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PERFORMANCE SPECIFICATION

PROPELLANT, HYDRAZINE – WATER (70 % HYDRAZINE – 30 % WATER)



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AMSC N/A

FSC 9135

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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 hydrazine - water propellant blend, 70 percent hydrazine and 30 percent water by weight (H-70).

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

DEPARTMENT OF DEFENSE SPECIFICATIONS

MIL-PRF-25604	Propellant, uns-Dimethylhydrazine
MIL-PRF-26536	Propellant, Hydrazine
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.dla.mil> 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

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ASTM D2276	Standard Test Method for Particulate Contaminant in Aviation Fuel by Line Sampling (DoD Adopted)
ASTM E29	Standard Practice for 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 ASTM International, 100 Barr Harbor Drive, West Conshohocken PA 19428-2959).

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY (EPA)

EPA 300.0	Determination of Inorganic Anions by Ion Chromatography.
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(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 mixture shall conform to those listed in Table I when tested according to 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. A filter with a rating of at least 2 micrometer (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	Test Paragraph
Hydrazine (% by weight)	69 - 70	4.3.2
Water (% by weight)	30 min	4.3.2
Particulate (mg/L)	1.0 max	4.3.3
Chloride (% by weight)	0.0005 max	4.3.4
Aniline (% by weight)	0.40 max	4.3.5
Iron (% by weight)	0.002 max	4.3.6
Non-volatile residue (mg/L)	40 max	4.3.7
Carbon dioxide (% by weight) ⁽¹⁾	0.002 max	4.3.8
Other volatile carbonaceous material ⁽²⁾ (Total as UDMH, IPA & MMH, % by Weight)	0.02 max	4.3.9
<p>Note:</p> <p>¹ Determination of CO₂ content must be performed before all other analyses to prevent further absorption of CO₂.</p> <p>² Unsymmetrical dimethylhydrazine (UDMH), Isopropyl alcohol (IPA), and Monomethylhydrazine (MMH).</p>		

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 1500 mL of propellant. 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 glass narrow mouth bottles 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. The bottle must be dried with filtered nitrogen after cleaning. The sampling of drums and other shipping containers shall be conducted in such a manner that neither the contents of the container nor the sample is exposed to the atmosphere. The use of a plastic bag purged with nitrogen to cover the container is mandatory.

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 to ensure that the material conforms to 3.4. The examination shall be conducted after a representative aliquot of the sample has been transferred to a clear glass vessel and compared to the same type vessel containing the same volume of purified water.

4.3.2 Hydrazine assay and water. The hydrazine and water content of the sample shall be determined by the Gas Chromatographic method described in Appendix A.

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

- a. Mix the sample thoroughly without exposure to air. Immediately pour 1000 mL of the sample into a clean 1000 mL graduated cylinder.
- b. Pass the 1000 mL sample aliquot through a Mitex disc polytetrafluoroethylene (PTFE) hydrophobic, 5 µm, 0.47 mm diameter, white filter or equivalent.
- c. Set the oven temperature to 70°C (158°F).
- d. Filtered American Chemical Society (ACS) reagent grade isopropyl alcohol shall be used for rinsing the sample bottle and filter holder instead of petroleum ether specified in ASTM D2276. Use a suitable solvent resistant filter disc with an absolute rating of at least 1.0 µm. Wet the filter with the filtered isopropyl alcohol prior to filtering the sample.

4.3.4 Chloride. The chloride (Cl⁻) level shall be determined by a calibrated ion chromatograph (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.

4.3.5 Aniline. The aniline content of the propellant shall be determined by one of the methods found in Appendix C or the OVCM method found in Appendix G. In case of a dispute, the spectrophotometric method (C.2.1) shall be the referee.

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

4.3.7 Non-volatile residue (NVR). The NVR of the propellant shall be determined in duplicate by one of the methods described in Appendix E. In case of a dispute, the hot plate method (E.2.1) shall be the referee.

4.3.8 Carbon dioxide. The carbon dioxide content of the propellant shall be determined by the method described in Appendix F.

4.3.9 Other volatile carbonaceous material (OVCM). OVCM 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 fuel for gas generators.

6.2 Acquisition requirements. Acquisition documents must specify the following:

- a. Title, number, and date of this specification.
- b. Quantity by weight in pounds (avoirdupois).
- c. When test methods are other than those specified (3.1).
- d. When a different sampling plan is required (4.2).

6.3 Safety Data Sheets. Contracting officers will identify those activities that require copies of completed Safety Data Sheets (SDS) prepared in accordance with the 29CFR1910.1200.

6.4 Subject term (key word) listing.

Fuel
Gas generator

6.5 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 a Gas Chromatographic method for the determination of hydrazine 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 METHOD

A.2.1 Gas chromatographic method – capillary column.

A.2.1.1 Procedure. A 60 meter (m) x 0.53 millimeters (mm), 1.00 micrometer (μ m) film thickness Agilent DB-Wax capillary column, a TCD, with a split injector and a glass wool packed split liner shall be used. Table A-1 provides a summary of the critical operating parameters. These parameters may vary depending on GC system, detector brands, and column length and may be adjusted to optimize component resolution.

TABLE A-1. GC and method parameters

PARAMETER	CONDITION
Injector Port Temp.	150 °C
Injection Mode	Split injection
Sample Volume	1 μ L
Split Ratio	1:50
Carrier Gas	He
Control Flow	10 mL/min
Control Mode	Flow
TCD Detector Temp.	210 °C
Equilibration Time	2.00 min
Initial Temp. (T_0)	60 °C
Initial Time (t_0)	3.00 min
Rate (1)	10 °C/min
Final Temp. (T_{f1})	100 °C
Final Time (t_{f1})	0.00 min
Rate (2)	20 °C/min
Final Temp. (T_{f2})	185 °C
Final Time (t_{f2})	3.75 min

The elution order of possible sample components is as follows:

Air > ammonia > water > hydrazine > aniline

A.2.1.2 Standard preparation.

Determine the hydrazine and water content of a sample of high purity hydrazine (HPH) using procedures in the latest revision of MIL-PRF-26536. Use this analyzed hydrazine to prepare a mixture with purified water which is approximately 70% hydrazine and 30% water. Use an analytical balance that is accurate to 0.1 mg to determine the weight of each component used to make the standard. (Use approximately 0.5 mL H₂O for each 1 mL of N₂H₄).

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APPENDIX A

A.2.1.3 Calculations.

$$\%N_2H_4 = \frac{W_{N_2H_4} \times \% \text{ HPH (from A.2.1.2)}}{\text{Total Weight}}$$

$$\% H_2O = \frac{W_{H_2O} + \left[\frac{W_{N_2H_4} \times \% H_2O \text{ (from A.2.1.2)}}{100} \right]}{\text{Total Weight}} \times 100$$

A.2.1.4 Quality control. Verify the HPH analysis falls within 10% of historical values. Analyze the H-70 prepared standard with the samples to be tested. The following performance criteria must be met for fuel purity analysis,

GC replicate analyses (3 consecutive)	H ₂ O content RSD ^a ≤ 1 %
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a. RSD = Standard Deviation * 100% / Mean

A.2.1.5 Equipment and reagents. The following equipment and reagents shall apply as test conditions of A.2.

a. Equipment:

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

(2) Agilent ChemStation or equivalent.

(3) A 60 m x 0.53 mm ID and 1 µm film thickness DB-wax capillary column (Agilent P/Ns 125-7062 or equivalent).

(4) Glass wool packed split liner (Agilent P/N 5183-4647 or equivalent).

(5) Analytical balance calibrated to 0.0001g.

b. Reagents:

(1) High Purity Hydrazine (HPH) conforming to MIL-PRF-26536.

(2) Helium conforming to MIL-PRF-27407.

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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 4.3.7 with a 5 mL aliquot of 1N sulfuric acid (H_2SO_4). 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 Calibration. Add 50 mL of purified water plus one drop of 0.1 N H_2SO_4 to each of five 100 mL volumetric flasks. Then add 0.5, 1.0, 2.5 and 5.0 mL of a 1000 ppm chloride standard sequentially to four of the five flasks. Add 2-3 drops of bromocresol green indicator to each of the five flasks and if necessary adjust with 0.1 N H_2SO_4 or 0.1N NaOH to obtain a green endpoint. Dilute each to the mark with purified water and mix the solutions thoroughly. The calibration standards are equivalent to a blank, 5, 10, 25 and 50 ppm Cl^- respectively. Pour enough of the standards into a small beaker to cover the electrode tips and record the resulting millivolt reading. Prepare a calibration curve of Cl^- concentration to mV and use this to determine Cl^- concentration in the sample.

B.2.1.3 Calculation. Calculate the percent chloride in the sample using the following formula:

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

where,

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

V_p = Volume of propellant used in NVR analysis in mL.

D = Density of H-70 (1.03 g/mL).

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APPENDIX B

B.2.1.4 Reagents and equipment. The following shall apply as test conditions of B.2.1:

B.2.1.4.1 Reagents.

a. Purified water free of interfering substances; the water is considered free of interfering substances if a 100 mL sample used to dissolve 0.1 g of silver nitrate shows no turbidity after standing in the dark for 24 hours. The purified water as described in this paragraph shall be used throughout the procedure.

b. Standard sodium chloride (NaCl) solution, 1 mL = 1.00 mg Cl⁻; weigh 1.648 g of 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. A 1000 mg/L (ppm) chloride standard may be commercially obtained; must be certified.

c. 1N H₂SO₄; prepare by pouring 29 mL of ACS reagent grade concentrated H₂SO₄ into 300 mL of purified water contained in a 1000 mL volumetric flask. Cool the solution to room temperature, dilute to the mark with the purified water, and mix thoroughly. Transfer the solution to a plastic bottle.

d. 1N NaOH; prepare by dissolving 40 g of ACS reagent grade, low carbonate, NaOH in 300 mL of purified water contained in a 1000 mL volumetric flask. Cool the solution to room temperature, dilute to the mark with the purified water, and mix thoroughly. Transfer the solution to a plastic bottle and protect from prolonged exposure to the atmosphere.

e. Bromocresol green indicator; 1% aqueous solution. Use purified water.

B.2.1.4.2 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, Orion 420A+ or equivalent.

B.2.2 Colorimetric method.

B.2.2.1 Procedure. Add to the propellant residue container in one vessel from 4.3.7 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 versus 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.2.1.3.

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B.2.2.3 Reagents and equipment. The following shall apply as test conditions of B.2.2:

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 ($\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) ACS reagent grade in approximately 50 mL of purified water. Add 10 mL of ACS reagent 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

ANILINE

C.1 SCOPE

C.1.1 Scope. This Appendix describes two 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.

C.2 METHODS

C.2.1 Spectrophotometric method.

C.2.1.1 Procedure. Pipet or syringe 0.25 mL (250 μ L) of propellant into a 25 mL volumetric flask containing approximately 15 mL of purified water, 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 flat then 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 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.

C.2.1.2 Calibration. Pipet or syringe 0.025 mL (25 μ L) of ACS reagent grade 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 standard is equivalent to 0.025%. Use this aniline standard to prepare a series of calibration standards by adding 2.0, 4.0, 6.0 and 8.0 mL to separate 25 mL volumetric flask, fill to the mark with purified water and mix thoroughly. The aniline concentrations are equivalent to 0.2, 0.4, 0.6 and 0.8% respectively. 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 shall be prepared fresh daily to check the calibration standards. If the check standard falls outside of $\pm 5\%$ of the expected value, fresh calibration standards shall be prepared and the calibration check repeated until the required accuracy is demonstrated.

C.2.1.3 Equipment. Spectrophotometer, double beam, ultra violet, narrow band width, recording, equipped with 1 cm silica cells.

C.2.2 Gas chromatographic method – capillary column.

C.2.2.1 Procedure. Aniline concentration may also be determined using the OVCM GC method described in Appendix G of this specification.

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APPENDIX D

IRON

D.1 SCOPE

D.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.

D.2 METHODS

D.2.1 Atomic absorption.

D.2.1.1 Procedure. Rinse the propellant residue contained in one vessel from 4.3.7 as follows: Add 5 mL of 5N H₂SO₄ to the vessel and place on a hotplate. Heat the mixture to near boiling, maneuver the beakers so the acid contacts the surface area of the glass that the fuel mixture came in contact with and maintain at that temperature for three to five minutes. Allow the solution to cool and transfer to a 200 mL volumetric flask. Rinse the vessel at least three times with 5 mL aliquots of 0.1N H₂SO₄ combining all of the rinses in the volumetric flask. Dilute to the mark with purified water and mix thoroughly. 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.

D.2.1.2 Calibration. Prepare a 1000 ppm iron standard by dissolving 1.00 g of 99.99% purity 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 1000 ppm standard solution may be used; must be certified). 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 versus iron concentration.

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

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

where:

ppmv Fe = The iron content of the sample solution, using the calibration curve.

V_d = Final dilution volume taken from NVR in mL.

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

D = Density of the H-70 (1.03 g/mL)

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D.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 shall be used as the laboratory control sample.

D.2.1.5 Reagents and equipment. The following equipment shall apply as test conditions of D.2.1.

D.2.1.5.1 Reagents.

a. Iron Standard – A minimum of 99.99% purity wire or shot or a 1000 µg/mL commercially obtained solution (must be certified).

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

D.2.1.5.2 Equipment.

a. Hotplate – controllable heat.

b. Atomic absorption spectrophotometer with an iron hollow cathode lamp.

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

D.2.2.1 Procedure. Prepare the sample solution in the same manner as described in D.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 D.2.1.2 to determine the slope.

D.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 with the analyses.

D.2.2.3 Calculations. Calculate the iron content of the propellant using the formula in D.2.1.3.

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

D.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).

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

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

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D.2.3 Colorimetric method.

D.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 4.3.7 by adding 1 mL of concentrated H_2SO_4 , 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 H_2SO_4 , and 50 mL purified water to at least four empty 150 mL evaporating dishes for the standards.
- NOTE: Make sure the 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 .

D.2.3.2 Calculations. Calculate the iron content of the propellant using the formula in D.2.1.3.

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

- a. Sodium acetate solution. Dissolve 200 g $\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$ in a 1 L volumetric flask in 700 mL of 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 E

NON-VOLATILE RESIDUE (NVR)

E.1 SCOPE

E.1.1 Scope. This Appendix describes two methods for the determination of non-volatile residue of the propellant. This Appendix is a mandatory part of the specification. The information contained herein is intended for compliance.

E.2 METHOD

E.2.1. Hot plate. This method involves the gradual evaporation of an H-70 sample on an explosion proof hot plate in a fume hood. The difference in weight before and after evaporation is calculated as NVR.

E.2.1.1 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 A1 and A2. Remove evaporation dishes from the oven, place in a desiccator to cool for 15 minutes, and then place next to a five place balance long enough to equilibrate (usually around 30 min). Weigh each clean, dry evaporating dish to the nearest 0.0001 g until the weight remains constant to ± 0.1 mg. Record the sample evaporating dish weight as A1, A2 and the blank evaporating dish weight as C. Add 30 mL of purified water to each one of the evaporating dishes. Transfer 50 mL of the H-70 sample into the evaporating dishes marked A1 and A2. Place the evaporating dishes 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 an oven set at 110°C for 30 minutes. Remove dishes from the oven and place in a desiccator for 15 minutes to cool; then place them next to a five place balance long enough to equilibrate. Weigh each evaporating dish as before to a constant weight. Record the sample evaporating dish weight as B1, B2 and the blank evaporating weight as D.

NOTE

Save the propellant residue for chloride (4.3.4) and iron (4.3.6) determinations.

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

$$NVR, \text{ mg/L} = \left[\frac{(Wt_B - Wt_A) - (Wt_D - Wt_C)}{\text{Sample volume, mL}} \right] 1 \times 10^6$$

where,

A = Weight of the sample evaporating dish, g.

B = Weight of the sample evaporating dish and residue, g.

C = Weight of blank evaporating dish, g.

D = Weight of blank and water residue, g.

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E.2.1.3 Equipment.

- a. Hot plate, explosion proof.
- b. High efficiency fume hood.
- c. Five decimal place analytical balance (semi-micro balance).

E.2.2 Dropwise method.

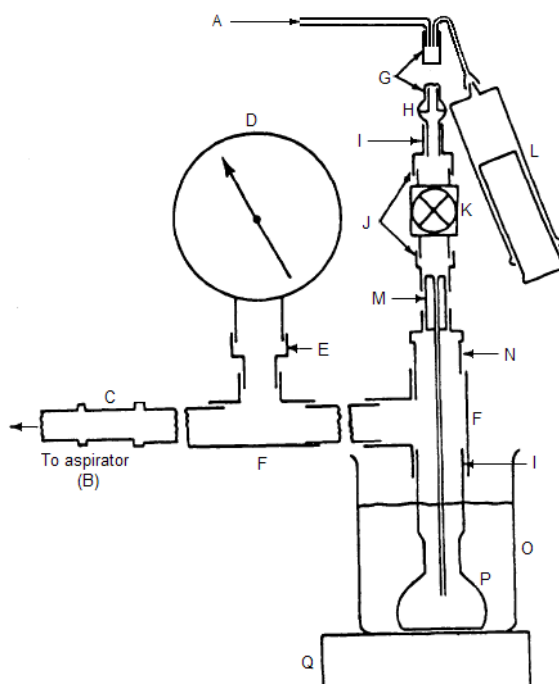
E.2.2.1 Procedure. Clean the unassembled apparatus with detergent and rinse thoroughly with purified water. Dry the parts in an oven at 110°C. Assemble the apparatus as shown in Figure E-1. Fill the water bath with purified water and turn on the heater. Adjust the water level of the bath to approximately one-half inch below the lowest fitting and mark this level on the bath. When the bath temperature 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 carefully and place it near the analytical balance. After at least twenty minutes, accurately weigh the residue vessel until the weight remains constant to ± 0.1 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. 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 insure 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 ACS grade H_2SO_4 (or equivalent) 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 (4.3.6) 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 E-1. NVR apparatus

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E.2.2.2 Calculations. Calculate the non-volatile residue of the propellant as follows:

$$NVR, mg/L = \left[\frac{W_2 - W_1}{V} \right] 1 \times 10^6$$

where:

W_1 = Weight of clean vessel in grams (g).

W_2 = Weight of residue and vessel in g.

V = Volume of sample used in mL.

Report the averaged result of duplicate NVR determinations.

E.2.2.3 Equipment. The following equipment shall apply as test conditions of E.2.1.

- a. Components described in Figure E-1.
- b. Tubing – polyethylene, ½ inch OD, borosilicate glass, ½ inch OD.
- c. Clamps – hose, to fit ½ inch OD tube.
- d. Five decimal place analytical balance (semi-micro balance).

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APPENDIX F

CARBON DIOXIDE

F.1 SCOPE

F.1.1 Scope. This Appendix describes a method 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. Determination of CO₂ content in H-70 must be performed before all other analyses to prevent further absorption of CO₂.

F.2 METHOD

F.2.1 Determination of carbon dioxide by non-dispersive IR analysis. This method is to be utilized to determine the carbon dioxide concentration in H-70 within a 10 – 100 mg/kg (ppm) range. The sample of propellant is injected into a solution of 30% 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 silica gel drying tube to remove water vapor, and is measured by an infrared technique.

F.2.1.1 Calibration procedure.

- a. Assemble the apparatus as shown in Figure F-1.
- b. Adjust the flow of nitrogen purge gas according to the manufacturer's recommendation by use of a control valve and flow meter.
- c. Add an appropriate amount of 30% phosphoric acid containing several drops of bromocresol green indicator to the CO₂ reaction flask, turn on the nitrogen (N₂) gas to give vigorous, constant mixing. The nitrogen flow (approximately 200 mL/min) should be kept constant throughout the analysis.
- d. After the apparatus has stabilized, adjust the zero on the infrared analyzer.

F.2.1.2 Standardization. Direct instrument response (flow technique),

- a. Inject, via the septum on the phosphoric acid containing unit, an appropriate amount (approximately 200 µL) of the 100 ppm working CO₂ carbonate standard into the phosphoric acid solution to get a reading of 100 ppm on the instrument. Repeat the injection to ensure reproducibility is within ± 10 ppm.
- b. Repeat as above with approximately 100 µL (50 ppm) and 50 µL (25 ppm).

Alternatively if an integrator is used, a calibration curve may be prepared using the 100 ppm stock standard and plotting the absorbance counts of the prepared working standards versus concentration. The correlation coefficient shall be ≥ 0.995. Use this curve to determine the CO₂ concentration in the sample.

F.2.1.3 Sample analysis. Inject an appropriate amount of H-70 sample into the phosphoric acid reaction flask to obtain a reproducible result within the standards range. Record the reading from the infrared analyzer scale or strip chart recorder (from the zero point). Perform the sample analysis in triplicate (verifying reproducibility) and use the average to determine the CO₂ concentration.

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F.2.1.3.1 Calculation.

$$CO_2 \text{ Wt\%} = \frac{(Std \text{ conc}_{(ppmw)})(Std \text{ vol}_{(\mu L)})(Sample \text{ response})}{(Sample \text{ vol}_{(\mu L)})(Std \text{ response})(1 \times 10^4)}$$

F.2.1.4 Reagents.

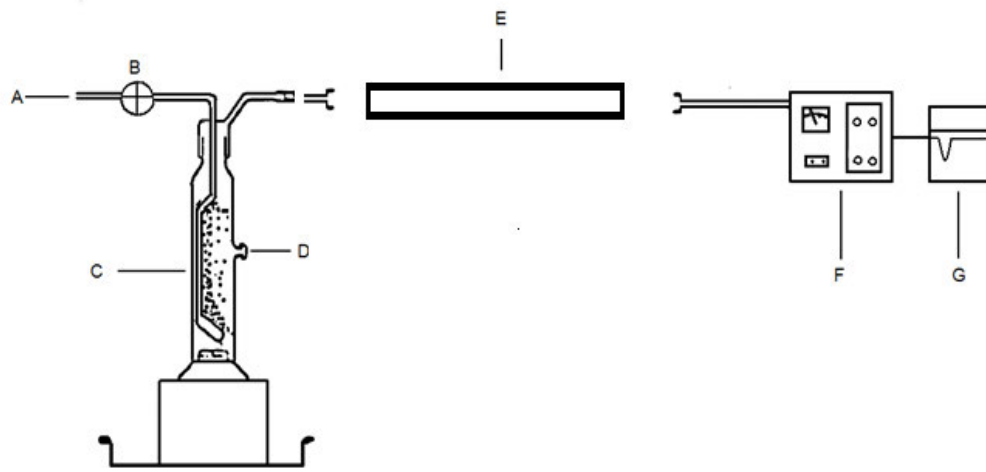
- a. Purified water, CO₂ free - Prepare by boiling purified water vigorously for 15 minutes or by bubbling nitrogen through it for several hours.
- b. Carbon Dioxide Stock Solution, 1000 ppm - Dissolve 2.4083 g sodium carbonate, dried for one hour at 100°C, in CO₂ free purified water in a 1 L volumetric flask; fill to the mark and mix thoroughly. Transfer 1 mL of this solution to a 10 mL volumetric flask, fill to the mark with CO₂ free purified water to prepare a 100 ppm standard. Prepare fresh daily.
- c. Phosphoric Acid, 30% by volume - Dilute 355 mL of 85% H₃PO₄ to 1 L with purified water. Add enough indicator to this solution to readily determine when the acid solution is depleted.
- d. Dry nitrogen gas supply.
- e. Silica gel desiccant.

F.2.1.5 Equipment.

- a. Non-dispersive infrared analyzer, Rosemount Analytical Model XStream-X2GP or equivalent.
- b. Glass reaction tube with replaceable septum.
- c. Glass drying tube.
- d. Needle valve to control flow into reaction tube.
- e. PTFE tubing.
- f. Fittings to achieve air-tight connections.
- g. Operating fume hood
- h. Suitable data acquisition device.

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A	-	Sparge gas inlet	E	-	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		-	

FIGURE F-1. CO₂ apparatus

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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 60 m x 0.53 mm x 1 μ m film thickness Stabilwax®-DB megabore column, a flame ionization detector (FID), a split injector and a deactivated glass wool split liner shall be used. GC parameters are listed in Table G-1. The analysis requires approximately 15 min for elution of all components.

TABLE G-1. GC conditions

PARAMETER	CONDITION
Injector Port Temp.	175°C
Injection Mode	Split injection
Sample Volume.	3 μ L
Split Ratio	1:50
Carrier Gas	He
Column Flow	10 mL/min
Control Mode	Flow
FID Detector Port Temp.	210 °C
H ₂ Flow	~ 40 mL/min
Air Flow	~ 400 mL/min
Initial Temp (T ₀)	60°C
Initial Time (t ₀)	3.00 min
Rate (1)	10 °C/min
Final Temp. (T _{f1})	100 °C
Final Time (t _{f1})	0.00 min
Rate (2)	20 °C/min
Final Temp. (T _{f2})	185 °C
Final Time (t _{f2})	3.75 min

The elution order is as follows:

UDMH < IPA < MMH < water < hydrazine < aniline

NOTE; Water and hydrazine co-elute.

G.2.1.2 Calibration. Prepare a standard stock solution, and a working standard of UDMH, IPA, and MMH in H-70 as described in G.2.1.2.1 and G.2.1.2.2. Run a HPH blank (meeting this specification) and subtract the areas of UDMH, IPA, MMH and aniline (if detected) from the areas of the standard. If

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any of the contaminants are found in a propellant sample, analyze the standard and sample(s) in triplicate; the RSD \leq 10%.

G.2.1.2.1 Standard stock solution.

1. Weigh a 200 mL borosilicate glass bottle with a PTFE cap to the nearest 0.0001g and tare.
2. Add approximately 69 mL of HPH to the tared bottle; cap and weigh to the nearest 0.0001g.
3. Add approximately 30 mL of purified water to the bottle and weigh to the nearest 0.0001g. Subtract the weight of the HPH from the weight obtained to determine the weight of water added.
4. Follow same procedure as above with the additions of 200 μ L UDMH, IPA and MMH and approximately 4.7 mL aniline.
5. Mix the solution thoroughly and store it tightly sealed.

G.2.1.2.2 Working standard. Make a 1:10 dilution of the stock standard in a suitable borosilicate glass volumetric flask and mix the solution thoroughly.

G.2.1.3 Calculations.

- a. Standard stock solution:

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

where,

$$Wt_{\text{Total}} = Wt_{N_2H_4} + Wt_{UDMH} + Wt_{IPA} + Wt_{MMH} + Wt_{\text{aniline}}$$

- b. Sample calculation:

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

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

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

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$$Aniline\ ppmw = \frac{Aniline_{Std\ Conc} \times A_s}{A_{Aniline} - A_s}$$

where,

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

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

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

$A_{Aniline}$ = The area of the aniline peak times its signal attenuation factor.

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

$$Wt\% OVCM = Wt\% UDMH + Wt\% IPA + Wt\% MMH$$

G.2.1.4 Reagents and equipment. The following reagents and equipment shall apply as test conditions of G.2.1.

G.2.1.4.1 Reagents.

- a. N_2H_4 - high purity grade conforming to MIL-PRF-26536.
- b. UDMH - conforming to MIL-PRF-25604.
- c. IPA - ACS reagent grade.
- d. MMH - conforming to MIL-PRF-27404.
- e. Aniline - ACS reagent grade.

G.2.1.4.2 Equipment.

- (1) Gas chromatograph equipped with a flame ionization detector (FID) and a split injector.
- (2) Agilent ChemStation or equivalent.
- (3) A 60 m x 0.53 mm ID and 1 μ m film thickness Stabilwax®-DB column (Restek catalog No. 10858 or equivalent).
- (4) Deactivated glass wool packed liner (Restek catalog no. 23309 or equivalent).
- (5) Analytical balance calibrated to 0.0001g.

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CONCLUDING MATERIAL

Custodians

Navy – AS
Air Force – 68
DLA – PS

Preparing Activity

Air Force – 68
(Project: 9135-2012-002)

Review Activities

Air Force - 19

Civil Agency

NASA - NA

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