If the propellant is essentially water white (minimal red-brown tint), then the propellant may actually be nitric acid. The analyst should seek guidance from KSC/CCAS Joint Propellants Contractor (JPC) Fluids Management before proceeding with this analysis.

4. QUALITY ASSURANCE PROVISIONS

4.1 Responsibility for Inspection. - Unless otherwise specified in the contract, the KSC/CCAS Joint Propellants Contractor shall be responsible for the performance of all inspection requirements as specified herein. Except as otherwise specified in the contract, the JPC may use its own or any other facilities suitable for the performance of the inspection requirements specified herein, unless disapproved by the Government. The Government reserves the right to perform any of the inspections set forth in the specification where such inspections are deemed necessary to ensure that supplies and services conform to prescribed requirements.

4.2 Classification of Tests. - The inspection and testing of the propellant shall be classified as quality conformance tests.

4.3 Quality Conformance Tests. - Quality conformance tests shall consist of:

a. Individual tests (4.3.1)

b. Sampling tests (4.3.2)

4.3.1 Individual Tests. - The propellant shall be sampled by the Examination of Product test described in 4.5.1.

4.3.2 Sampling Tests. - The propellant shall be selected in accordance with 4.3.2.1 and subjected to the following tests:

a. NO assay (4.5.2)

b. N_2O_4 assay (4.5.3)

c. HNO_3 and water (H_2O) assay (4.5.4)

d. Chlorides (4.5.6)

e. Sodium (4.5.7)

f. Nonvolatile residue (4.5.8)

g. Particulate (4.5.9)

h. Density (4.5.10)

4.3.2.1 Sampling Plan.

4.3.2.1.1 Lot. - A lot shall consist of one of the following:

a. The propellant recovered from an individual batch process that filled recovery containers directly from the process output.

b. The recovered propellant is consolidated into a larger volume from recovery containers filled in a batch process (a. above) to form a new homogenous mixture.

4.3.2.1.2 Sample. - A sample shall consists of not less than 800 milliliters (mL) of propellant. Two 400-mL samples may be taken for the test specified in 4.3.2. One sample may be used for tests a, b, and c and the other for tests d, e, f, and h (see 4.5.9.3 for test g). Unless otherwise specified, quality conformance tests shall be performed on each sample of the propellant taken directly from the recovery or consolidation containers.

4.3.2.1.2.1 Sampler. - The sampler shall be capable of accepting a 400-mL or 800-mL sample and shall be 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 cleaned and handled in accordance with the procedure described in KSC-C-123, Level 500.

4.3.2.1.3 Nonbulk Cylinders. - Nonbulk cylinder sampling shall be at the discretion of JPC Fluids Management if the individual recovery cylinders are each provided with an identification tag in accordance with 5.4.1 of the propellant contained therein. Cylinders whose contents and/or origins are not otherwise known shall each be considered a lot and shall be individually sampled.

4.3.2.1.4 Bulk Cylinders, Portable Tanks, and Cargo Tanks. - Each bulk cylinder, portable tank, or cargo tank shall constitute a lot. JPC Fluids Management may defer container sampling until an adequate inventory of recovered propellant has been accumulated in that container. This will preclude repetitive sampling of partial tank loads of recovered propellants.

4.3.2.1.5 Other Containers. - Unless otherwise specified, other containers of 454-liter (120-gallon) or less water capacity shall be sampled in accordance with 4.3.2.1.3 and other containers equal to greater than 455-liter (121 gallon) water capacity shall be sampled in accordance with 4.3.2.1.4.

4.4 Rejection. - When any sample of the propellant tested in accordance with 4.5 fails to conform to the requirements specified herein, the entire lot represented by the sample shall be rejected.

4.5 Test Methods.

4.5.1 Examination of Product. - The sample (4.3.2.1.2) 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.

4.5.2 NO Content. - If the recovered propellant has a green tint when visually examined, then the NO content shall be determined by referring to this paragraph. If the propellant is red-brown in color, then this paragraph shall be ignored and the NO content shall be reported as zero. The NO content of the sample shall be determined by the following method.

4.5.2.1 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 60 to 80 g of the sample. Close all valves and 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 re-weigh the sample bomb to the nearest 0.001 g, obtaining the sample weight by difference. If the sample weight is below 60 g, another sample shall be taken.

4.5.2.2 Procedure. - Attach a rotameter with stainless-steel tubing to the reducing valve of a cylinder of oxygen (O_2). Connect a length of 1.6 millimeter (mm) [1/16 inch (in)] stainless-steel tubing and, using the reducing valve, adjust the oxygen pressure to 207 kilopascals (kPa's) [30 pounds per square inch (psi)]. Close the cylinder valve. Place the sample bomb in an ice bath and maintain the temperature at approximately 0 degree Celsius (°C) [32 degrees Fahrenheit (°F)]. After the sample has been allowed to cool for 10 minutes, permit oxygen to flow into the sample bomb by first opening the cylinder valve and then opening the bomb valve.

Occasionally shake the bomb to hasten absorption and oxidation. Lack of oxygen flow through the rotameter indicates completion of the reaction. Allow the sample bomb to remain in the ice bath for 15 minutes, with the valves open after the reaction has been completed. Disconnect the sample bomb, remove it from the bath, warm it to ambient temperature, and wipe it dry. Place the sample bomb on a balance and record the weight to the nearest 0.001 g.

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

$$x = B-A$$
$$y = C-B$$

$$\text{NO, percent by weight} = \frac{\left[y - 0.003857\left(z - \frac{x+y}{1.49}\right)\right] 187.5}{x} - 0.015$$

Where:

x = sample weight in grams

y = O_2 weight in grams

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

A = weight of sample bomb in grams

B = weight in sample bomb plus sample in grams

C = weight in sample bomb plus sample and O_2 in grams

4.5.2.4 Reagents and Equipment. - The following reagents and equipment or their equivalent shall apply as test conditions of 4.5.2.1:

a. Reagents

(1) Nitrogen, MIL-P-27401, Type 1

(2) Oxygen, MIL-P-25508, Type 1

b. Equipment

(1) Valve, needle, 3.2 mm (1/8 in) national pipe thread (NPT) male inlet x 6.4 mm (1/4 in) Swagelok outlet, stainless steel

(2) Bomb, sample, 51 mm (2 in) diameter with 3.2 mm (1/8 in) NPT female, 302 stainless steel, 24 gage

(3) Stand, ring

(4) Tubing, polyethylene, length as required

(5) Rotameter, glass-ball, with 0 to 1.0 liter (L) per minute (min) capability

(6) Tubing, stainless steel 1.6-mm (1/16 in) diameter

(7) Bath, ice

(8) Balance, analytical, plus or minus 0.1 milligram (mg) sensitivity, 0.1-mg accuracy

4.5.3 Nitrogen Tetroxide Assay. - The N_2O_4 content of the sample shall be determined by the following procedure.

4.5.3.1 Preparation of Sample.

4.5.3.1.1 Oxidation State. - Prior to the weighing and sealing of the assay sample, one of the following requirements shall be complied with.

4.5.3.1.1.1 Red-Brown N_2O_4/Solution. - N_2O_4 shall be assayed without further chemical treatment. Proceed to 4.5.3.1.2.

4.5.3.1.1.2 Green N_2O_4/Solution. - The N_2O_4 assay of NO containing propellant shall be performed without further chemical treatment of the oxidized sample generated in 4.5.2.1. Proceed to 4.5.3.1.2 and 4.5.3.2.

4.5.3.1.2 Sample Sealing. - Cool the sample to approximately 0 °C (32 °F) with crushed ice. Introduce the cooled sample into a clean, weighed 2-mL glass ampoule directly from the sampler through a 1.6-mm (1/16 in) stainless-steel tube. Insert the ampoule tip into an adequate size polyvinylchloride tube, approximately 150 mm (6 in) 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, wrap it with a piece of soft paper, and remove the polyvinylchloride tube. Seal the ampoule in the hot flame of a methane (CH_4)/O_2 or hydrogen (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 0.5 normalility (N) alkali is used in 4.5.3.1.3.

4.5.3.1.3 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 percent hydrogen peroxide. Chill the 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 it vigorously, keeping the stopper firmly in place. Continue shaking until all the 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 place it on a steam bath or hot plate at a moderate heat setting [approximately 120 °C (250 °F)] 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 to 5 drops of methyl red or methyl orange indicator and titrate with 0.5 N sodium hydroxide (NaOH) solution to the yellow end point. Run a reagent blank in the same manner as the sample.

4.5.3.2 Calculation.

Red-Brown N_2O_4 solution

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

Where:

a = mL NaOH for sample

b = mL NaOH for blank

N = normality of NaOH

W = grams of N_2O_4 in ampoule

Green N_2O_4 solution

N_2O_4, percent by weight = 1.534 (A-B)

Where:

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

(see Red-Brown N_2O_4 solution above for a, b, N definitions)

W = grams of oxidized N_2O_4 in ampoule

B = percent by weight NO

4.5.3.3 Reagents and Equipment. - The following reagents and equipment shall apply as test conditions of 4.5.3.

a. Reagents

(1) Sodium hydroxide solution, 0.5 N: 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 0.5 N hydrochloric acid (HCl) or acid phthalate to the methyl red or methyl orange end point. Quantitatively transfer 30 to 50 mL of the standard acid into a beaker from a 100-mL buret. Titrate the acid with the 0.5 N NaOH using the same buret after cleaning. Store the 0.5 N NaOH in a polyethylene container and ensure the exclusion of carbon dioxide during storage.

(2) Distilled water

(3) Methyl red or methyl orange indicator solution: 0.1 percent by weight in ethanol and distilled water

(4) Hydrogen peroxide, ACS, or equivalent, reagent grade, 30 percent weight

(5) Standard acid solution 0.5 N: 0.5 molarity (M) HCl standardized with primary standard grade diphenyl guanidine to the methyl red 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

4.5.4 Nitric Acid and Water Assay. - The nitric acid and water assay of the sample shall be determined by the following near infrared absorption procedure.

N_2O_4 solution may have a water and nitric acid content above the limits of the infrared instrument. If so, the analyst shall report the nitric acid as part of N_2O_4 determined in 4.5.3. The water shall be determined by difference [100 - N_2O_4 weight percent (wt %)].

4.5.4.1 Preparation. - Set the conditions of a lambda 9 spectrophotometer as specified in table 2. These are suggested parameters and may be varied by the analyst to optimize the procedure. Set the temperature of a circulating low temperature bath to -6 °C ±1 °C (21.2 °F ±1.8 °F). Attach the cell to the cooling bath and start the circulation. Purge the sample compartment with nitrogen so the cells do not become coated with moisture.

4.5.4.2 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 and then place the loaded cell in the 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 bandpass 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 atmospheric (free) water can be found by entering 1404 PEAK FIND. Record the absorbency.

Table 2. Conditions for Lambda 9 Spectrophotometer

Method		Scan/Manual
01	Ord/Absc Mode	Abs/WL
02	Slit/Gain/Sens	2.00 nanometer/2
03	Scan Speed	240 nanometer/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	Abscessa Format	20 nm/cm
12	Printer	/SCALE/

4.5.4.3 Calculation. - The wt % nitric acid and water shall be calculated by one of the following formulas:

Brown composition

$$\text{Water (wt \%)} = \frac{A_{H_2O}}{ab}$$

$$\text{Nitric acid (wt \%)} = \frac{A_{HNO_3}}{hb}$$

Green composition

$$\text{Water (wt \%)} = \frac{A_{H_2O}}{ab} X \frac{100 + C(\%\ NO)}{100}$$

$$\text{Nitric acid (wt \%)} = \frac{A_{HNO_3}}{hb} X \frac{100 + C(\%\ NO)}{100}$$

Where:

$^{A}HNO_3$ = Absorption of HNO_3

$^{A}H_2O$ = Absorption of free water

h = Absorption coefficient of HNO_3 = 0.178

b = Thickness of sample (cm)

a = Absorption coefficient of free water = 0.55

C = Calculation coefficient (NO to N_2O_4) = 0.534

4.5.4.4 Reagents and Equipment. - The following reagents and equipment shall apply as test conditions of 4.5.4.

a. Reagent

(1) Nitrogen: conforming to MIL-P-27401, Type 1

b. Equipment

(1) Circulating low temperature bath

(2) Two 1-cm cells with cooling jackets

(3) Syringe, 2 mL

(4) Erlenmeyer flask, 50 mL

(5) Spectrophotometer, lambda 9

4.5.5 NO + N_2O_4 + HNO_3 + H_2O + Assay. - The NO, N_2O_4, HNO_3, and H_2O percent determined in paragraphs 4.5.2, 4.5.3, and 4.5.4, respectively, shall be added together.

4.5.6 Chlorides. - The chloride content of N_2O_4 is determined by one of the following methods. In the event of a dispute, refer to the procedure specified in 4.5.6.1.

4.5.6.1 Silver Nitrate ($AgNO_3$) Titration Method.

4.5.6.1.1 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 1-M NaOH solution. Activate the stirrer. Weigh a sampler containing oxidized N_2O_4 solution material to 0.1 g. 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 g) of sample, via the tube below the surface of the caustic. The rate should be low enough so 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. While stirring, slowly add 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. While stirring, slowly add 1:1 HNO_3 until gas evolution ceases or a pH of 2.5 to 3.0 is reached. The pH of the solution should be checked often while adding the acid to make sure that the pH does not go below 2.5. Allow the solution to stand 15 minutes in preparation for titration.

4.5.6.1.2 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 0.5 M $AgNO_3$ 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 the sample stirring, turn on the meter, recorder, and pump. Chart speed should be approximately 2.5 cm (1 in) per minute. Mark the point where the syringe pump delivery begins. As soon as the "S" shaped 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/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 buret and detection of millivolts from the millivolt meter. The millivolts versus 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.

4.5.6.1.3 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 $AgNO_3$ titrant

W = sample weight in mg

4.5.6.1.4 Calibration. - The $AgNO_3$ molarity is obtained by titrating, in triplicate, a standard sodium chloride solution by the procedure in 4.5.6.1.2.

4.5.6.1.5 Reagents and Equipment. - The following reagents and equipment shall apply as test conditions of 4.5.6.1.

a. Reagents

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

(2) Standard sodium chloride solution, 1 mL = 1.00 mg C1: weigh 1.648 g dry sodium chloride into a 1-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, 1 M: dissolve 40-g ACS reagent grade or equivalent, sodium hydroxide in distilled water. Dilute to 100 mL.

(4) HNO_3 solution, 1:1: mix 500-mL ACS reagent grade or equivalent, nitric acid with 500-mL distilled water.

(5) $AgNO_3$, 0.05 M: dissolve 8.494-g ACS reagent grade or equivalent, silver nitrate in distilled water to which has been added 10 mL of 1:1 HNO_3 solution. Dilute to 1000 mL. Store the well-mixed solution in a lightproof bottle.

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

b. Equipment

(1) Balance, analytical, 0.1-g sensitivity

(2) Chloride ion selective elective 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

4.5.6.2 Colorimetric Method.

4.5.6.2.1 Procedure. - Weigh the cylinder containing the oxidizer sample prepared in 4.5.2.1 to the nearest 0.10 g. Slowly bubble 1 to 50 g of N_2O_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 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 1 g of N_2O_4 per milliliter of solution by evaporating it on a hot plate. Into three other 25-mL volumetric flasks, add 0.010 mg Cl^-, and 0.020 mg Cl^-, and 0.040 mg Cl^- of the dilute standards solution, using a 5-mL microburet. Add chloride-free distilled water to all flasks so 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 5.00-cm cell at 460 nm, after setting the blank in a 5.00-cm cell at zero absorbance (100 percent transmittance). Plot the absorbance of the standards versus mg Cl^- and draw a curve through the origin.

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

$$\text{Chloride, percent by weight} = \frac{(\text{mg } Cl^- \text{ from curve}) \times F \times 100}{\text{mg } N_2O_4}$$

Where:

F = aliquot factor (i.e., 1/1 to 5/1)

4.5.6.2.3 Reagents and Equipment. - The following reagents and equipment shall apply as test conditions of 4.5.6.2.

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 percent weight in alcohol and water.

(3) Ammonia, ACS reagent grade, 28 percent ammonia NH_3.

(4) Nitrate acid: ACS reagent grade, 70 percent HNO_3.

(5) Iron (III) ammonium sulfate, 0.25 M: Weigh 60.275 g of iron (III) ammonium sulfate dodecahydrate, $FeNH_4(SO_4)_2 \cdot 12H_2O$, ACS reagent grade, and make up to 500-mL volume with 9-M nitric acid. Filter or decant after 24 hours.

(6) Saturated mercury (II) thiocyanate: Dissolve 100-mg ACS reagent grade $Hg(SCN)_2$ in 100-mL 95-percent 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^-).

(8) Dilute standard Cl^- 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^-).

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

(4) Beakers, 250 mL

(5) Analytical balance, 0 to 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 110 °C (230 °F)

(9) Ringstand and clamps, as required

(10) Microburet, 5.00-mL capacity

(11) Hot plate

(12) Fleming gas absorbers, 250-mL size

4.5.7 Sodium. - The sodium content of the propellant shall be determined by the following method.

4.5.7.1 Procedure. - Thoroughly clean and dry two 250-mL beakers per sample. Transfer 25 mL of the N_2O_4 to each beaker. Using the hot plate, evaporate the sample to near dryness. Let the beaker cool, then dissolve the residue in 100 mL of distilled water. Set up atomic absorption spectrophotometer using standard conditions for sodium: air/acetylene flame and 589.0 nm. Aspirate the sample and standards, record the absorbencies, and graph the standards.

4.5.7.2 Calculation. - Determine ppm sodium (Na) in the sample from a standard graph and calculate the ppm by weight in N_2O_4 as follows:

$$\text{ppm Na} = \frac{(\text{ppm from graph})\ (4)}{1.44}$$

4.5.7.3 Standard Solution. - Prepare the sodium standard solutions as follows. Dissolve 3.7 g $NaNO_3$ in 1 liter of demineralized water to create a 1000-ppm sodium solution. Dilute the solution as follows to prepare the working standards:

0.1 to 100 mL: 1 ppm Na

0.2 to 100 mL: 2 ppm Na

0.4 to 100 mL: 4 ppm Na

4.5.7.4 Reagents and Equipment. - The following reagents and equipment shall apply as test conditions of 4.5.7.

a. Reagents

(1) Demineralized water

b. Equipment

(1) 250-mL beakers

(2) Hot plate, porcelain topped

(3) Atomic absorption spectrophotometer, Perkin-Elmer no. 2380, or equal.

4.5.8 Nonvolatile Residue. - The nonvolatile residue of the propellant shall be determined by the following method.

4.5.8.1 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 mg. Place a hot plate in an exhaust hood and place the weighed dishes on the plate. Transfer 500 mL of the N_2O_4 to each dish. Using the hot plate, evaporate the sample until only 1 to 2 mL remain in each dish. Oven-dry the dishes for 1 hour beyond the point when no liquid remains in each dish. After drying, cover the dishes with a watch glass and allow to cook next to the balance for 30 minutes. Weigh each dish to the nearest 0.01 mg.

4.5.8.2 Calculation. - The % wt nonvolatile residue shall be calculated by the following formula:

$$\text{NVR (\% wt)} = \frac{(Wr - Wx)}{V * D}$$

where:

Wr = dish weight with residue (grams)

Wx = dish weight empty (grams)

V = volume of sample used (liters)

D = density of propellant at measured temperature

4.5.8.3 Reagents and Equipment. - The following reagents and equipment shall apply as test conditions of 4.5.8.

a. Reagents

(1) Sulfuric acid, reagent grade

b. Equipment

(1) Platinum evaporating dishes

(2) Hot plate, porcelain topped

(3) Graduated cylinder, 50 mL

(4) Oven, 110 °C (230 °F)

(5) Analytical balance, 0.01-mg sensitivity

(6) Watch glasses

4.5.9 Particulate. - The particulate matter of the propellant shall be determined as follows.

4.5.9.1 Preparation of Test Membrane Filter. - Using forceps, place a 47-mm membrance filter of nominal pore size (10 μm) in a clean petri dish. Place the petri dish, with its lid slightly ajar, in an overn 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 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.

4.5.9.2 Sampling. - When possible, 400 to 500 mL of sample should be passed through the filter assembly during sampling of the propellant container. The sample volume actually employed must be reported.

4.5.9.3 Procedure. - Assemble the filter holder with the weighed membrane filter and position it so the filter membrane is in a horizontal position. Pass 400 to 500 mL of sample through the filter holder. Follow with clean, dry nitrogen or helium gas to purge the 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 the surface. The drying procedure described in 4.5.9.1 should be followed in detail.

4.5.9.4 Calculation. - Subtract the initial weight of the test membrane filter, W1, from the final weight, W2. Divide the corrected weight of contaminant (W2 - W1) by the volume of sample filtered and report the result as total contaminate expressed in milligrams per liter. Report the result to the nearest 0.01 mg/L and also report the sample volume used in the test.

4.5.9.5 Equipment. - The following equipment shall apply as test conditions of 4.5.6.

a. Analytical balance, single or double pan, the precision standard deviation must be 0.07 mg or better

b. Oven, of the static type (without fan-assisted air circulation), controlling to 90 ±5 °C

c. Petri dishes, approximately 50 mm (2 in) in diameter with removable glass supports for membrane filters

d. Forceps, flat-bladed with unserrated, nonpointed tips

e. Vacuum system

f. Test membrane filters, 47-mm diameter, polytetrafluoroethylene, filter disc with rating of 10 ±3 µm

g. Filter apparatus

h. Air ionizer, for the balance case

i. Disc filter holder, in-line, reagent resistant plastic, 47 mm

4.5.10 Density Hygrometer Method. - The propellant density shall be determined by the general procedure described in specification ASTM D287. Density shall be reported at 25 °C (77 °C) reported in kilogram per liter (kg/L) units pound per gallon (lb/gal). The analyst shall make whatever changes necessary to the procedure commensurate with the hazards of N_2O_4 and nitric acid. Use the propellant left over from the particulate analysis in 4.5.9.

4.6 Preparation for Delivery Inspection. - The preservation, packaging, packing, and marking for shipment and storage of the propellant shall be inspected to determine compliance with the requirement of section 5 of this specification.

5. PREPARATION FOR DELIVERY

5.1 Packaging. - The propellant shall be packaged in containers as specified by the JPC. Packaging shall comply with the requirements of the Department of Transportation (DOT) Regulations 49 CFR 170-190 or a waiver from the KSC/CCAS Safety Organizations obtained by the JPC.

5.2 Preparation of Containers. - The JPC shall establish the condition of all containers to ensure they are free from contamination and suitable for shipment and storage. Leased or Government-owned containers shall be cleaned and repaired in accordance with the schedule established in the contract. Internal

inspections on portable tanks used in exclusive continuous service need be made only upon initial entry into that service or at any required retest or overhaul.

5.3 Filling. - Containers shall not be entirely filled. Typically a 10 percent-by-volume ullage space shall be left in each container to ensure that no leakage or over-pressurization of the container occurs. After filling of containers, the space above the liquid level shall be filled with nitrogen conforming to MIL-P-27401, Type I, to not less than 34.4 kPa (5 psi) or as specified in the container's operating procedure.

5.4 Labeling and Marking. - Each container shall be marked, labeled, and/or placarded in accordance with DOT regulations and/or 81K04331 as appropriate. In addition, an identification tag and precautionary label shall be used.

5.4.1 Identification Tag. - An identification tag, KSC Form 28-688, shall be secured to each container and shall contain the following information: propellant name, quantity, facility of origin, name of generating contractor or program, and date of recovery from a propellant system.

5.4.2 Precautionary Label. - A precautionary label prepared in accordance with ANSI Z129.1 shall be applied to each container.

6. NOTES

6.1 Intended Use. - The recovered propellants covered by this specification are intended for reprocessing to conform to MIL-P-26539.

6.2 Definition. - For the purposes of this specification, the following definitions apply.

a. Particulate. The undissolved solids retained on a 10-mm filter membrane.

b. Homogeneous liquid. A homogeneous liquid is devoid of any visible layers or foreign liquid but may contain solid material as permitted within this specification.

6.3 Pollution Control. - US Public Laws dictate increased effort to improve air, land, and water pollution control of toxic propellant vapors, leaks, spills, and disposal during all phases of manufacture, transfer, storage, and transportation operations. KSC/CCAS propellants users should consult KHB 8800.7 (on KSC) or OPLAN 19-14 [on Cape Canaveral Air Station (CCAS)] for information regarding waste management, disposal and minimization.

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