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MILITARY SPECIFICATION

PROPELLANT, uns-DIMETHYLHYDRAZINE

This amendment forms a part of Military Specification MIL-P-25604D, dated 23 May 1969, and is approved for use by all Departments and Agencies of the Department of Defense.

Page 1, 2.1: Add following Federal Specifications:

BB-H-886	Hydrogen
BB-A-1034	Air, Compressed, For Breathing Purposes

Page 2, 2.2: Delete "Manufacturing Chemists' Association, Inc." and "MCA Manual L-1" and replace with the following:

"American National Standards Institute (ANSI) Standards

ANSI Standard 2129.1	The Precautionary Labeling of Hazardous Industrial Chemicals

Page 3, 3.1: Delete Table I and substitute:

TABLE I. Chemical and Physical Properties

PROPERTY	LIMIT	TEST PARAGRAPH
UDMH (Percent by weight)	98.0 min	4.5.2
H_2O (Percent by weight)	0.3 max	4.5.2
Amines (Percent by weight)	1.5 max	4.5.2
N-nitrosodimethylamine (Percent by weight)	0.01 max	4.5.6
Chloride (Percent by weight)	0.003 max	4.5.3
Density (g/ml) @ 60°F	0.795 to 0.797	4.5.4
Particulate (mg/l)	10 max	4.5.5

Page 4, 4.4.2: Delete subparagraph (c) and add the following:

(c)	Amines	4.5.2
(d)	N-nitrosodimethylamine	4.5.6
(e)	Chloride	4.5.3
(f)	Density	4.5.4
(g)	Particulate	4.5.5

Page 4, 4.4.2.1.1: Change first line to read as follows:

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Lot. For containers of 100 gallons or less (water capacity), a lot shall consist of one of the following:

Page 5, 4.4.2.1.2: Change the number at the end of the last sentence from 4.5.3 to 4.5.5.

Page 5, 4.4.2.1.4: Delete last sentence and substitute:

The sample shall be drawn from the sample port of the tank.

Page 6, 4.5: Delete and substitute:

4.5 Test Methods.

4.5.1 Examination of Product. The propellant shall be visually examined while performing test specified in 4.5.5 to determine requirements as specified herein. Examination to ensure that the material conforms to paragraph 3.4 shall be conducted after the sample has been transferred to the 500 ml graduated cylinder.

4 5.2 UDMH Assay, Water, and Amines. The propellant, water and amine content shall be determined by the following method.

4.5.2.1 Column Preparation. Weigh 5 grams of polyethylene glycol 400 and 45 grams of 60/80 mesh Fluoropak 80 into separate beakers. Dissolve the polyethylene glycol 400 in a volume of reagent grade dichloromethane which is approximately one-half the volume of the Fluoropak 80. Pour the Fluoropak 80 into the polyethylene glycol 400 solution with gentle stirring. Spread the resulting damp powder in a tray and dry the mixture in a vacuum oven at 100°C and less than 50 mm Hg for at least one hour.

Cap one end of an 1/8 inch O.D. by 6 foot stainless steel tube and using a small funnel fill the tube with the prepared column packing. Tap or mechanically vibrate the tube to insure 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 ~120°C for one hour. After conditioning the column, connect the other end to the detector and set the carrier gas flow to approximately 25 ml/min, and the column oven to 100°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.

4.5.2.2 Analysis. Equilibrate the column with propellant by injection of two or more 5 microliter samples into the inlet. If more than 30 minutes elapse between analyses a single 5 microliter injection of propellant should reequilibrate the column. Inject 1 to 2 microliters of propellant for analysis and record the areas of all peaks in the chromatogram. Each analysis should require less than 15 minutes for elution of all components. The elution order of possible sample components is as follows: Air, NH_3, methylamine,

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dimethylamine, formaldehyde dimethylhydrazone, UDMH, water, methylhydrazine, and hydrazine.

4.5.2.3 Calculations. The following formula shall be used to calculate the percent by weight of each component appearing in the chromatogram.

$$\% C = \frac{A_c}{\Sigma Ai} \times 100$$

Where: Ac = the measured area of a peak multiplied by its signal attenuation factor.

Σ Ai = the sum of all of the measured areas multiplied by their respective signal attenuation factors.

% C = weight percent of the component corresponding to Ac.

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

4.5.2.4 Equipment and Reagents. The following equipment and reagents shall apply as test conditions of 4.5.2.

(a) Equipment

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

(2) Recorder: potentiometric strip chart, 0-1 millivolt, 1 second F.S. response, with integrator (mechanical or electronic).

(3) Tubing: stainless steel, 1/8 inch O.D. x 6 feet.

(4) Hypodermic syringe: 10 microliter, fixed needle.

(5) Regulator: helium, to fit the cylinder.

(6) Standard Screens: 60 mesh and 80 mesh.

(7) Vacuum oven, capable of 100°C.

(b) Reagents

(1) Fluoropak 80, Analabs, Inc., 80 Republic Dr., North Haven, CT 06473, or equivalent.

(2) Polyethylene glycol 400, or equivalent

(3) Methylene chloride: ACS reagent grade.

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(4) Helium gas: conforming to MIL-P-27407

4.5.3 Chloride:

4.5.3.1 Procedure. Evaporate 2.0 ml of propellant and 0.2 ml 1N-NaOH contained in a 25 ml volumetric flask using a steambath or hot plate located in a fume hood. Purge the flask with nitrogen gas to facilitate evaporation. Dissolve the residue with 2.0 ml of ferric ammonium sulfate reagent and 2 ml of chloride-free distilled water. Add 1.0 ml saturated mercuric thiocyanate reagent, mix by swirling, and dilute to the 25 ml mark with chloride-free distilled water. Mix again by inverting the flask several times and allow to stand in darkness for 15 to 30 minutes. Measure the absorbance of the reagent blank and sample solutions at 460nm in a 5.0cm cell, after setting distilled water to "0" absorbance. Subtract the absorbance of the reagent blank from the sample absorbance. The chloride content is determined from the calibration curve constructed according to 4.5.3.3.

4.5.3.2 Calculation. The chloride content shall be calculated as follows:

$$Cl^-, \text{ weight } \% = \frac{(\text{mg } Cl^- \text{ from calib. curve})}{1.57} \times 10^{-1}$$

4.5.3.3 Calibration Curve. A calibration curve shall be prepared as follows Syringe 0, 1 ml, 2 ml, 4 ml, and 8 ml of the dilute chloride standard solution (0.010 mg/ml) into separate 25 ml volumetric flasks. Add 0.20 ml of 1N sodium hydroxide to each. Add 2.0 ml ferric ammonium sulfate and 5 ml chloride-free water and swirl. Add 1.0 ml saturated mercuric thiocyanate and mix. Add chloride-free distilled water to the 25 ml mark and mix by inverting several times. Place standards and blank in darkness for 15 to 30 minutes. Measure the absorbance of the blank and each of the four standards in a 5.00 cm cell at 460 nm after setting distilled water to "0" absorbance. Subtract the absorbance of the blank from that of each standard. Plot this difference against the corresponding mg of Cl^-.

4.5.3.4 Reagents and Equipment.

(a) Reagents

(1) Sodium hydroxide solution, 1N; dissolve 40 g of ACS reagent grade sodium hydroxide pellets in sufficient chloride-free distilled water to make 1 liter of solution.

(2) Ferric ammonium sulfate: Mix 240 ml concentrated nitric acid and 160 ml of chloride-free distilled water. Dissolve 48.2 g of ferric ammonium sulfate, ACS grade, in the nitric acid solution and allow the precipitate to settle out. Decant the liquid for use in the analysis.

(3) Saturated mercuric thiocyanate: Saturate ACS reagent grade ethyl alcohol (95 percent) with ACS reagent grade mercuric thiocyanate. Allow

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the excess to settle out and decant the supernatant liquid for use in the analysis.

(4) Chloride stock solution: Dissolve exactly 165 mg (0.165g) of dried, primary standard grade, sodium chloride in chloride-free distilled water contained in a 100 ml volumetric flask and dilute to the mark (1.0 mg Cl^-/ml).

(5) Chloride standard solution: Syringe exactly 10.0 ml of the chloride stock solution into a 1000 ml volumetric flask, and dilute to the mark with chloride-free water (0.010 mg Cl^-/ml).

(6) Chloride-free water: This shall be double-distilled, or distilled deionized water, which tests negative (no cloudiness) with silver nitrate.

(b) Equipment

(1) Syringes: 1, 2, and 10 ml capacity.

(2) Volumetric flasks: 25-, 100-, and 1000-ml capacity.

(3) Reagent bottles as necessary.

(4) Steam bath, or hot plate.

(5) Analytical balance.

(6) Spectrophotometer or filter photometer: Single or double beam, capable of accommodating 5.0cm cells.

4.5.4 Density. The density of the propellant shall be determined in accordance with ASTM-D-1298-67, using the hydrometer calibrated at 25°C.

4.5.5 Particulate. The propellant sample shall be tested for contamination in accordance with ASTM Designation D-2276-65T, Method A, with the following exceptions:

4.5.5.1 Mix the sample thoroughly by shaking the sample container. Immediately pour 500 ml of the sample into a clean 500 ml graduated cylinder. Use this 500 ml of propellant for the particulate analysis.

4.5.5.2 Use a solvent resistant filter disc made from such materials as Millipore LSWP 04700, (Mitex-Teflon), Millipore URWP 04700, (Solvinert), or Gelman VF-6, (Fluoride-Metricel), plain white, 10 + 3 microns, 47 mm diameter instead of the filter specified in Method 2276-65T.

4.5.5.3 The drying oven temperature shall be 158°F (70°C) instead of the 194°F (90°C) specified in Method 2276-65T.

4.5.5.4 Filtered isopropyl alcohol shall be used for rinsing the sample bottle and filter holder instead of petroleum ether specified in Method 2276-65T.

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4.5.6 N-Nitrosodimethylamine. The N-nitrosodimethylamine (NDMA) content of the propellant shall be determined as follows.

4.5.6.1 Column preparation. Weight 10 grams of Amine 220 and 20 grams of support material into separate beakers. Dissolve the Amine 220 in a volume of reagent grade dichloromethane which is approximately equal to the volume of the support material. Pour the support material into the Amine 220 solution with gentle stirring, spread the resulting damp powder in a tray, and dry the mixture in a vacuum oven at 100°C and less than 50 mm Hg for at least one hour.

Cap one end of a 1/8 inch by 6 foot stainless steel tube and fill the tube with the prepared column packing by pouring through a small funnel attached to one end. Tap or mechanically vibrate the tube to insure 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 ~150°C for one hour. After conditioning the column connect the other end of the column to the detector and set the carrier gas flow to ~30 ml/min and the column oven to 115°C. The inlet temperature and detector temperature, if separately heated, should be set at 120°C and 150°C, respectively. The hydrogen and air flowrates should be set to those recommended by the instrument manufacturer.

4.5.6.2 Analysis. Inject 1-3 microliters of the calibration standard into the chromatograph and record the area of the NDMA peak (retention time = approximately 8 min.). Inject the same volume of propellant and record the area of the NDMA peak.

4.5.6.3 Calibration Standard. Place 0.10 ml of NDMA (0.10 grams) into a 1000 ml volumetric flask containing ~500 ml of distilled water, mix, and dilute to the mark. The calibration standard contains 0.1 micrograms of NDMA per microliter of solution.

4.5.6.4 Calculation. Calculate the results as follows:

$$\% \text{ NDMA} = \frac{A \times S}{0.785 \times V} \times 10^{-1}$$

where: A = area of NDMA peak in sample chromatogram multiplied by the signal attenuation.

S = 0.1 x volume of standard injected (microliters) / Area of Standard NDMA peak multiplied by the signal attenuation.

V = volume of sample injected (microliters)

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4.5.6.5 Reagents and Equipment. The following shall apply as test conditions of 4.5.6.

a. Reagents

(1) Support Material. White diatomaceous earth. Acid and Base washed, silanized, 70/80 mesh.

(2) Amine 220, Alltech Associates, 202 Campus Drive, Arlington Heights, IL 60004, or equivalent.

(3) Dichloromethane, ACS Reagent Grade.

(4) Helium Gas, conforming to MIL-P-27407.

(5) Hydrogen Gas, conforming to BB-H-886.

(6) Breathing Air, conforming to BB-A-1034.

b. Equipment

(1) Gas chromatograph, equipped with a flame ionization detector.

(2) Recorder, potentiometric, strip chart, 0-1 millivolt span, 1 sec. F. S. response with integrator (mechanical or electronic).

(3) Tubing, 1/8 inch O.D. x 6 feet, stainless steel.

(4) Hypodermic syringe, 10 microliter, fixed needle.

(5) Regulators, to fit cylinders of helium, hydrogen, and air.

(6) Vacuum oven, capable of 100°C.

Page 10, 5.3: Change last sentence to read as follows:

After filling of containers, the space above the liquid level shall be filled with contractor furnished nitrogen conforming to MIL-P-27401, Type I, Grade A, or equivalent (99.5% + pure), at not less than atmospheric pressure.

Page 11, 5.4.2: Replace MCA Manual L-1 in second line with ANSI Standard 2129.1.

Page 11, 6.3: Delete.

Page 11, 6.4 (d): Change RPORS in last line to LKCP.

Page 12, 6.6: Replace MCA Manual L-1 in second line with ANSI Standard 2129.1.

Custodians:

Army - MI
Navy - AS
Air Force - 12

Preparing Activity

Air Force - 12

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Review Activities:

Air Force - 19, 68
Army - MI
Navy - AS, OS
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User Activities:

Navy - SH

Civilian Agency Interest:

NAS

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