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PERFORMANCE SPECIFICATION

PROPELLANT, HYDRAZINE



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

1. SCOPE

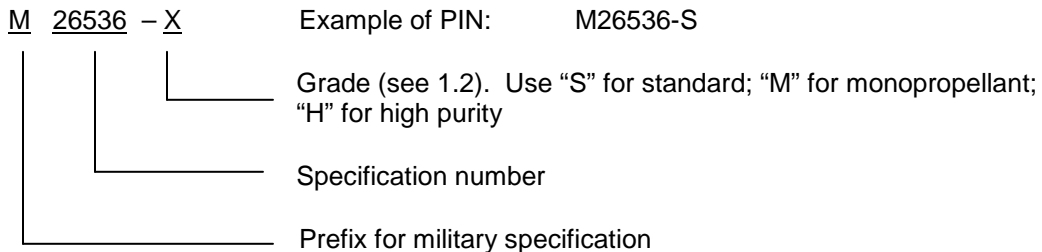
1.1 Scope. This specification covers the requirements for three grades of hydrazine (N₂H₄).

1.2 Classification. Hydrazine will be of the following designated grades as specified (6.2).

GRADES

Standard	-	For uses other than those required by monopropellant and high purity grades.
Monopropellant	-	Normal product with strict control of specified impurities. To be specific only for monopropellant catalytic engines where extended life is a requirement.
High Purity	-	Special production with strict control of specified impurities.

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



2. APPLICABLE DOCUMENTS

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

2.2 Government documents.

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 cited in the solicitation or contract.

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DEPARTMENT OF DEFENSE SPECIFICATIONS

MIL-PRF-25604	Propellant, uns-Dimethylhydrazine
MIL-PRF-27401	Propellant Pressurizing Agent, Nitrogen
MIL-PRF-27404	Propellant, Monomethylhydrazine
MIL-PRF-27407	Propellant Pressurizing Agent, Helium

(Copies of these documents are available online at <https://assist.daps.dla.mil/quicksearch/> or from the Standardization Document Order Desk, 700 Robbins Avenue, Bldg 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 these documents are those cited in the solicitation or contract.

ASTM International

ASTM D1068	Standard Test Methods for Iron in Water (DoD Adopted)
ASTM D1193	Standard Specification for Reagent Water (DoD Adopted)
ASTM D1976	Standard Test Method for Elements In Water by Inductively-Coupled Argon Plasma Atomic Emission Spectroscopy
ASTM D2276	Standard Test Method For Particulate Contaminant in Aviation Fuel by Line Sampling (DoD Adopted)
ASTM E29	Standard Practice Using Significant Digits in Test Data to Determine Conformance with Specifications (DoD Adopted)
ASTM E394	Standard Test Method for Iron in Trace Quantities Using the 1,10-Phenanthroline Method

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

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY (EPA)

EPA 300.0 Determination of Inorganic Anions by Ion Chromatography.

(Copies of these documents are available online at <http://water.epa.gov> or call EPA New England Customer Call Center at (888) 372-7341 for New England States or (617)918-111 for all others)

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

3. REQUIREMENTS

3.1 Chemical and physical properties. The chemical and physical properties of the propellant shall conform to those listed in Table I when tested in accordance with the applicable test methods.

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 E29, Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications.

3.3 Filter.

3.3.1 Standard grade. A filter with a rating of at least 10 micrometer (μm) nominal and 40 μm absolute rating shall be installed between the manufacturer's plant system and the container to be filled for delivery.

3.3.2 Monopropellant and high purity grades. A filter with a rating of at least 2 μm nominal and 10 μm absolute rating shall be installed between the manufacturer's plant system and the container to be filled for delivery.

3.4 Qualitative. The propellant shall be colorless, homogeneous liquid when examined visually by transmitted light.

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TABLE I. *Chemical and physical properties*

Properties	Limits			
	Standard grade	Monopropellant grade	High purity grade	Test paragraph
Hydrazine (% by wt)	98 min	98.5 min	99.0 min	4.3.2
Water (% by wt)	1.5 max	1.0 max	1.0 ⁽¹⁾ max	4.3.2
Ammonia (% by wt)	---	---	0.3 max	4.3.2
Particulate (mg/L)	10 max	1.0 max	1.0 max	4.3.3
Chloride (% by wt)	---	0.0005 max	0.0005 max	4.3.4
Aniline (% by wt)	---	0.50 max	0.003 max	4.3.5
Iron (% by wt)	---	0.002 max	0.0004 max	4.3.6
Nonvolatile residue (% by wt)	---	0.005 max	0.001 max	4.3.7
Carbon dioxide (% by wt)	---	0.003 max	0.003 max	4.3.8
Other volatile carbonaceous material ⁽²⁾ (Total as UDMH, MMH, & IPA % by wt)	---	0.02 max	0.005 max	4.3.9

Note:
¹ High purity grade is available with a range of 0.5 to 1.0 % by wt water upon request to the procuring activity (DLA Aerospace Energy).
² Unsymmetrical dimethylhydrazine (UDMH), Monomethylhydrazine (MMH), and Isopropyl Alcohol (IPA).

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 (see 4.2.1)
- b. Sampling tests (see 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 (see 4.3.1)

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4.2.2 Sampling tests. The propellant shall be selected according to 4.2.2.1 and subjected to the tests indicated in Table I as described under 4.3.

4.2.2.1 Sampling plan. Unless otherwise specified (6.2), each filled shipping container shall be considered a lot and shall be sampled.

4.2.2.1.1 Sample. A sample consists of not less than 600 milliliters (mL) of propellant when tested to standard grade requirements and not less than 1500 mL when tested to monopropellant and high purity grade requirements. Unless otherwise specified, quality conformance tests shall be made on the sample of propellant taken directly from the shipping container. When required, the sample shall be forwarded to a laboratory designated by the procuring activity for subjection to the quality conformance tests specified herein. The bottle intended for sampling shall be specially cleaned and handled according to the procedure described in ASTM D2276 Section 10 with the exception listed in 4.3.3d. Sampling shall be conducted in such a manner that atmospheric exposure of the contents of the shipping container and the sample is minimized.

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 propellant shall be visually examined while performing test specified in 4.3.3 to determine compliance with the requirement as specified herein. Examination to ensure that the material conforms to 3.4 shall be conducted after the sample has been transferred to the 500 mL calibrated cylinder for standard grade or to a 1000 mL graduated cylinder for monopropellant and high purity grades.

4.3.2 Hydrazine assay and water. The propellant and water content of the sample shall be determined by one of the Gas Chromatographic (GC) methods described in Appendix A. In case of a dispute, the packed column method (A.2.1) shall be the referee.

4.3.3 Particulate. The propellant sample shall be tested gravimetrically for contamination in accordance with ASTM D2276, with the following exceptions:

a. Mix the sample thoroughly without exposure to air. Immediately pour 500 mL of the sample into a clean 500 mL graduated cylinder for standard grade. For monopropellant and high purity grades pour 1000 mL of sample into a clean 1000 mL graduated cylinder.

b. Use a Mitex disc polytetrafluoroethylene (PTFE) hydrophobic, 10 μm , 0.47mm, white filter for standard grade, and a 5 μm , 0.47mm, white filter for monopropellant and high purity grades or equivalent.

c. Set oven temperature to 70°C (158°F).

d. Filtered isopropyl alcohol shall be used for rinsing the sample bottle and filter holder instead of petroleum ether specified in ASTM D2276.

4.3.4 Chloride. The chloride level shall be determined by methods based on accepted scientific chemical principles, such as ion chromatographic techniques (EPA 300.0), or one of the methods described in Appendix B (colorimetric with mercuric thiocyanate or combinations of silver nitrate and/or specific ion electrodes (Ag^+/AgCl)). In case of a dispute, the specific ion electrode method (B.2.1) shall be the referee.

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4.3.5 Iron. The iron content of the propellant shall be determined by one of the methods described in Appendix C. In case of a dispute, the atomic absorption method (C.2.1) shall be the referee.

4.3.6 Non Volatile Residue (NVR). The nonvolatile residue of the propellant shall be determined in duplicate by either of the methods in Appendix D. In case of a dispute, the dropwise method (D.2.1) shall be the referee.

4.3.7 Aniline. The aniline content of the propellant shall be determined by one of the methods found in Appendix E. In case of a dispute the spectrophotometric method (E.2.1) and the wide bore capillary method (E.2.3) shall be the referee methods for monopropellant and high purity grades respectively

4.3.8 Carbon dioxide. The carbon dioxide content of hydrazine shall be determined by one of the methods described in Appendix F. In case of a dispute, the gas chromatographic method (F.2.1) shall be the referee.

4.3.9 Other volatile carbonaceous material (OVCM). Other volatile carbonaceous material shall be determined by the gas chromatographic method found in Appendix G.

5. PACKAGING

5.1 Packaging. For acquisition purposes, the packaging requirements shall be as specified in the contract or order (see 6.2). When actual packaging of materiel is to be performed by DoD or in-house contractor personnel, these personnel need to contact the responsible packaging activity to ascertain packaging requirements. Packaging requirements are maintained by the Inventory Control Point's packaging activities within the Military Service or Defense Agency, or within the Military Service's System Commands. Packaging data retrieval is available from the managing Military Department's or Defense Agency's automated packaging files, CD-ROM products, or by contacting the responsible packaging activity.

6. NOTES

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

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

6.2 Acquisition requirements. Acquisition documents must specify the following:

- a. Title, number, and date of this specification.
- b. Grade of the propellant required (see 1.2).
- c. Method of shipment, type and capacity of containers.
- d. Quantity by weight.
- e. When a different sampling plan is required (see 4.2.2.1).
- f. Packaging requirements (see 5. 1).

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6.3 Subject term (key word) listing.

Catalytic Engine
Fuel
Monopropellant
Rocket Engine

6.4 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.

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APPENDIX A

HYDRAZINE ASSAY AND WATER

A.1 SCOPE

A.1.1 Scope. This Appendix describes two Gas Chromatographic methods for the determination of propellant and water content in the sample. This Appendix is a mandatory part of the specification. The information contained herein is intended for compliance.

A.2 METHODS

A.2.1 Gas chromatographic method - packed column.

A.2.1.1 Assay column preparation. Cap one end of a 1/8 inch (in) OD by 6 foot (ft) nickel tube and fill the tube with the Tenax GC column packing by pouring through a small funnel attached to the other end. Tap or mechanically vibrate the tube to ensure uniform packing. When the tube is filled, plug both ends with a small wad of glass wool, bend the column to the configuration required by the column oven, and connect the column to the inlet fitting in the oven. Condition the column with carrier gas flowing and the oven set at 200°C for one hour. After conditioning the column, connect the other end to the detector and set the carrier gas flow to approximately 25 milliliters per minute (mL/min), and the column oven to 50°C. The inlet and detector temperatures, if separately heated, shall be set to 100°C and 150°C, respectively. The detector current should be set to a nominal sensitivity value recommended for helium by the instrument manufacturer. The column temperature and carrier gas flow may be adjusted by the analyst to provide adequate component resolution for minimum analysis time.

A.2.1.2 Procedure. Equilibrate the column with propellant by injection of three or more 1 - 2 microliter (µL) samples into inlet. If more than 30 minutes (min) elapse between analyses, a single 1 µL injection of propellant should re-equilibrate the column. Inject 1 - 2 µL of propellant for analysis and record the areas of all peaks in the chromatogram, using the following time/temperature program:

Helium carrier gas flow	20 – 25 mL/min
Initial temperature	50°C
Rate	20°C/min
Final temperature	155°C
Final time hold	4 min

Each analysis should require less than 20 min for elution of all components. The elution order of possible components is as follows:

Air, ammonia, methylamine, water, and hydrazine.

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APPENDIX A

A.2.1.3 Calculations.

$$\% N_2H_4 = \frac{A_{N_2H_4} \times 100}{\sum A_i}$$

$$\% H_2O = \frac{A_{H_2O} \times 100}{\sum A_i}$$

$$\% NH_3 = \frac{A_{NH_3} \times 100}{\sum A_i} \quad (\text{For high purity grade only})$$

where,

$A_{N_2H_4}$ = The measured area of the N_2H_4 peak multiplied by its signal attenuation factor.

A_{H_2O} = The measured area of the H_2O peak multiplied by its signal attenuation factor.

A_{NH_3} = The measured area of the NH_3 peak multiplied by its signal attenuation factor.

$\sum A_i$ = The sum of all measured peak areas times their signal attenuation factors.

NOTE: For monopropellant and high purity grades substitute $\sum A_i [100 / (100 - \% \text{aniline})]$ for $\sum A_i$ to correct for the aniline content of the propellant.

Assumption: The thermal conductivities of all components in the sample are equal.

A.2.1.4 Equipment and Reagents. The following equipment and reagents shall apply as test conditions of 4.3.2.

a. Equipment:

(1) Gas chromatograph equipped with a thermal conductivity detector (TCD).

(2) Hewlett Packard (HP) Chemstation or equivalent.

(3) Packed column, may be commercially obtained from W.R. Grace & Co.-Conn., Alltech Division, 2051 Waukegan Road, Deerfield IL 60015-1899

b. Reagents:

Tenax GC 60/80 mesh or equivalent.

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APPENDIX A

A.2.2 Gas chromatographic method - capillary column.

A.2.2.1 Procedure. A 30 meters (m) x 0.53 millimeters (mm) DB-Wax, Agilent J & W capillary column, a TCD, and a split/splitless injector with a glass wool packed split liner shall be used. Table A-1 depicts recommended parameters for initial setup. These parameters may vary depending on GC system and detector brands, and may be adjusted by the chemist to provide adequate component resolution.

Allow the instrument to stabilize, condition the column and perform check runs by processing three consecutive injections of 1 - 3 μ L of sample. The checks must meet the quality control criteria in A.2.2.2.

This method may be used for aniline quantification for monopropellant hydrazine; for high purity refer to section E.2.4.

TABLE A-1. GC Recommended parameters

PARAMETER	CONDITION
Carrier Gas	He
Carrier Flow	10 mL/min
Sample Volume.	1 μ L (10:1 split)
Inlet Temp.	150 °C
TCD Detector Temp.	200 °C
Carrier + Aux. Flow	~25 mL/min
Carrier + Aux. + Ref. Flow	~65 mL/min
Total (Splitter Bypass) Flow	~90 mL/min
Purge	On
Oven Max	200 °C
Equilibration Time	2.00 min
Initial Temp.(T ₀)	60 °C
Initial Time (t ₀)	4.00 min
Rate (1)	10 °C/min
Final Temp. (T _f)	100 °C
Final Time (t _f)	0.00 min
Rate (2)	20 °C/min
Final Temp. (2)	185 °C
Final Time (2)	2.75 min

A.2.2.2 Quality control. The following performance criteria must be met for fuel purity analysis,

GC replicate analyses (3 consecutive)	RSD ^a \leq 5 %
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a. RSD = Standard Deviation * 100 / Mean

A.2.2.3 Equipment.

- (1) Gas chromatograph equipped with a thermal conductivity detector (TCD) and a split/splitless injector.
- (2) Hewlett Packard (HP) Chemstation or equivalent.

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APPENDIX A

- (3) A 30 m x 0.53 mm DB-Wax capillary column.
- (4) Glass wool packed split liner.

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APPENDIX B

CHLORIDE

B.1 SCOPE

B.1.1 Scope. This Appendix describes two methods for the determination of chloride content of the propellant. This Appendix is a mandatory part of the specification. The information contained herein is intended for compliance.

B.2 METHODS

B.2.1 Specific ion electrode method.

B.2.1.1 Procedure. Rinse the propellant residue container in one vessel from 4.3.6 with a 5 mL aliquot of 1N sulfuric acid (H₂SO₄). Briefly stir and heat the liquid to boiling and cover with an inverted watch glass to prevent the condensate from escaping. Transfer the solution to a 25 mL volumetric flask. Rinse vessel with a second 5 mL aliquot of acid followed by one 5 mL aliquot of purified water. Combine the aliquots in the 25 mL volumetric flask and add two to three drops of bromocresol green indicator. Dropwise titrate the contents of the flask to a green endpoint with 1N sodium hydroxide (NaOH) and dilute to the mark with purified water. Mix the solution and transfer approximately 10 mL to a 25 mL beaker. Immerse the electrodes in the sample solution and record the millivolt reading. Compare the millivolt reading from the sample to a calibration curve prepared from chloride standards and record the concentration (ppmv) of the sample.

B.2.1.2 Calculation. Calculate the percent chloride in the sample using the following formula:

$$\%Cl^{-} = \frac{(ppmv Cl^{-})(V_d)}{(V_h)(D)(1 \times 10^4)}$$

where,

V_d = Final dilution volume taken from NVR residue in mL.

V_h = Volume of hydrazine used in NVR analysis in mL.

D = Density of hydrazine (1.01 g/mL).

B.2.1.3 Reagents and equipment. The following shall apply as test conditions of 4.3.4:

B.2.1.3.1 Reagents.

a. Chloride-free purified water; the water is considered chloride free if a 100 mL sample used to dissolve 0.1 gram (g) of silver nitrate, shows no turbidity after standing in the dark for 24 hours.

b. 1N H₂SO₄; prepare by pouring 29 mL of American Chemical Society (ACS) grade concentrated H₂SO₄ into 300 mL of chloride free water contained in a 1000 mL volumetric flask. Cool the solution to room temperature, dilute to the mark with the chloride free water, and mix thoroughly. Transfer the solution to a plastic bottle.

c. 1N NaOH; prepare by dissolving 40 g of ACS grade, low carbonate, NaOH in 300 mL of chloride-free water contained in a 1000 mL volumetric flask. Cool the solution to room temperature, dilute

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APPENDIX B

to the mark with chloride free purified water, and mix thoroughly. Transfer the solution to a plastic bottle and protect from long exposure to the atmosphere.

d. Standard sodium chloride (NaCl) solution, 1 mL = 1.00 mg Cl⁻; weigh 1.648 g dry NaCl into a 1 liter (L) volumetric flask. Dilute to the mark with purified water. Transfer the thoroughly mixed solution to a clean polyethylene bottle for storage.

B.2.1.3.2 Equipment.

- a. Chloride electrode – solid state Orion 9417BN, or equivalent.
- b. Reference electrode - Orion 900200 Sure-Flow® double junction with 1M potassium nitrate (KNO₃) outer compartment filling solution, or equivalent.
- c. pH/millivolt meter.

B.2.2 Colorimetric method.

B.2.2.1 Procedure. Add to the propellant residue container in one vessel from 4.3.6 five milliliters of ferric alum indicator and transfer to a 100 mL volumetric flask. Rinse the vessel with three 5 mL purified water aliquots and combine into the volumetric. Set samples aside.

Prepare a calibration blank and at a minimum two standards to bracket the expected chloride concentration in the samples in 100 mL volumetric flasks, and add 5 mL of ferric alum indicator. Add 2.5 mL of mercuric thiocyanate solution to each volumetric, samples and standards, and dilute to the mark with purified water. Mix the solutions thoroughly and allow to stand in darkness for 15 – 30 min. Analyze in a UV-Vis spectrophotometer at 460nm, at the wavelength recommended by the instrument manufacturer, or at that which provides the highest sensitivity using 5 cm cells. Use the blank to set the instrument to zero absorbance and determine the absorbances of standards and samples. Prepare a calibration curve of absorbance vs concentration and determine the chloride concentration in the samples. The calibration correlation coefficient shall be ≥ 0.999 .

B.2.2.2 Calculation. Calculate the chloride content of the propellant using the formula in B.2.1.2.

B.2.2.3 Reagents and equipment. The following shall apply as test conditions of 4.3.4:

B.2.2.3.1 Reagents.

- a. Purified water of 18M-ohm or greater resistivity.
- b. Ferric alum indicator, Volhard (oxidation reduction indicator) –, Dissolve 10 g of ferric ammonium sulfate dodecahydrate (FeNH₄(SO₄)₂•12H₂O) ACS grade in approximately 50 mL of purified water. Add 10 mL of ACS grade nitric acid, and dilute to 100 mL with purified water. (may be commercially obtained).
- c. Mercuric thiocyanate, 4.17 g/L in methanol for chloride determination (commercially available).
- d. Chloride standard, 1000 mg/L (may be commercially obtained; must be certified).

B.2.2.3.2 Equipment. UV-Vis Spectrophotometer, double beam, equipped with 5 cm cells.

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APPENDIX C

IRON

C.1 SCOPE

C.1.1 Scope. This Appendix describes three methods for the determination of iron content of the propellant. This Appendix is a mandatory part of the specification. The information contained herein is intended for compliance.

C.2 METHODS

C.2.1 Atomic absorption.

C.2.1.1 Procedure. Rinse the propellant residue contained in one vessel from 4.3.6 as follows:

Add 5 mL of 5N H₂SO₄ to the vessel and place on a hotplate stirrer. Heat the mixture to boiling, while stirring and maintain at that temperature for three to five minutes. Allow the solution to cool and transfer to a 100 mL volumetric flask. Rinse the vessel at least three times with 5 mL aliquots of 0.1N H₂SO₄ combining all rinses in the volumetric flask. Dilute to the mark with purified water and mix thoroughly. (For atomic absorption only, hydrazine may be diluted 1:2 and used directly.) Determine the absorbance of the sample at an iron wavelength closest to 2480 Å on a suitable atomic absorption spectrophotometer, after setting the instrument to zero absorbance, with 0.1N H₂SO₄. Compare the results to a calibration curve prepared from iron standards and record the iron concentration of the sample.

C.2.1.2 Calibration. Prepare a 1000 ppm iron standard by dissolving 1.00 g of iron wire or shot in 50 mL of 6N H₂SO₄. Use heat. Quantitatively transfer the resulting solution to a 1000 mL volumetric flask with 0.1N H₂SO₄ and dilute to the mark with 0.1N H₂SO₄ (a commercial standard solution may be used). Prepare a minimum of three calibration standards to bracket the expected iron concentration range of the samples by combining appropriate volumes of the stock solution in 200 mL volumetric flasks with 0.1N H₂SO₄, and mix thoroughly. Prepare a mid range check standard to verify the calibration. After setting the instrument to zero absorbance with 0.1N H₂SO₄, determine the absorbance of the calibration standards and check standard. Prepare a calibration curve of absorbance vs iron concentration.

C.2.1.3 Calculation. Calculate the iron content of the propellant using the following formula:

C.2.1.3.1 Iron from NVR residue.

$$\% Fe = \frac{(ppmv Fe)(V_d)}{(V_h)(D)(1 \times 10^4)}$$

where

V_d = Final dilution volume taken from NVR in mL.

V_h = Volume of hydrazine used in NVR analysis in mL.

D = Density of hydrazine (1.01 g/mL).

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APPENDIX C

C.2.1.3.2 Iron from direct hydrazine analysis.

$$\% Fe = \frac{(ppmv Fe)(DF)}{(D)(1 \times 10^4)}$$

where,

DF = Dilution factor used to dilute hydrazine.

D = Density of hydrazine (1.01 g/mL).

C.2.1.4 Quality control. Follow the guidelines described in ASTM D1068 Method A with the following exceptions:

- a. A mid-range standard, different than those used to calibrate the instrument shall be used to verify calibration.
- b. The mid-range standard from C.2.1.4b shall be used as the laboratory control sample.

C.2.1.5 Equipment.

- a. Hotplate/stirrer – controllable heat and stir settings.
- b. Atomic absorption spectrophotometer with an iron hollow cathode lamp.

C.2.2 Inductively Coupled Argon Plasma-Atomic Emission Spectrometry. For each instrument interference effects must be evaluated, and corrected as applicable (ASTM D1976), and instrument performance validated. The argon gas supply must have a purity of 99.99% or better.

C.2.2.1 Procedure. Prepare the sample solution in the same manner as described in C.2.1.1. Choose the iron wavelength recommended by the instrument manufacturer or that which provides the highest sensitivity (most commonly used is 259.940 nm). Calibrate the zero point with the acid matrix blank. Make a 1.0 ppm standard in the same manner as the standards described in C.2.1.2 to determine the slope.

C.2.2.2 Quality control. The instrumental drift shall be checked using the acid matrix blank and standard at the beginning of each run, at least every ten readings during the run, and at the end of the run. The blank shall read ≤ the detection limit and the standard shall fall within ± 10% of the standard value. If the recovery of the analyte falls outside of the required control limits, the source of the problem must be identified and resolved before continuing analyses.

C.2.2.3 Calculations. Calculate the iron content of the propellant using the formula in C.2.1.3.1.

C.2.2.4 Reagents and equipment. The following shall apply as test conditions of B.2.2.

C.2.2.4.1 Reagents.

- a. Purified water of 18M-ohm or greater resistivity.
- b. Iron standard, 1000 µg/mL (may be commercially obtained; must be certified).

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c. Sulfuric acid, concentrated, suitable for trace metal analysis.

C.2.2.4.2 Equipment. Inductively-coupled argon plasma atomic emission spectrometer (ICP-AES).

C.2.3 Colorimetric method.

C.2.3.1 Procedure. ASTM E394 shall be followed with the following exceptions:

a. Add 5 mL of the ammonium acetate-acetic acid buffer solution to each empty 100 mL volumetric flasks (for standards and samples) and set aside.

b. Dissolve the residue of each vessel from 4.3.6 by adding 1 mL of concentrated H₂SO₄, and carefully adding 50 mL purified water (instead of the 80 mL called out in the method). Mix thoroughly.

c. Add 1 mL of concentrated H₂SO₄, and 50 mL purified water to at least four empty 150 mL evaporating dishes for the standards.

NOTE: Make sure solution is thoroughly mixed after each component addition.

d. Add the 2 mL of hydroxylamine hydrochloride and the 5 mL of 1,10-phenanthroline as described in the method.

e. Add enough sodium acetate (instead of the buffer called out in the method) to bring the pH of the mixture to between pH 3 and pH 4 while swirling (add ~20 mL initially and then continue adding drop wise until desired pH is reached).

f. Transfer the solutions to their respective 100 mL volumetric flask from step a above, dilute to the mark, and mix thoroughly. Allow the flasks to set at room temperature in the dark for a minimum of 15 minutes.

g. Determine iron concentrations from the calibration curve prepared from the iron standards; the correlation coefficient shall be ≥ 0.990 .

C.2.3.2 Calculations. Calculate the iron content of the propellant using the formula in C.2.1.3.1.

C.2.3.3 Reagents. The following reagents are in addition to those reagents listed in ASTM E394,

a. Sodium acetate solution. Dissolve 200 g CH₃COONa•3H₂O in 1 L volumetric flask with 700 mL with purified water and dilute to the mark. An equivalent solution may be obtained commercially.

b. Sulfuric acid, concentrated, suitable for trace metal analysis.

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APPENDIX D

NON-VOLATILE RESIDUE (NVR)

D.1 SCOPE

D.1.1 Scope. This Appendix describes three methods for the determination of nonvolatile residue of the propellant. This Appendix is a mandatory part of the specification. The information contained herein is intended for compliance.

D.2 METHODS

D.2.1 Dropwise method.

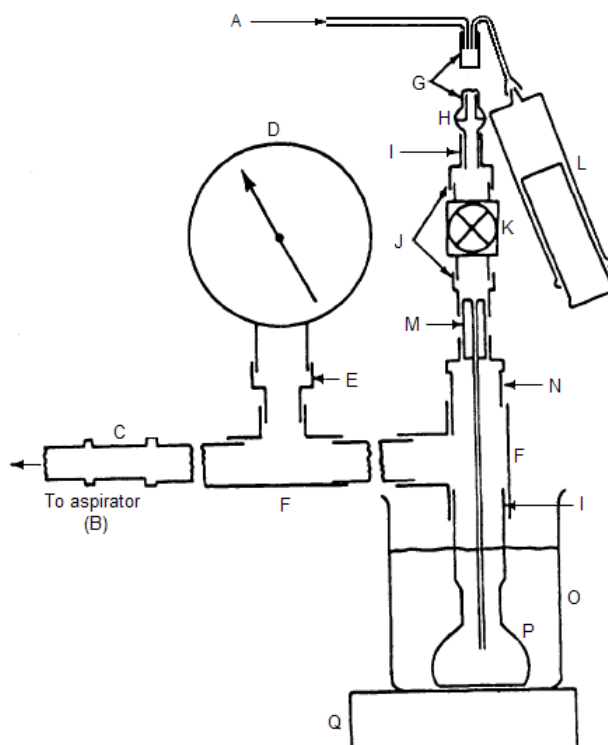
D.2.1.1 Procedure. Clean the unassembled apparatus with detergent and rinse thoroughly with purified water. Dry the parts in an oven at 110°C. Assemble the apparatus as shown in Figure D-1. Fill the water bath with purified water and turn on the heater. Adjust the water level of the bath to approximately one-half inch below the lowest fitting and mark this level on the bath. When the temperature bath reaches boiling, adjust the nitrogen purge to approximately 2 L/min and turn on the aspirator. With the sample delivery valve closed, the pressure in the apparatus should be below 30 mmHg. Open the sample delivery valve slowly to adjust the apparatus pressure to approximately 60 mmHg. Allow the apparatus to purge for approximately five minutes to remove traces of water. Remove the water bath and dry the outside of the residue vessel with a clean lintless tissue. Disconnect the aspirator from the apparatus and remove the residue vessel using a tissue to hold the vessel. Wipe the outside of the vessel and place it near the analytical balance. After at least twenty minutes, accurately weigh the residue vessel until the weight remains constant to ± 0.5 mg. Record the weight. Reassemble the apparatus and close the sample delivery valve. Replace the water bath, adjust the water level to the mark, and heat the water to boiling. Transfer 100 mL of propellant to the apparatus using a 100 mL volumetric pipette. With the nitrogen purge in place, turn on the water aspirator and reduce the apparatus pressure to less than 30 mmHg. Slowly open the sample delivery valve to admit propellant to the residue vessel and adjust the flow such that the apparatus pressure does not exceed 60 mmHg (approximately 2 drops per second). The quantity of propellant in the residue vessel should not exceed 2 - 4 mL at the equilibrium evaporation rate. Adjust the sample delivery valve to maintain the evaporation pressure at less than 60 mmHg. After 100 mL of propellant have been evaporated (approximately 30 min), allow the residue vessel to purge for an additional five minutes to ensure complete evaporation of volatile material. Remove the water bath, disconnect the aspirator, wipe the outside of the residue vessel, and remove it from the apparatus. Allow the residue vessel to stand near the analytical balance for at least twenty minutes before weighing. Weigh the residue vessel as above, and record the weight. To clean the residue vessel reflux 5 mL of 5N H₂SO₄ in the vessel for several minutes followed by several rinses of purified water. The vessel may be dried as described above or by gently heating the vessel with a burner while purging with dry nitrogen. Regardless of the drying method used, allow at least twenty minutes for the vessel to equilibrate to ambient temperature and humidity before weighing.

NOTE

Save the propellant residue for chloride (4.3.4) and iron (4.3.5) determinations.

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- | | |
|--|---|
| A - GN ₂ | J - Connector (Swagelok SS-400-7-2 or equivalent) |
| B - Water aspirator (glass or polyethylene) | K - Valve (Swagelok SS-ORM2 or equivalent) |
| C - Connector (polyethylene, separable) | L - Syringe (100 mL glass with an 8 – 12 in PTFE needle). |
| D - Gauge (stainless steel, absolute pressure, 0 - 760 mmHg range) | M - Rod (PTFE or polyethylene, 1/4 inch OD & a 1/16 OD x 0.025 in wall tube inserted) |
| E - Adapter (Swagelok SS-8-TA-7-4 or equivalent) | N - Reducer (Swagelok SS-400-R-8 or equivalent) |
| F - Union Tee (Swagelok SS-810-3 or equivalent; 2 ea.) | O - Beaker (glass, 1000 mL capacity) |
| G - Pipette (100 mL, volumetric, borosilicate glass) | P - Flask (25 mL volumetric, borosilicate glass) |
| H - Joints (borosilicate glass, spherical, 12/5, ball, socket and clamp) | Q - Hotplate (adjustable heat range) |
| I - PTFE Ferrules (Swagelok T-814-1, T-813-1, T-404-1, T-403-1, or equivalent) | |

NOTE: All fittings, stainless steel, Swagelok or equivalent.

FIGURE D-1. NVR apparatus

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D.2.1.2 Calculations. Calculate the nonvolatile residue of the propellant as follows:

$$\% NVR = \frac{(W_2 - W_1) \times 100}{V \times D}$$

where,

W_1 = Weight of clean vessel in grams.

W_2 = Weight of residue and vessel in grams.

V = Volume of sample used in milliliters.

D = Density of hydrazine (1.01 g/mL).

Report the averaged result of duplicate NVR determinations.

D.2.1.3 Equipment. The following equipment shall apply as test conditions of D.2.1.

- a. Components described in Figure D-1.
- b. Tubing – polyethylene, ½ inch OD, borosilicate glass, ½ inch OD.
- c. Clamps – hose, to fit ½ inch OD tube.

D.2.2 Rotary evaporation.

D.2.2.1 Procedure. Dry a 250 mL round bottom flask in an oven at 110°C for one hour. Allow the flask to cool in a desiccator and weigh on the analytical balance until the weight remains constant to ± 0.5 mg. Transfer 100 mL of hydrazine into the 250 mL flask. Place the flask on the evaporator using a standard taper Teflon sleeve as a seal. Attach a water aspirator pump to the evaporator via a one liter suction flask and evaporate the hydrazine to dryness. A water bath may be placed around the rotating flask to aid evaporation.

WARNING

The contact of hydrazine vapor with metal surfaces, as in a metal rotary evaporator, must be avoided. Do not exceed 40°C during the initial evaporation phase when hydrazine liquid is present. Chemical splash proof goggles must be worn throughout the entire evaporation process.

When no more hydrazine distills over, the water bath is lowered. Final high boiling components (mainly aniline) are distilled under vacuum at temperatures up to 100°C using a hot air gun for heating. The flask is then removed and dried in an oven at 110°C for one hour and weighed as before to a constant weight.

NOTE

Save the propellant residue for chloride (4.3.4) and iron (4.3.5) determinations.

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D.2.2.2 Calculations. Use equation in D.2.1.2

D.2.2.3 Equipment.

- a. All glass rotary evaporator, BÜCHI Rotavapor or equivalent.
- b. Flask, round bottom, 250 mL, with standard neck to fit evaporator.
- c. Water aspirator – glass or polyethylene.

D.2.2.4 Hotplate. This method involves the gradual evaporation of a hydrazine sample on an explosion proof hot plate in a fume hood. The difference in weight before and after evaporation is calculated as nonvolatile residue.

D.2.2.4.1 Procedure. Place three clean borosilicate glass or platinum evaporation dishes in an oven at 110°C for 30 minutes. Label one as a blank and the others as samples 1 and 2. Remove evaporation dishes from the oven and place in a desiccator to cool for one hour. Weigh each clean, dry evaporating dish to the nearest 0.0001 g until the weight remains constant to ± 0.5 mg. Record the sample evaporating dish weight as A and the blank evaporating dish weight as C. Pipette 40 mL of hydrazine sample into the evaporating dishes marked 1 and 2. Add 40 mL of water to each sample of hydrazine in evaporating dishes 1 and 2. Hydrazine and water form an azeotrope (constant boiling mixture) with a maximum boiling point of 120.5°C (771 mmHg pressure). Therefore, when anhydrous hydrazine and water are mixed, a corresponding eutectic of 76.0 mole percent hydrazine is the maximum concentration obtained. This eliminates any significant hazard in evaporating a hydrated sample of hydrazine to dryness. Pipette the same volume of purified water into the blank evaporating dish as was pipetted into the sample dish. Place each evaporating dish on a hot plate which is set to a temperature of 150 – 200°C. Evaporate to dryness, but do not bake. Remove the evaporating dishes from the explosion-proof hot plate and place them in oven set at 110°C for 30 minutes. Remove dishes from oven and place in a desiccator for one hour to cool. Weigh each evaporating dish as before to a constant weight while monitoring the room temperature with a narrow range viscosity thermometer (dishes must be weighed at the same temperature). Record the sample evaporating dish weight as B and the blank evaporating weight as D.

NOTE

Save the propellant residue for chloride (4.3.4) and iron (4.3.5) determinations.

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D.2.2.4.2 Calculations. Calculate the nonvolatile residue of the propellant as follows:

$$\% NVR = \frac{(Weight\ B - Weight\ A) - (Weight\ D - Weight\ C) \times 100}{Sample\ size, mL \times density\ of\ N_2H_4, g / mL}$$

where,

A = Weight of the sample evaporating dish.

B = Weight of the sample evaporating dish and residue.

C = Weight of blank evaporating dish.

D = Weight of blank and water residue.

D.2.2.4.3 Equipment.

- a. Hot plate, explosion proof.
- b. High efficiency fume hood.

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APPENDIX E

ANILINE

E.1 SCOPE

E.1.1 Scope. This Appendix describes four methods for the determination of aniline content of the propellant. This Appendix is a mandatory part of the specification. The information contained herein is intended for compliance.

E.2 METHODS

E.2.1 Spectrophotometric method.

E.2.1.1 Procedure. For high purity, pipette or syringe 5 mL of propellant into a 25 mL volumetric containing approximately 15 mL of purified water; for monopropellant pipette or syringe 0.10 mL (100 μ L) of propellant. Dilute to the mark with purified water, and mix the solution thoroughly. Fill two 1 cm pathlength silica spectrophotometer cells with purified water and place one in each position for sample and reference cells. Using the appropriate source and detector for the spectrophotometer, set the recorder pen to zero absorbance at 320 nm and scan the region between 320 and 240 nm. If the baseline is relatively stable, the cells and purified water can be considered free from interfering substances. Exchange the water in the sample cell with the previously prepared sample, using several rinses with the sample solution, and rescan the 320 to 240 nm region, first ensuring that the recorder pen is set at zero absorbance at 320 nm. Draw a baseline under the aniline peak at 280 nm, measure, and record the net absorbance of the peak. Determine the aniline content of the sample by comparing the net absorbance obtained to a calibration curve of net absorbance versus percent aniline.

E.2.1.2 Calibration. Pipette or syringe 0.025 mL (25 μ L) of aniline into a 100 mL volumetric flask containing 50 mL of purified water. Shake the mixture to dissolve the aniline and dilute the solution to the mark with purified water. Mix the standard thoroughly. This calibration standard is equivalent to 0.025%. Prepare a series of calibration standards in the aniline range expected to find in the samples. Determine the net absorbance of standards versus purified water in the same manner as with the sample. Plot net absorbance versus percent aniline and draw a curve through the points. A check standard should be prepared fresh daily to check the calibration standards. If the check standard falls outside of $\pm 5\%$ of the expected value, the calibration standards shall be prepared anew.

E.2.1.3 Equipment. Spectrophotometer, double beam, ultra violet, narrow band width, recording, equipped with 1 cm silica cells, Cary 14 or equivalent.

E.2.2 Gas chromatographic method - packed column.

E.2.2.1 Procedure. Prepare a gas chromatographic column consisting of 9.5 g Apiezon L and 0.5 g Alltech AT-220 (formerly Amine 220) coated upon 20 g of a white, silanized diatomaceous earth support 60/80 mesh. Condition the column for four hours at 150°C prior to connection to the detector. Use a gas chromatograph equipped with a flame ionization detector. The inlet, if separately heated, should be adjusted to 130°C or greater, the column and detector temperatures should be 130°C and 150°C, respectively. After the instrument has stabilized, inject 0.5 μ L of propellant and record the area of the aniline peak. Compare the area of the aniline peak with that of a calibration standard and calculate the percent aniline of the sample.

E.2.2.2 Calibration (monopropellant hydrazine). Pipette or syringe 0.5 mL (500 μ L) of aniline into a 100 mL volumetric flask containing approximately 50 mL of purified water, shake the mixture, dilute to the mark with purified water, and mix the solution thoroughly. This calibration standard is equivalent to

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0.5% aniline in propellant. Inject 0.5 μ L of the standard into the inlet of the chromatograph and record the area of the aniline peak. Prepare the standard fresh daily.

E.2.2.3 Calculation. Use the following formula for calculation of the aniline content of the propellant:

$$\% \text{ aniline} = \frac{0.5A_s}{A_c}$$

where,

A_s = Area of the sample aniline peak times its attenuation factor.

A_c = Area of the standard aniline peak times its attenuation factor.

E.2.2.4 Equipment. The following equipment shall apply as test conditions to E.2.2.1.

- a. Gas chromatograph, equipped with a flame ionization detector.
- b. Hewlett Packard (HP) Chemstation or equivalent.
- c. Packed columns, available from W.R. Grace & Co.-Conn., Alltech Division, 2051 Waukegan Road, Deerfield IL 60015-1899

E.2.3 Gas Chromatographic method - wide bore capillary.

E.2.3.1 Procedure. A 0.53 mm OD x 15 m crosslinked "Carbowax 20M" capillary column shall be used. Helium is used as a carrier gas. A gradient temperature program is used from 40°C to 130°C. Splitless injection is used. Sample size should be 0.4 to 1 μ L. Condition the column with several injections of the calibration mixture 3 minutes apart. After the fifth injection, allow sufficient time for the final injection of aniline to elude, approximately 10 min. Adjust flow rate to allow for baseline separation of the trace monomethylhydrazine from hydrazine.

E.2.3.2 Calibration (high purity hydrazine). Pipette or syringe 0.5 mL of aniline into a 1.0 L volumetric flask containing approximately 500 mL of purified water, and mix the solution thoroughly. Fill to the mark with purified water and thoroughly mix. Pipette 10 mL of this solution into a 100 mL volumetric flask and dilute to the mark. This calibration standard is equivalent to 0.005% aniline in propellant. Inject 1.0 μ L of the standard into the inlet of the chromatograph and record the area of the aniline peak. Use a similar calculation method described in E.2.2.3 allowing for the less concentrated standard solution of 0.005%.

E.2.3.3 Equipment. The following equipment shall apply o test conditions of E.2.3.

- a. Gas chromatograph, equipped with a flame ionization detector.
- b. Hewlett Packard (HP) Chemstation or equivalent.
- c. Packed columns, available from W.R. Grace & Co.-Conn., Alltech Division, 2051 Waukegan Road, Deerfield IL 60015-1899

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E.2.4 Alternate capillary methods

E.2.4.1 Procedure for monopropellant grade hydrazine. Aniline may also be obtained using the assay capillary column method described in Appendix A of this specification (A.2.2).

E.2.4.2 Procedure for high purity hydrazine. Aniline may also be obtained using the OVCM GC capillary method described in Appendix G of this specification.

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APPENDIX F

CARBON DIOXIDE

F.1 SCOPE

F.1.1 Scope. This Appendix describes two methods for the determination of carbon dioxide content of the propellant. This Appendix is a mandatory part of the specification. The information contained herein is intended for compliance.

F.2 METHODS

F.2.1 Determination of carbon dioxide by gas chromatographic analysis.

F.2.1.1 Procedure. Assemble the apparatus as shown in Figure F-1 and connect a burette to the gas exit. Adjust the needle valve so that the flow at the gas exit is 50 – 100 mL/min. Adjust the gas chromatograph carrier gas flow to 30 – 60 mL/min, the column temperature to 100 to 150°C, and the detector temperature to 150 to 200°C. Adjust the detector current to the manufacturer's recommended level of nominal sensitivity. Position the gas sampling valve and the stopcocks so that the sparge gas passes through the CO₂ trap to liquid nitrogen temperature to collect a sample for background CO₂ determination. Collect the sample for 30 to 45 min and then position the stopcocks so that the sparge gas bypasses the cooled portion of trap. Position the gas sampling valve so that the carrier gas will flow through the bypass line of the trap, and warm the lower portion to ambient temperature. Inject the trapped gases into the gas chromatograph by rotation of the stopcocks to the collect position. Determine the CO₂ peak height or area and record the results. Position the gas sampling valve so that the sparge gas is again flowing through the trap and cool the trap to liquid nitrogen temperature. Immediately inject a 0.25 mL propellant sample into the septum inlet of the apparatus and allow 30 to 45 min for complete transfer of the CO₂ from the sulfamic acid bubbler to the trap. Repeat the trapped sample sequence described earlier for the background determination and record the sample CO₂ peak height or area.

F.2.1.2 Propellant transfer. To achieve accurate CO₂ results, all propellant transfers must be performed in a CO₂-free atmosphere (i.e. a gaseous nitrogen dry box). Propellant in the sampler shall be transferred in an inert atmosphere to septum sealed vials. The vials shall be stored in an inert gas purged container when not actually being sampled. Use an ordinary 0.5 mL glass syringe with a small amount of "Apiezon L". The gas tight syringe shall be cleaned and dried between each propellant sample injection into the apparatus.

F.2.1.3 Calculation. Calculate the CO₂ level of the propellant as follows:

$$\% CO_2 = (R_s - R_b) \times S$$

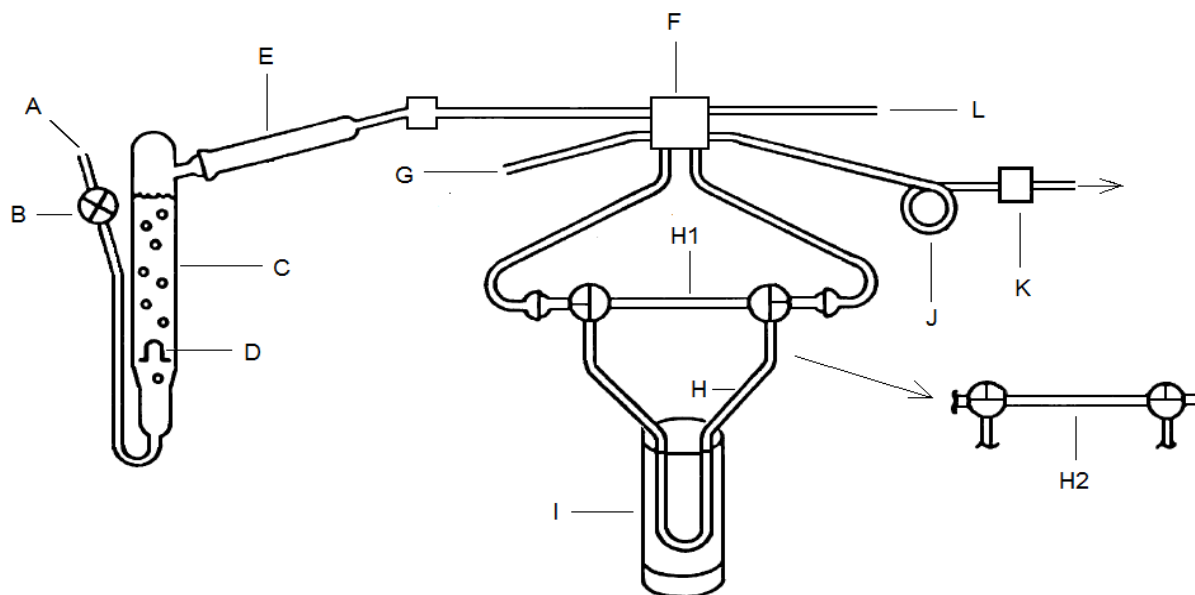
where,

$R_s - R_b$ = CO₂ response due to the sample minus CO₂ response due to the background, peak height or area.

S = Sensitivity, %CO₂ per unit response.

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- | | | |
|---|---|-------------------------|
| A - Sparge gas inlet | E - $\text{Mg}(\text{ClO}_4)_2$ drying tube | I - LN_2 Dewar |
| B - Needle valve | F - 6 or 8 port gas sampling valve | J - Charcoal GC column |
| C - Reactor with coarse frit and sulfamic acid solution | G - Sparge gas vent | K - TCD |
| D - Septum inlet for propellant | H - LN_2 trap for CO_2
H1 - collect position
H2 - bypass position | L - Carrier gas inlet |

FIGURE F-1. CO_2 apparatus

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F.2.1.4 Calibration. Accurately weigh 0.130 g ammonium carbonate monohydrate (ACS) $[(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}]$ into a tared glass vessel which will accept a vapor tight cap and will contain 100 mL of liquid. Place the vessel in the propellant transfer apparatus (dry box) which contains the propellant sample. Transfer 100 mL of propellant to the vessel, cap the vessel. Use sample or other known hydrazine. Dissolve and thoroughly mix the ammonium carbonate solution. Remove the vessel from the sample apparatus and weigh the container. Calculate the CO_2 added as follows:

$$\% \text{CO}_2 \text{ added} = \frac{0.130 \times 44.01 \times 100}{[\text{total wt} - (\text{tare} + 0.130)] \times 114.1}$$

Transfer an aliquot of the calibration standard to a septum sealed vial and use the procedure described in F.2.1.1 to determine the response due to the CO_2 sensitivity of the apparatus as follows:

$$S = \frac{\% \text{CO}_2 \text{ added}}{R_{std} - R_s}$$

where,

$R_{std} - R_s$ = The response due to the CO_2 in the standard minus the response due to the sample, peak height or area.

F.2.1.5 Reagents and equipment.

F.2.1.5.1 Reagents.

- a. Sulfamic acid, aqueous, 90% saturated solution.
- b. Bromocresol green indicator, several drops added to the sulfamic acid solution will provide a visual indication of when the solution is spent.
- c. Charcoal, coconut, 60/80 mesh, activated, or column of equivalent resolution.

F.2.1.5.2 Equipment.

- a. Reactor, sulfamic acid, constructed so that the volume is approximately 75 mL, borosilicate glass. (See Figure F-1).
- b. Drying tube, $\text{Mg}(\text{ClO}_4)_2$, approximately 6" x 1/2", borosilicate glass.
- c. Trap, CO_2 , borosilicate glass, constructed with 6 mm OD tubing, the lower loop should contain glass beads to increase the condensing surface area.
- d. Valve, gas sampling, 6 or 8 port.
- e. Valve, needle, for regulation of the sparge gas.
- f. Dewar, conical, to fit trap.

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g. Gas chromatograph, equipped with a thermal conductivity detector, 6' x 1/8" 60/80 mesh charcoal column.

h. Recorder, potentiometric, 1mv span, 1sec FS pen speed.

i. Integrator, mechanical or digital, optional.

F.2.2 Determination of carbon dioxide by non-dispersive IR analysis. This method is to be utilized to determine the carbon dioxide concentration in hydrazine within a 1 – 2 mg/kg (ppm) range. The sample of propellant is injected into a solution of 20% phosphoric acid which absorbs the hydrazine and ammonia. Carbon dioxide is liberated from the acidic solution and is swept out of the solution by a stream of nitrogen through a sulfuric acid solution to remove water vapor and measured by infrared technique.

F.2.2.1 Calibration procedure.

a. Assemble the apparatus as shown in Figure F-2.

b. Adjust the flow of nitrogen purge gas to 200 mL/min by use of a flowmeter.

c. Add 200 mL of 20% phosphoric acid containing several drops of bromocresol green indicator to the CO₂ reaction flask, turn on the magnetic stirrer to give vigorous, constant stirring. Once set, the stirring rate and nitrogen flow should be kept constant throughout the analysis.

d. After the apparatus has purged for 30 minutes, set the power to range 1 position. Adjust the zero on the infrared analyzer by using one zero adjusting knob and the shutter setting.

F.2.2.2 Standardization.

a. Inject 25 µL of standard anhydrous sodium bicarbonate solution into the phosphoric acid (25 ppm level) solution via the septum on the phosphoric acid containing unit.

b. Adjust the gain control so the 25 mg/kg standard will read 50% of the scale on the infrared analyzer or the strip chart recorder. (It takes two minutes to reach maximum deflection from the infrared analyzer. 1 scale unit = 0.5 mg/kg CO₂). Wait ten minutes or until the infrared analyzer scale goes back to zero.

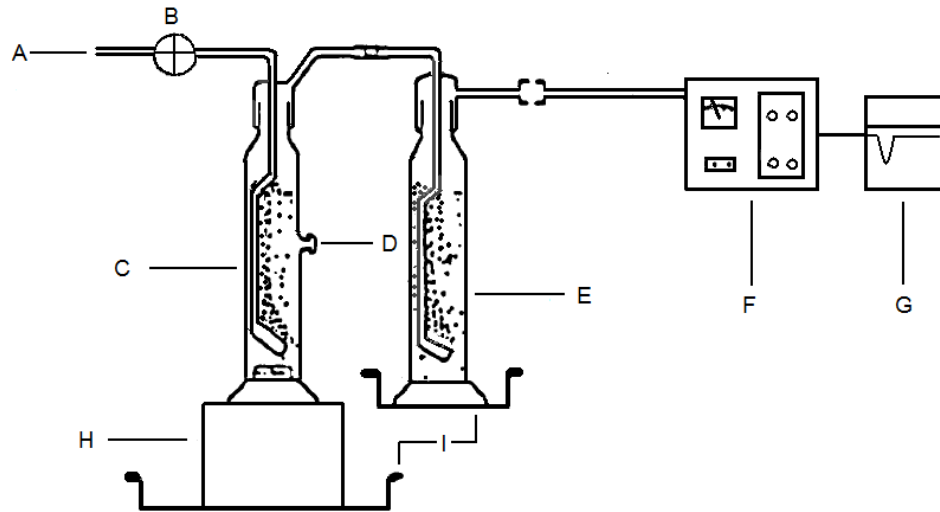
c. Repeat with an injection of 10 µL – scale on infrared analyzer should read 20 units (10 mg/kg CO₂).

F.2.2.3 Sample analysis. Inject 1 mL of hydrazine sample into the phosphoric acid reaction flask. Record the reading from the infrared analyzer scale or strip chart recorder (from the zero point).

F.2.2.4 Reagents. Accurately weigh 0.19 g of ACS reagent grade anhydrous sodium bicarbonate (NaHCO₃) into a 100 mL volumetric flask and dilute to volume with purified water. A 25 mL sample of this solution will provide 0.25 mg of CO₂ per mL of the phosphoric acid solution.

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- | | |
|--|--|
| A - Sparge gas inlet | E - Concentrated H ₂ SO ₄ trap for removing H ₂ O |
| B - Needle valve | F - Infrared analyzer |
| C - Reactor and phosphoric acid solution | G - Recorder |
| D - Septum inlet for propellant | H - Magnetic stirrer |
| | I - Plastic spill trays |

FIGURE F-2. CO₂ apparatus

F.2.2.4 Equipment.

- a. Reactor, phosphoric acid, 250 mL glass wash bottle.
- b. Drying bottle, 200 mL glass wash bottle filled with concentrated sulfuric acid solution.
- c. Non-dispersive infrared analyzer (Beckman model 865 or equivalent).

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APPENDIX G

OTHER VOLATILE CARBONACEOUS MATERIAL (OVCM)

G.1 SCOPE

G.1.1 Scope. This Appendix describes the method for the determination of other volatile carbonaceous material content of the propellant. This Appendix is a mandatory part of the specification. The information contained herein is intended for compliance.

G.2 METHOD

G.2.1 Gas chromatographic method.

G.2.1.1 Procedure. A 30 m x 0.53 mm Stabilwax DB column, a FID equipped with a split/splitless injector, and a glass wool packed split liner shall be used. The UDMH peak will elute first followed by the IPA and MMH peaks respectively. Subsequent peaks are those of hydrazine and aniline and shall be ignored. Table G-1 depicts recommended parameters for initial setup. These parameters may vary depending on GC system and detector brands, and may be adjusted by the chemist to provide adequate component resolution.

G.2.1.2 Calibration. Prepare a standard stock solution, and a working standard of UDMH, IPA, and MMH in propellant as depicted in G.2.1.2.1 and G.2.1.2.2. Run a blank of pure N_2H_4 (high purity meeting this specification) and subtract the areas of UDMH, IPA, and MMH from the areas of the standard. If any of the contaminants are found in a propellant sample, analyze the standard and sample(s) in triplicates; the RSD \leq 15%.

G.2.1.2.1 Standard stock solution.

1. Weigh a 40 mL volatile organic analysis type septa vial to the nearest 0.0001g and tare.
2. Add 30 mL of pure N_2H_4 to the tared vial; cap and weigh to the nearest 0.0001g.
3. Using a gas-tight glass syringe add approximately 190 μ L UDMH to the vial and weigh to the nearest 0.0001g. Subtract the weight of the pure hydrazine from the weight obtained to determine the weight of UDMH added.
4. Follow same procedure as above with the additions of 190 μ L IPA and 170 μ L MMH.
5. Mix solution thoroughly and store in the fuel hood under a gaseous nitrogen purge.

G.2.1.2.2 Working standard.

1. Weigh two autosampler vials (without caps) to the nearest 0.0001g and tare; label one standard.
2. Add 1.5 mL of pure N_2H_4 to the vial labeled standard; crimp both vials and weigh. The difference in weight between the two will be the amount of N_2H_4 added.
3. Shake the standard stock solution and inject enough to the standard vial to obtain a mid range concentration based on the maximum allowed limits for high purity and monopropellant hydrazine. Subtract weight from the N_2H_4 weight to obtain weight of added standard stock solution.

G.2.1.3 Calculation. Calculate the concentration by weight of UDMH, IPA, and MMH separately using the following equations,

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a. Standard stock solution:

$$\text{Analyte ppmw} = \frac{Wt_{\text{Analyte}} \times 10^6}{Wt_{\text{Total}}}$$

where,

$$Wt_{\text{Total}} = Wt_{\text{N}_2\text{H}_4} + Wt_{\text{UDMH}} + Wt_{\text{IPA}} + Wt_{\text{MMH}}$$

b. Working standard:

$$\text{Analyte ppmw} = \frac{\text{Analyte}_{\text{Stock Std Conc}} \times Wt_{\text{Analyte added}}}{Wt_{\text{Analyte added}} + Wt_{\text{N}_2\text{H}_4}}$$

c. Sample calculation:

$$\text{UDMH ppmw} = \frac{\text{UDMH}_{\text{Std Conc}} \times A_s}{A_{\text{UDMH}} - A_s}$$

$$\text{MMH ppmw} = \frac{\text{MMH}_{\text{Std Conc}} \times A_s}{A_{\text{MMH}} - A_s}$$

$$\text{IPA ppmw} = \frac{\text{IPA}_{\text{Std Conc}} \times A_s}{A_{\text{IPA}} - A_s}$$

where,

A_{UDMH} = The area of the UDMH peak times its signal attenuation factor

A_{MMH} = The area of the MMH peak times its signal attenuation factor

A_{IPA} = The area of the IPA peak times its signal attenuation factor.

A_s = The area of the respective analyte in the sample times its signal attenuation factor.

Report OVCM in weight percent using following equation,

$$Wt\% \text{ OVCM} = Wt\% \text{ UDMH} + Wt\% \text{ MMH} + Wt\% \text{ IPA}$$

G.2.1.4 Reagents and equipment. The following reagents and equipment shall apply as test conditions of G.2.1.2.

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G.2.1.4.1 Reagents.

- a. N₂H₄ - High purity grade conforming to this specification
- b. UDMH - Conforming to MIL-PRF-25604
- c. MMH - Conforming to MIL-PRF-27404
- d. IPA - ACS Reagent grade

G.2.1.4.2 Equipment.

- (1) Gas chromatograph equipped with a flame ionization detector (FID) and a split/splitless injector.
- (2) Hewlett Packard (HP) Chemstation or equivalent.
- (3) A 30 m x 0.53 mm Stabilwax DB column.
- (4) Glass wool packed split liner.
- (5) Analytical balance calibrated to 0.0001 g

TABLE G-1. GC Recommended parameters

PARAMETER	CONDITION
Carrier Flow (Helium)	10 mL/min
Sample Volume.	1 µL (10:1 split)
Inlet Temp.	175 °C
FID Detector Temp.	250 °C
Aux. + Column Flow	~25 mL/min
H ₂ Flow	~60 mL/min
Air Flow	375 - 400 mL/min
Purge	On
Oven Max	200 °C
Initial Temp.(T ₀)	60 °C
Initial Time (t ₀)	3.00 min
Rate (1)	10 °C/min
Final Temp. (T _f)	100 °C
Final Time (t _f)	0.00 min
Rate (2)	20 °C/min
Final Temp. (2)	185 °C
Final Time (2)	3.75 min

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CONCLUDING MATERIAL

Custodians

Navy – AS
Air Force – 68
DLA – PS

Preparing Activity

Air Force – 68
(Project: 9135-2011-001)

Review Activities

Air Force - 19

Civil Agency

NASA - NA

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