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JOINT ARMY-NAVY SPECIFICATION

ACID, NITRIC

(For Ordnance Use)

Army Number
50-11-3C

Navy Number
51A22

This specification was approved by the War Department and the Navy Department for use of procurement services of the Army and the Navy and supersedes the following specification:

U. S. Army	Navy Department
50-11-3B	----------
11 June 1941	----------

A. APPLICABLE SPECIFICATIONS.

A-1. The following specifications, of the issue in effect on the date of invitation for bids, form a part of this specification:

U. S. ARMY SPECIFICATION

100-2—Standard Specification for Marking Shipments by Contractors.

NAVY DEPARTMENT SPECIFICATION

General Specifications for Inspection of Material.[1]

B. CLASSES.

B-1. This specification covers nitric acid furnished in the following classes (see par. H-1):

Class a—For use in manufacture of mercury fulminate.
Class b—For use in manufacture of PETN and nitramines.
Class c—For use in manufacture of picric acid.
Class d—For use in manufacture of ammonium nitrate.
Class e—For use in manufacture of mixed acids, and for other purposes.

C. MATERIALS AND WORKMANSHIPS.

C-1. See section E.

D. GENERAL REQUIREMENTS.

D-1. See section E.

E. DETAIL REQUIREMENTS.

E-1. *Color.*—Nitric acid shall be not darker than the standard color solution described in paragraph F-4a.

E-2. *Appearance.*—Nitric acid shall be clear and free from sediment, suspended matter, and separated material.

E-3. *Chemical requirements.*—Nitric acid shall conform to the chemical requirements of table I.

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TABLE I.—*Chemical requirements*

	Class a	Class b	Class c	Class d	Class e
	Percent	*Percent*	*Percent*	*Percent*	*Percent*
Nitric acid content, minimum [1]	(2)	[4] 98.0	(2)	(2)	(2)
Nitrobodies	None	None	None	None	[3] None
Chlorides (as HCl), maximum	0.01	None	0.20	0.01	0.10
Sulfates (as H_2SO_4), maximum	0.01	0.05	.....	0.25	0.20
Oxides of nitrogen (as NO_2), maximum	0.02	0.18	0.50	0.0	.....
Lead salts, maximum	0.01	None	None	0.01	0.10
Ash, maximum	0.01	0.01	0.01	0.01	0.10

[1] See paragraph H-3.
[2] As specified in the contract or order. (See par. H-1).
[3] Not applicable to recovered nitric acid used only in the manufacture of trinitrotoluene, dinitrotoluene or tetryl.
[4] The titration method described in paragraph F-4c(2) shall be used to determine nitric acid content.

F. METHODS OF SAMPLING, INSPECTION, AND TESTS.

F-1. *Size of lots.*—Maximum, 50,000 pounds, unless delivered in tank cars, in which case one tank carload shall constitute a lot. Each lot shall contain acid of one class only.

F-2. *Sampling.*—

F-2a. *Other than carload lots.*—A minimum of 10 percent of the containers in the lot shall be selected by the Government inspector in such a manner as to be representative of the lot. When lots comprise less than 100 containers, either 10 containers or all containers in the lot shall be selected. Sufficient material shall be removed from each selected container by means of a thief to form a primary sample of approximately 1 quart. One-half of each primary sample shall be placed in a glass-stoppered bottle and so labeled that the container from which it was taken can be easily identified. The remaining portions of each primary sample shall be thoroughly mixed and a composite sample of approximately 1 quart shall be placed in a glass-stoppered bottle and labeled to show the name of the material, class, manufacturer, plant, contract or order number, lot number, and number of pounds in the lot. All acceptance tests shall be made on the composite sample representative of the lot.

F-2b. *Carload lots.*—A portion of approximately 1 quart from each tank car shall be removed by lowering a weighted, unstoppered bottle by means of a cord, chain, or rod to the bottom of the tank car shell and immediately withdrawing to the surface. In order to obtain a representative cross section sample, the speed of lowering and withdrawing shall be of uniform rate and so regulated that the bottle shall be just filled as it reaches the surface of the liquid. All samples shall be placed in glass-stoppered bottles labeled to show the name of the material, class, manufacturer, plant, contract or order number, lot number, and number of pounds in the lot. All acceptance tests shall be made on the sample representative of the lot.

F-3. *Inspection.*—Inspection shall be made at the point of delivery unless otherwise specified in the contract or order.

F-4. *Tests.*—The following tests shall be made at a Government laboratory unless otherwise specified in the contract or order.

F-4a. *Color.*—Put into a Nessler tube 100 ml. of a solution containing 0.8 gm. of cobalt chloride ($CoCl_2 6H_2O$), 6.25 gm. of ferric chloride

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and 3.85 ml. of 31 percent hydrochloric acid per liter. Place this tube containing the color standard on a white surface and place beside it a Nessler tube containing 100 ml. of the sample. The acid shall be no darker in color than the standard solution.

F-4b. *Appearance.*—Pour approximately 25 ml. of the thoroughly mixed sample into a clean test tube. Allow to stand for at least 10 minutes. Examine for clarity, sediment, and suspended or separated material.

F-4c. *Nitric acid content.*—Determine the nitric acid content by either the method described in paragraph F-4c(1) or the method described in paragraph F-4c(2) except that class b nitric acid content shall be determined by the method described in paragraph F-4c(2).

F-4c(1). *Nitrometer method.*—

F-4c(1)a. *Standardization of the nitrometer.*—Standardization shall be made by either of the following methods:

F-4c(1)a(1). *Absolute method.*—Assemble the nitrometer (du Pont or equivalent) after thoroughly cleaning and drying all parts. The various parts, with the exception of the reservoir bulbs, shall be completely filled with mercury. Place 25 ml. of 94.5+0.5 percent sulfuric acid in the generating bulb, draw air into the bulb to nearly the level of the lower shoulder by lowering the mercury reservoir and opening both stopcocks. Close both stopcocks and shake vigorously for 3 minutes. Connect the generating bulb to the compensating tube. Draw the dry air from the generating bulb into the compensating tube by adjustment of the two mercury reservoirs, keeping open the stopcock of the measuring tube. Continue the introduction of the air until the mercury in the reading tube is nearly at the 12.50 mark. Seal the compensating tube by means of a small blow pipe flame. Desiccate similarly in the generating bulb another portion of air and transfer this to the reading tube until the mercury in the reading tube, compensating tube, and their mercury reservoirs is at the same level, the mercury in the reading tube being approximately at the 12.50 mark. It is not necessary that these gas volumes be exact or equal. Fill a small U-tube manometer with sulfuric acid and attach to the reading tube. Allow the apparatus to come to constant temperature and then adjust the mercury levels in the reading tube, compensating tube, and their mercury reservoirs so that the air in the reading tube is under atmospheric pressure, as shown by the acid levels in the arms of the manometer tube. Take the reading on the graduated scale of the calibrated reading tube, and at the same time note the temperature and barometric pressure. From these readings calculate the volume of air at 20° C. and 760 millimeters pressure in the reading tube by means of the following formula:

$$V = V' \times \frac{P' \times 293 \times (1 - 0.00018t')}{760 \times (273/T') \times (1 - 0.00018 \times 20)}$$

where

V = volume at 20° C. and 760 millimeter, barometer at 20° C.
V' = volume at the observed temperature (T') and pressure (P')
t' = temperature of the barometer.

The factor 0.00018 represents the correction to be applied for the coefficient of expansion of mercury in the barometer. When V has

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been calculated, adjust the heights of the reading tube, compensating tube, and their reservoirs so that, with the mercury in the reading and compensating tubes on a level, the mercury in the reading tube marks the calculated volume of the air. Paste a strip of paper on the tube so as to mark the height of the mercury in the compensating tube. Take this as the standard volume of air with which every volume of gas to be measured is compared.

NOTE.—The use of dry air tends to form a scum around the reading level of the compensating tube, thus requiring frequent restandardization of the nitrometer. This scum is caused by reaction of oxygen in the air with mercury or caused by impurities. Dry nitrogen eliminates this condition and should be used, if available. A half drop of sulfuric acid will also prevent this scum.

F-4c (1) a (2). *Potassium nitrate method.*—Recrystallize 3 times from 95 percent alcohol a sample of chemically pure grade of potassium nitrate, and grind this to pass through a No. 100 (149 micron) U. S. Standard sieve. After drying at 135° to 150° C. for 2 or 3 hours, weigh a portion of exactly 1 gm. into a small weighing bottle and transfer this portion to the cup of the generating bulb. Wash the potassium nitrate into the generating bulb by means of 8 to 10 portions of 94.5±0.5 percent sulfuric acid free from nitrogen, using a total of 25 ml. of acid. With the lower stopcock of the generating bulb open and the mercury reservoir low enough to maintain a slightly reduced pressure in the generating bulb, shake the sample until most of the gas has been generated. Adjust the mercury reservoir until the mercury drops nearly to the lower shoulder of the generating bulb. Close the lower stopcock and shake the bulb vigorously for 3 minutes. Replace the bulb on the rack, open the lower stopcock, and allow the tube to stand for 5 minutes, the levels in the generating bulb and reservoir being approximately the same; having previously introduced desiccated air into the compensating tube as described in the absolute method of paragraph F-4c(1)a(1). Close the lower stopcock, and shake the generating bulb for an additional minute. Transfer the gas to the reading tube, and adjust the levels of the mercury in the reading and compensating tubes to approximately the same height. Allow the gas to stand for approximately 20 minutes to permit equalization of the temperature. With sulfuric acid U-tube leveling device, make careful adjustment so that the mercury in both tubes is at the same level and that in the reading tube is at the 13.85 mark (the percentage of nitrogen in potassium nitrate). Make a mark on the compensating tube to show the volume occupied by the air equivalent to the volume of nitric oxide gas liberated from exactly 1 gm. of potassium nitrate. This mark is usually made on a strip of gummed paper attached to the compensating tube.

NOTE 1.—In order to avoid any doubt regarding the purity of the potassium nitrate, it is desirable to check the standardization obtained by the use of potassium nitrate by means of the absolute method. If the agreement is within 1 or 2 hundredths of a percent, the potassium nitrate can be considered as of satisfactory quality and used in subsequent periodic standardizations. It has been found by actual experimentation that the solubility of nitric oxide in sulfuric acid of the strength prescribed is so small that no correction need be applied to bring the value in agreement with the mark set by the absolute method.

NOTE 2.—If the nitrometer is standardized by both the absolute and potassium nitrate methods the results may not be in agreement by 0.01 to 0.04

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percent nitrogen due to expansion of the brass barometer scale. Such difference may be removed by applying the brass scale correction corresponding to the temperature. (See par. H-2.)

F-4c(1)b. *Procedure.*—Place approximately 5 ml. of special nitrogen-free sulfuric acid (94.5±0.5 percent) in the cup of the generating bulb of the nitrometer. By means of a tared acid weighing pipette, rapidly introduce a known weight of the sample, of aproximately 0.50 to 0.55 gm. of nitric acid, into the cup, stirring the acid mixture by means of a small glass rod. As soon as the sample has been added, close the stopcocks of the acid pipette, quickly replace the cap on the pipette, and draw the acid into the generating bulb. Use four 5-ml. portions of sulfuric acid to thoroughly wash the sample into the generating bulb, making a total consumption of 25 ml. sulfuric acid used in the test. It is customary to reweigh the pipette with as little delay as possible after the first washing with 5 ml. of sulfuric acid to minimize any evaporation losses or absorption of moisture from the air. When the sample has been completely drawn into the generating bulb, close the upper stopcock, allow the lower stopcock to remain open, and adjust the mercury reservoir so as to give a slightly reduced pressure in the generating bulb. Shake the bulb gently until most of the gas has been generated. Adjust the mercury reservoir so that the mercury in the generating bulb drops nearly to the lower shoulder, and close the lower stopcock. Shake the bulb vigorously for 3 minutes. Replace the bulb on the rack with the lower stopcock open and adjust the mercury reservoir until the mercury in the generating bulb is approximately the same height as the reservoir. This adjustment is for the purpose of bringing the pressure inside of the generating bulb to approximately one atmosphere, so that the solubility of nitric oxide gas in the sulfuric acid will not vary too widely. Close the lower stopcock and shake the bulb vigorously for an additional minute. Transfer the gas to the measuring tube and adjust the levels of the mercury in the compensating tube and measuring tube to approximately the same height. Allow the gas to stand for approximately 20 minutes in order to permit equalization of the temperature of gas in the two tubes, adjust the mercury levels closely with a leveling device and read the burette. Calculate percentage of nitric acid as follows:

$$\text{Percent } HNO_3 = \frac{4.4987}{W}$$

where

V = reading of gas burette of the nitrometer
W = weight of sample.

F-4c(2). *Titration method.*—Prepare glass bulbs from ordinary soft glass tubing by blowing so as to have a pear or globular shape, of suitable capacity, with a capillary stem several inches long. Cover the mouth of the bottle containing the sample with a thin piece of sheet lead which is perforated with two small holes far enough apart to permit the simultaneous filling of two bulbs. Weigh two bulbs separately and transfer a portion of the sample to each by gently heating the bulb over a flame and quickly inserting the tip of

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the capillary through the lead cover into the acid. Permit sufficient acid to neutralize from 80 to 90 ml. of N/3 sodium hydroxide solution to be drawn into the bulb. Withdraw the capillary stem from the bottle and quickly wipe it several times with a clean cloth to remove acid from the outer wall. Seal the tip of the capillary, using a flame and in this manner remove any trace of acid not removed by wiping. After cooling, weigh the bulb. Hold the bulb stem upward and submerge it in approximately 100 ml. of neutral distilled water contained in a specimen jar or heavy-walled beaker, until it rests on the bottom of the vessel. By means of a glass rod break off the stem at a point approximately ½ inch from the bulb proper. When the bulb turns over and floats on the water, allow the acid to flow out through the broken stem for 5 minutes and then break the bulb against the side or bottom of the vessel and crush the bulb and stem. Titrate the solution with N/3 sodium hydroxide solution, using phenolphthalein indicator, as soon as possible in order to avoid loss of nitric acid. Apply any necessary temperature and calibration corrections to the burette reading and calculate the percentage of the total nitric acid as follows:

$$\text{Percent } HNO_3 = \frac{6.302VN}{W}$$

where

V = ml. of sodium hydroxide used
N = normality of sodium hydroxide used
W = weight of sample.

F-4d. *Nitrobodies.*—Place approximately 50 gm. of a saturated solution of sodium hydroxide in a tall 250 ml. beaker. Weigh out approximately 25 gm. of the well-agitated sample, pour into 100 ml. of water, and cool the mixture. Hold the 250-ml. beaker in an inclined position and carefully pour the acid-water mixture down the side of the beaker so that it rests upon the layer formed by the sodium hydroxide solution. Note if a red ring, indicating the presence of a nitro compound, is formed at the junction of the two solutions.

F-4e. *Chlorides (as HCl).*—Neutralize a weighed portion of approximately 3 gm. of the sample with approximately N/2 sodium hydroxide. Add 2 or 3 drops of potassium chromate solution (60 to 70 gm K_2CrO_4 per 100 ml. water). Titrate the solution with approximately N/10 silver nitrate solution until the faintest blood-red tinge is imparted to the liquid. Calculate the chloride content of the sample as percentage of hydrochloric acid as follows:

$$\text{Percent HCl} = \frac{3.647VN}{W}$$

where

V = ml. of silver nitrate solution used
N = normality of silver nitrate solution
W = weight of sample.

F-4f. *Sulfates (as H_2SO_4).*—In a platinum or silica dish evaporate a weighed portion of approximately 50 gm. of the sample until nearly dry. Add 20 ml. of distilled water and transfer to a 250-ml. beaker. Wash out the dish with five 20-ml. portions of distilled water. Boil the solution in the beaker and slowly add 10 ml. of a hot 2-percent solution of barium chloride. Continue to heat for approximately 10 minutes.

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Set the solution aside to cool. Filter through a tared filtering crucible. Wash the precipitate with five successive portions of distilled water, or until the filtrate gives no test for chlorides with silver nitrate. Dry the crucible for 3 hours at 135° C., cool in a desiccator, and weigh. Calculate the sulfate present as percentage of sulfuric acid as follows:

$$\text{Percent } H_2SO_4 = \frac{42.02A}{W}$$

where

A = weight of precipitate
W = weight of sample.

F-4g. *Oxides of nitrogen* (*as* NO_2).—Weigh out carefully approximately 5 gm. of the sample. Transfer this to a 300-ml. Erlenmeyer flask containing 75 ml. distilled water slightly acidified with sulfuric acid. Titrate with a standardized N/10 potassium permanganate solution. Add this solution until a permanent pink coloration is observed. Calculate the oxides of nitrogen as NO_2 as follows:

$$\text{Percent oxides of nitrogen} = \frac{4.601VN}{W}$$

where

V = ml. of $KMnO_4$ used
N = normality of the $KMnO_4$
W = weight of sample.

F-4h. *Lead salts.*—Mix the sample thoroughly and weigh out in a 250-ml. beaker a portion of approximately 100 gm. Add 2 ml. of a 5-percent solution of sulfuric acid. Evaporate nearly to dryness. Dilute the residue with 20 ml. of distilled water. Add 50 ml. of ethyl alcohol. Stir the solution and set aside for 2 hours to allow the precipitate of lead sulphate to settle. Filter through a tared filtering crucible, wash free of acid with ethyl alcohol, dry for 2 hours at 100° C., cool in a desiccator and weigh. Calculate the percentage of lead in the sample as follows:

$$\text{Percentage of lead} = \frac{68.32A}{W}$$

where

A = weight of precipitate
W = weight of sample.

F-4i. *Ash.*—Evaporate in a tared platinum or silica dish a weighed portion of approximately 50 gm. of the sample, evaporating slowly at first on a steam bath or hot-plate. When no liquid remains, heat the dish to a dull red color with a blast burner or a muffle furnace for at least 15 minutes. Cool the dish in a desiccator and weigh. Calculate the increase in weight as the percentage of ash.

F-5. *Retests.*—If the composite sample representative of the lot fails to pass the inspection tests, the manufacturer shall have the option of having an analysis of each primary sample made at his own expense. The manufacturer may then remove or replace defective portions of the lot represented by the primary samples which fail to meet the requirements and submit the lot for acceptance, provided that the markings on the containers are such that complete removal or replacement of defective portions of the lot can be made to the satisfaction of the Government inspector.

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G. PACKAGING, PACKING, AND MARKING FOR SHIPMENT.

G-1. *Packing.*—Unless otherwise specified, nitric acid shall be delivered in tank cars or standard commercial containers as specified (see par. H-1), so constructed and protected as to conform to applicable regulations of the Interstate Commerce Commission, and insure acceptance by common or other carriers for safe transportation, at the lowest rate, to the point of delivery.

G-2. *Marking.*—Unless otherwise specified, each container shall be plainly marked with the following information completed:

MATERIAL _____
PERCENT HNO_3 _____
CLASS _____
SPECIFICATION NO. _____
QUANTITY _____
CONTRACTOR _____
MANUFACTURER _____
CONTRACT NO. _____
GROSS WEIGHT _____
DATE _____
LOT NO. _____

In addition, shipments for the Army shall be marked in accordance with the requirements of U. S. Army Specification 100-2; for the Navy, in accordance with the requirements of the latest issue of the Navy Shipment Marking Handbook.

H. NOTES.

H-1. Requests, requisitions, schedules, and contracts or orders should specify the following:

Title, number, and date of specification.
Class desired and nitric acid content.
Shipping container desired.

H-2. An explanation of the procedure for making the brass scale correction will be found in Lange's Handbook of Chemistry, page 1368, 1937 edition.

H-3. The term "nitric acid content" as used in this specification differs from the true nitric acid content since the titration method is not corrected for other acidic impurities or oxides of nitrogen and the nitrometer method is not corrected for oxides of nitrogen. The basis for procurement of nitric acid will therefore conform to previous practice. If it is desired to determine true nitric acid content, the calculation of paragraph F-4c(1)b would be as follows where the nitrometer is used:

$$\text{True percentage nitric acid} = \frac{4.498\,V}{W} - (1.368B)$$

where

V = reading of gas burette of the nitrometer
B = percent NO_2 in the sample (see par. F-g)
W = weight of sample.

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Using the titration method, the calculation of paragraph F-4c(2) would be as follows:

$$\text{True percentage nitric acid} = \frac{6.302VN}{W} - (1.368B + 1.728C + 1.285D)$$

where

V = ml. of sodium hydroxide used
N = normality of sodium hydroxide used
B = percent NO_2 in the sample (see par. F-4g)
C = percent HCl in the sample (see par. F-4e)
D = percent H_2SO_4 in the sample (see par. F-4f)
W = weight of sample.

H-4. Copies of Navy Shipment Marking Handbook may be obtained upon application to the Bureau of Supplies and Accounts, Navy Department, Washington 25, D. C.

H-5. Copies of Joint Army-Navy specifications (required for Army purchases) and U. S. Army specifications may be obtained, as indicated in the "Index of United States Army and Federal Specifications Used by the War Department." Copies of this Index may be obtained from the Superintendent of Documents, Government Printing Office, Washington 25, D. C. Agencies within the War Department will obtain copies of Joint Army-Navy and United States Army specifications through established War Department channels. Both the title and identifying symbol number should be stipulated when requesting copies of specifications.

H-6. Copies of Joint Army-Navy specifications (required for Nav purchases) and Navy Department specifications may be obtained upon application to the Bureau of Supplies and Accounts, Navy Department, Washington 25, D. C., except that naval activities should make application to the Supply Officer in Command, Naval Supply Depot, Bayonne, N. J. Both the title and identifying symbol number should be stipulated when requesting copies of specifications.

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