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JOINT ARMY-NAVY SPECIFICATION

ACID, SULFURIC, AND OLEUM

Army Number	Navy Number
50-11-1B	51A25

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
50-11-1A	----------------
25 March 1938	

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. GRADES.

B-1. This specification covers the following grades of sulfuric acid and oleum as specified in the contract or order (see par. H-2).

Grade I
Grade II

C. MATERIAL AND WORKMANSHIP.

C-1. See section E.

D. GENERAL REQUIREMENTS.

D-1. See section E.

E. DETAIL REQUIREMENTS.

E-1. Sulfuric acid shall conform to the chemical requirements shown in Table I.

TABLE I.—*Chemical requirements*

Grade	Nitrobodies	Total acidity as H_2SO_4	Suspended matter (max.)	Ash (max.)	Arsenic (max.)
		Percent	*Percent*	*Percent*	*Percent*
I	None	As specified ±0.5	0.05	0.50	0.01
II	None	As specified ±0.5	.10	.65	.025

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[1] Applicable only to Navy purchases.

F. METHODS OF SAMPLING, INSPECTION, AND TESTS.

F-1. *Size of lots.*—A lot shall consist of a maximum of 100,000 pounds, except when shipment is made in tank cars, the capacity of the tank car shall be made the lot size for inspection purposes.

F-2. *Sampling.*—In case shipment is made in containers, 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. The sample shall be taken from each container or tank car by means of a thief and transferred as rapidly as possible to a small-neck bottle of the ground glass stopper type. The top, middle and bottom levels of the container or tank car shall be represented in the sample. If preferred, the sample may be taken by lowering the above type bottle, properly secured to the bottom of the container or tank car. The stopper shall then be removed and the bottle withdrawn through the entire height of the liquid at a uniform rate, arising at the surface of the liquid just short of full. (See pars. H-6 and H-7).

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. *Nitrobodies.*—Place approximately 50 gm of a saturated solution (containing 40-50 percent by weight) 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. Hold the 250 ml beaker containing the sodium hydroxide solution 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. (See par. H-5.)

F-4b. *Total acidity.*—

F-4b(1). *Test.*—Transfer an accurately weighed portion of approximately 1.5 gm of the sample to a 400 ml glass stoppered bottle containing approximately 200 ml distilled water and 2 drops of methyl red indicator solution. For nonfuming acids, transfer is conveniently made by use of a Lunge pipette. For fuming acids, thin walled glass bulbs, each equipped with a capillary stem several inches long, are used and transfer is made as follows: Cover the mouth of the bottle containing the sample with a thin lead sheet. Warm a tared glass bulb over a nonluminous flame and then quickly insert the capillary stem through a small hole in the lead sheet into the sample. After the bulb is filled, withdraw it from the bottle and quickly seal the tip in the flame. Wipe any acid from the sealed tip and weigh the filled bulb. Shake well to absorb all fumes, cool, remove the stopper, and wash any liquid on the stopper and neck into the bottle with distilled water. Crush the fragments of the capillary with a glass rod so that the entire sample is mixed with water. Titrate with N/2 NaOH solution, adding 2 more drops of indicator near the end point. Run a blank on the distilled water, titrating the same quantity as used in the test to the same end point and correct the titer accordingly.

F-4b(2). *Calculation of total acidity (nonfuming acid or oleum).*—

F-4b(2)a. *Total acidity as percent H_2SO_4.*—

$$X=\frac{(A-B)\ N\times 4.904}{W}$$

where:

X=total acidity as percent H_2SO_4
A=ml of NaOH used for sample
B=ml of NaOH used for blank
N=normality of NaOH
W=weight of sample.

F-4b(2)b. *Total acidity as percent SO_3.*—

$$Y=0.8163X$$

where:

Y=total acidity as percent SO_3
X=total acidity as percent H_2SO_4

F-4b(3). *Calculation of percent actual H_2SO_4.*—

$$Z=5.444\ (100-Y)$$

where:

Z=percent actual H_2SO_4
Y=total acidity as percent SO_3

F-4b(4). *Calculation of percent free SO_3 in oleum.*—

$$\text{Percent free } SO_3=0.8163\ (X-Z)$$

where:

X=total acidity as percent H_2SO_4
Z=percent actual H_2SO_4

F-4c. *Suspended matter.*—Filter a portion of approximately 40 gm of the sample through a tared filtering crucible. Pour the portion of the sample filtered from a previously weighed acid weighing bottle, and weigh this after filtration in order to determine the weight of acid filtered. Wash the mud or suspended material with at least five 20 ml portions of anhydrous alcohol. The anhydrous alcohol used may be prepared by allowing 95 percent alcohol, denatured with 0.5 percent of benzene, to stand over anhydrous copper sulphate over night and filtering the alcohol before use. Dry the crucible for 8 hours at 125°C.±2°C., cool in a desiccator, and weigh. Calculate the increase in weight of the crucible as percentage of suspended matter.

F-4d. *Ash.*—Place the filtrate obtained from the determination of suspended matter (see par. F-4c), in a tared platinum, silica or other suitable type dish. Heat slowly with a Bunsen flame under a hood, until the evolution of fumes has ceased. Heat to a dull red for 2 or 3 minutes. Cool in a desiccator and weigh. Heat for a further short period to determine if a constant weight has been obtained. Calculate the increase in weight of the dish as percentage of ash in the sample. If the suspended matter is found to be 0.01 percent or less, an alternate time saving determination of ash may be made using 40 gm of the original sample instead of the filtrate as above and correcting the result for the percent of suspended matter found.

F-4e. *Arsenic.*—

F-4e(1). Weigh out a portion of approximately 5 gm of the sample and pour carefully into 15 ml of distilled water. Boil the solution for approximately 15 minutes to expel any hydrogen sulfide or sulfur dioxide. If nitric acid is present the heating must be continued until fumes of sulfur trioxide appear. This heating has been found not to expel any arsenic compounds. Cool the liquid and dilute to approximately 200 ml with distilled water to which a mixture of 2 ml of ferric ammonium sulfate solution (see par. F-4e(2)) with 0.5 ml of stannous chloride solution (see par. F-4e(3)) has been added. Put the solution in an 8-ounce bottle as shown on Figure 1, and add 25 to 40 pieces of arsenic-free zinc (see par. F-4e(4)). Place the three connected tubes in position immediately as shown on the figure. Shake the bottle gently and allow to stand for approximately 40 minutes. The temperature should be approximately 40° C. Free the arsine which is evolved from most of the hydrogen sulfide which may accompany it, by passing through lead acetate paper (see par. F-4e(5)) contained in a tube leading from the neck of the bottle. Remove all traces of hydrogen sulfide by passing through a second tube containing glass wool moistened with lead acetate solution. Absorb any arsine formed by passing through a third tube containing a test strip of mercuric chloride paper (see par. F-4e(6)). Remove the test paper, dip into molten paraffin, and compare it with standard stains (see par. F-4e(7)). Calculate the percentage of arsenic as As_2O_3 by means of the following formula:

$$\text{Percent Arsenic as } As_2O_3 = \frac{100A}{W}$$

where:

A=weight of As_2O_3 as estimated from stain
W=weight of sample.

Determine the colorations produced by the chemicals themselves by running blanks. To do this take 5 ml of arsenic-free sulfuric acid, place in the bottle and make the determination, using the same quantities of reagents as are regularly employed in the test. (See par. H-5.)

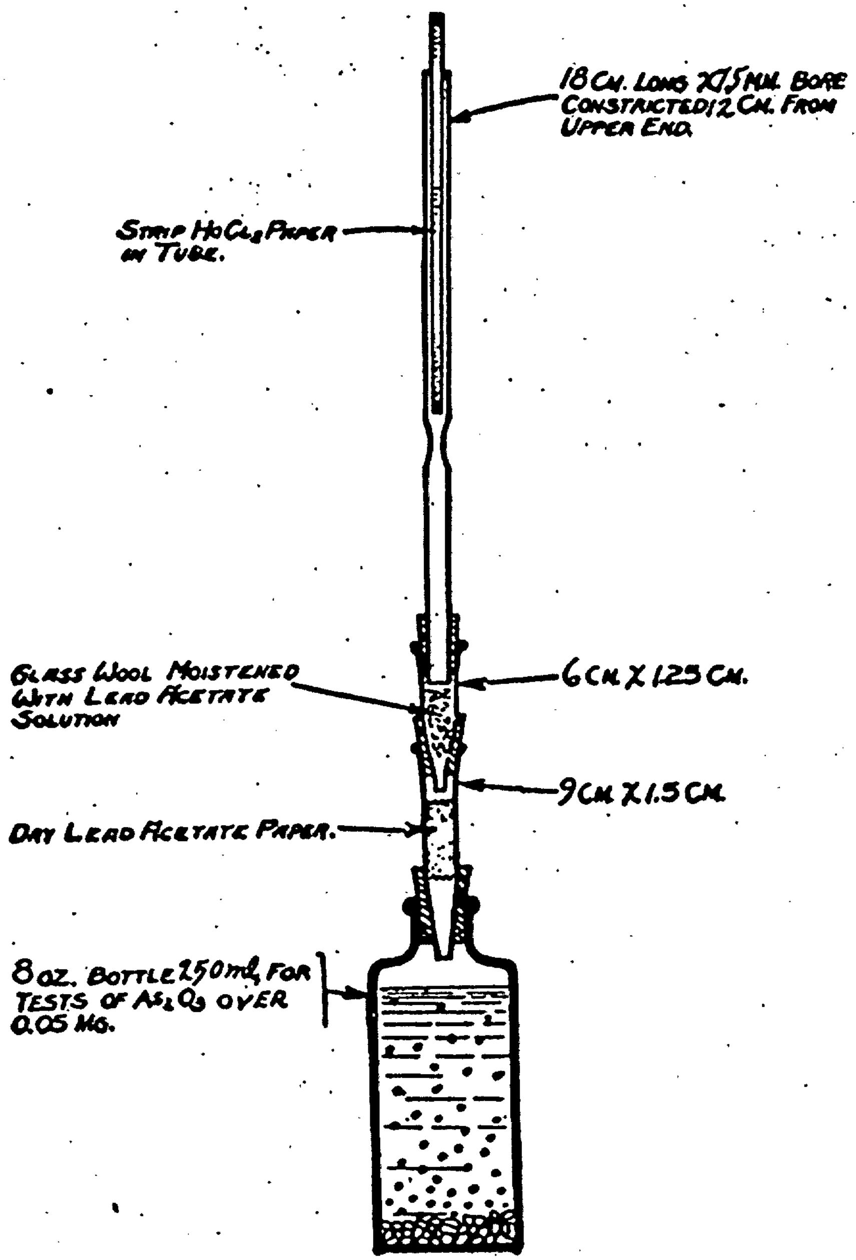
F-4e(2). *Ferric ammonium sulfate solution.*—Dilute one volume of arsenic-free sulfuric acid with four volumes of distilled water. Add 10 gm of sodium chloride to each 100 ml of diluted acid. Dissolve 10 ml of this solution and 84 gm of ferric ammonium sulfate in distilled water and make up to 1 liter. Two ml of this solution contains approximately 0.1 gm Fe_2O_3.

F-4e(3). *Stannous chloride solution.*—Dissolve 80 gm of stannous chloride in 100 ml of arsenic-free hydrochloric acid having a specific gravity of 1.2. Arsenic-free hydrochloric acid can be prepared by distilling 500 ml of commercial hydrochloric acid to which 10 gm of potassium chlorate have been added.

F-4e(4). *Arsenic-free zinc.*—Use shot having a granulation of approximately 3 to 6 mesh. Treat the zinc with C. P. hydrochloric acid until the surface of the zinc becomes clean and dull. Wash the shot and keep it covered with distilled water.

F-4e(5). *Lead acetate paper.*—Prepare a 1-percent solution of C. P. lead acetate adding sufficient acetic acid to clarify the solution. Soak filter paper in the solution of lead acetate, and dry. Cut the paper into strips 7 by 5 cm.

F-4e(6). *Mercuric chloride paper.*—Dip several sheets of acid-washed ashless filter paper approximately 10 by 10 inches into a 3.5-



APPARATUS FOR ARSENIC DETERMINATION.

FIGURE 1.

percent solution of mercuric chloride. Place each sheet on a clean glass plate and pass a squeegee roller gently over the impregnated paper to remove most of the reagent. Place the paper on a clean dry cloth and dry. Remove from the oven as soon as dry, since mercuric chloride is slightly volatile at 100° C. and trim off ½ inch of the outer edge. Cut the paper into strips 13 cm by 5 mm and store in bottles with tight-fitting stoppers. Prepare standards with each batch of paper. Do not use paper with a white deposit of mercuric chloride.

F-4e(7). *Standard arsenic stains.*—Produce standard stains on the mercuric chloride test paper by submitting a known amount of arsenic trioxide to the regular procedure of the test. Prepare a standard arsenic solution by dissolving 1 gm of resublimed arsenic trioxide in 25 ml of the 20 percent sodium hydroxide solution and neutralizing with dilute sulfuric acid. Dilute the solution to 1 liter in a measuring flask with distilled water to which 10 ml of arsenic-free sulfuric acid, specific gravity 1.84 has been added. Transfer 10 ml of this solution to a measuring flask and dilute to 1 liter with distilled water to which 10 ml of arsenic-free sulfuric acid, specific gravity 1.84, has been added. One ml of this solution contains 0.01 mg of arsenic trioxide. Add 2, 5, 10, 20, 30, 40, 50 ml portions of this solution to approximately 5 gm portions of arsenic-free sulfuric acid and test these samples in the manner specified in par. F-4e(1). The mercuric chloride strips will have 0.02, 0.05, 0.10, 0.20, 0.30, 0.40, 0.50 mg of arsenic trioxide, respectively. Dip these standard colored strips in molten paraffin (free from water) and mount them on a sheet of white paper, folded back to form a cylinder. Place this paper cylinder in a stoppered glass tube containing phosphorus pentoxide. Keep the strips dry and in a dark place in order to prevent fading.

F-5. *Retests.*—If the official sample representative of the lot fails to meet the requirements of this specification, the manufacturer shall have the option of having an analysis made on a sample from each separate container. The expense of such analysis shall be borne by the manufacturer. The manufacturer may then remove or replace defective portions of the lot represented by the primary samples which fail to meet the requirements of this specification and submit the lot for acceptance, provided that the markings on the container are such that complete removal or replacement of defective portions of the lot can be made to the satisfaction of the Government inspector.

G. PACKAGING, PACKING, AND MARKING FOR SHIPMENT.

G-1. *Packing.*—Sulfuric acid and oleum shall be loaded for shipment in accordance with Interstate Commerce Commission regulations in tank cars, carboys, or steel drums as specified in the contract or order (see par. H-2) or in other suitable containers so constructed as to 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 ------------------------------------
GRADE --
GROSS WEIGHT ------------------------------
NET WEIGHT ---------------------------------

PERCENT H_2SO_4 ________________________________
SPECIFIC GRAVITY ________________________________
MANUFACTURER ________________________________
CONTRACTOR ________________________________
CONTRACT NO. ________________________________
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 contain the title of the specification, the number and date.

H-2. Requests, requisitions, schedules and contracts or order should specify the grade of acid, and type of container desired (see pars. B-1 and G-1).

H-3. *Uses.*—Grade I material covered by this specification is intended for use in mixture with nitric acid in the manufacture of various explosives, in various sulfonating processes, and for other chemical processes. The term oleum, as used in this specification, refers to anhydrous sulfuric acid containing an excess of sulfuric anhydride (SO_3). Grade II material covered by this specification is intended for use in the manufacture of nitric acid and thionyl chloride and for special uses.

H-4. The sulfuric acid covered by this specification is not adapted for use in storage batteries or as a pickling acid. For these types, see Navy Department Specifications 51A2 and 51A6.

H-5. Pouring of oleum into water is a dangerous procedure due to the large heat of solution. Instead of using water as specified in paragraphs F-4a and F-4e (dilutions), a better method would be to pour the oleum into cool dilute (1:1) C. P. sulfuric acid on which a blank has been run to insure the absence of nitrobodies and arsenic.

H-6. Care must be taken to seal the inspection samples from the outside air at all times, as sulfuric acid and oleum are hygroscopic.

H-7. Tank cars shall not be emptied into Government storage tanks until the analysis to determine compliance with the requirements of this specification has been made.

H-8. 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-9. Copies of Joint Army-Navy specifications (required for Navy 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.

Notice.—When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

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