INCH-POUND
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MILITARY STANDARD

PROPELLANTS, SOLID:

SAMPLING, EXAMINATION AND TESTING

AMSC N/A

FSC 1376

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NUMERICAL INDEX OF TEST METHOD (Cont'd)

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GROUP 800

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804.1	Quickness and Force Measurement of Propellant (Alternate Closed Bomb Method)

1. SCOPE

1.1 Purpose. This standard describes the general methods of sampling, examining, and testing solid propellants.

1.2 Application. The test methods contained in this standard shall apply to the testing of solid propellants for conformance to the chemical and physical requirements of the applicable propellant specifications. In the event of conflict between these methods and those in the applicable propellant specifications, the latter shall take precedence.

2. APPLICABLE DOCUMENTS

2.1 Government documents.

2.1.1 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 listed in the issue of the Department of Defense Index of Specifications and Standards (DODISS) and supplement thereto, cited in the solicitation (see 6.2).

SPECIFICATIONS

FEDERAL

L-T-790	- Tube, Nonmetallic, Polyvinyl Chloride (PVC), Flexible (For Laboratory and Medical Use)
RR-P-54	- Pan, Aluminum Alloy

MILITARY

MIL-D-204	- Dinitroluene for Use in Explosives
MIL-D-218	- Dibutyl Phthalate, Technical
MIL-N-244	- Nitrocellulose
MIL-N-246	- Nitroglycerin
MIL-E-255	- Ethyl Centralite (Carbamite)
MIL-E-463	- Ethyl Alcohol (For Ordnance Use)
JAN-A-465	- Acid, Acetic (For Ordnance Use)
MIL-N-494	- Nitroguanidine (Picrite)
MIL-A-2550	- Ammunition, General Specification For
MIL-N-3399	- 2-Nitrodiphenylamine

STANDARDS

MILITARY

MIL-STD-12	- Abbreviations for Use on Drawings, and in Specifications, Standards and Technical Documents
MIL-STD-962	- Outline of Forms and Instructions for the Preparation of Military Standards Military Handbooks
MS36548	- Bottle, Solution
MIL-STD-45662	- Calibration System Requirements

(Unless otherwise indicated, copies of federal and military specifications, standards, and handbooks are available from the Naval Publications and Forms Center, (ATTN: NPODS), 5801 Tabor Avenue, Philadelphia, PA 19120-5099.)

2.2 Non Government publications. The following documents form a part of this document to the extent specified herein. Unless otherwise specified, the issues of the documents which are DOD adopted are those listed in the issue of the DODISS cited in the solicitation. Unless otherwise specified, the issues of documents not listed in the DODISS are the issues of the documents cited in the solicitation (see 6.2).

AMERICAN SOCIETY FOR TESTING AND MATERIALS (ASTM)

ASTM D 1193	- Reagent Water, Specification for
ASTM D 2015	- Gross Calorific Value of Solid Fuel by the Adiabatic by the Adiabatic Bomb Calorimeter, Test for
ASTM E 11	- Wire-Cloth Sieves for Testing Purposes, Specification for
ASTM E 203	- Water Using Karl Fischer Reagent, Test for (DOD Adopted)
ASTM E 323	- Perforated-Plate Sieves for Testing Purposes, Specification for
ASTM E 380	- Metric Practice, Standard for
ASTM E 438	- Glasses in Laboratory Apparatus, Specification for
ASTM E 694	- Volumetric Ware, Specification for

(Application for copies should be addressed to the American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103- 1187.)

AMERICAN CHEMICAL SOCIETY (ACS)

Reagent Chemicals

(Application for copies should be addressed to American Chemical Society, 1155 Sixteenth Street, NW, Washington, DC 20036)

2.3 Order of precedence. In the event of a conflict between the text of this document and the references cited herein, 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. DEFINITIONS

3.1 Definitions. Not applicable.

3.2 Abbreviations. Abbreviations shall be in accordance with MIL-STD-12.

4. GENERAL REQUIREMENTS

4.1 Sampling procedures.

4.1.1 Sample selection. Representative samples from each propellant lot shall be selected as specified in applicable propellant specifications. The following conditions shall be in effect:

a. Exercise extreme cleanliness in handling propellant samples.

b. Where moisture has been added to the propellantin the blending tower, the sample may not be taken sooner than 48 hours after the time of packing.

c. All samples are to be taken at the same time.

d. Exercise all safety precautions for handling chemical and energetic materials.

e. Handling and disposal of samples shall follow all environmental regulations.

4.1.2 Surveillance samples. Samples for surveillance tests shall be selected and forwarded to the appropriate agency in accordance with the detail specification.

4.2 Packing and marking.

4.2.1 Packing. Samples shall be transferred to approved airtight containers, and the containers shall be sealed immediately.

4.2.2 Marking. Each propellant sample container shall be labeled with the following information where applicable:

a. Complete propellant designation and specification number the propellant was manufactured to.

b. Lot number.

c. Batch number.

d. Grain number.

e. Weight of the lot.

f. Manufacturer's name and plant designation.

g. Contract number.

h. Date loaded.

i. Motor number.

j. Date sampled.

4.2.3 Sample container examination. The sample container shall be examined, before testing the propellant, to see that it is not broken, unstoppered, or otherwise damaged, and that it is labeled correctly. The contents of damaged or improperly labeled containers shall be discarded, and the condition reported to the government inspector or other proper official.

5. DETAILED REQUIREMENTS

5.1 Test and solution methods. Test methods included in this standard shall describe the examination and test procedures, including methods of analyses, for solid propellants. Solution methods included in this standard shall describe the direction for preparing the standard and indicator solutions that are required for these tests.

5.1.1 Tentative test methods. Tentative test methods included in this standard shall be in accordance with MIL-STD-962.

5.1.2 Modifications. Written permission from the technical agency identified by the applicable specification, and the contracting officer shall be obtained before using any modification of the procedures contained in this standard.

5.2 Numbering system. The numbering system shall be in accordance with MIL-STD-962. Each tests as well as each procedure for preparing the special solutions is considered as a separate method and is assigned an individual method number.

5.2.1 Method groups. Methods shall be arranged in groups according to type of test or type of solution. These groups shall be identified numerically by hundreds as follows:

Group 100 General Test Methods

Group 200 Quantitative Methods for Organic Ingredients

Group 300 Quantitative Methods for Inorganic Ingredients

Group 400 Stability Tests

Group 500 Physical Test Methods

Group 600 Standard Solutions

Group 700 Indicator Solutions

Group 800 Special Test Methods

5.2.2 Basic numbers. Method numbers in each group shall be arranged in subgroups, according to the ingredient or property to be determined, such as 201, 202, 203, and so on. Differences in the method of determination shall be differentiated by the addition of a tenths decimal to the subgroup numbers to form basic numbers, such as 201.1, 201.2, and 201.3.

5.2.3 Revision numbers. Revision numbers shall be assigned to basic numbers when changes are made in the method to improve it or to give additional details that will increase the accuracy or precision of the test results. Revision numbers shall appear as a second tenths decimal to the subgroup number, such as 201.1.2, which denotes the second revision of Method 201.1. Changes in a method which significantly alter the method of testing or the end result of the test shall be considered grounds for assigning a new basic number.

5.2.4 Numbering of tentative test methods. Tentative test methods shall be numbered by the same system as described above for standard test methods. In addition to the number, the capital letter "T" shall be prefixed to the number in accordance with MIL-STD-962.

5.3 Test equipment.

5.3.1 Glassware. This shall include equipment used for containers, reaction vessels, and volumetric measurement, and may be fabricated from plastic or ceramic as well as glass. The types of glasses commonly used to manufacture laboratory glass apparatus are specified in ASTM E 438. Borosilicate glass, Type I, Class A, shall be used wherever possible, unless a glass with other properties is required for special applications. The sizes of glassware given in the methods are only advisory and substitution may be made at the convenience of the analyst. In cases where volumetric measurements are involved, changes in size must not affect the concentrations of the compounds being determined or of standard solutions being prepared. Volumetric ware should conform to the specification requirements of ASTM E 694 for Class A ware to preclude the necessity for calibration.

5.3.2 Test sieves. Standard sieves for testing purposes shall conform to the requirements of ASTM E 11 and ASTM E 323 as applicable.

5.3.3 Instrumentation. This includes chromatographs, spectrometers, polarographs and other instruments used for quantitative measurements. Instruments of the same type but of different model or manufacturer may be used, provided they have the capability of producing data of the required accuracy and precision.

5.3.4 Calibration of test equipment. The accuracy of test instruments, apparatus and equipment used to control or monitor test conditions or parameters, and to measure and record test data shall conform with the calibration systems requirements of MIL-STD-45662, to the satisfaction of the user or contracting activity.

5.4 Reagents.

5.4.1 Chemicals. Wherever possible, the chemicals used in testing should conform to the specification requirements of the American Chemical Society (ACS) as described in the latest edition of their publication "Reagent Chemicals". Chemicals, including solvents, used for instrumental analysis should be of the reagent grade applicable to each test method. Reagents not covered by ACS specifications should be of the best grade available that are applicable to each test method, and shall not be used if interfering impurities are present.

5.4.2 Water. Water for general analytical use shall conform to the specification requirements of the ACS for reagent water as described in their latest edition of "Reagent Chemicals." Throughout the methods, the term "water", "distilled water", or "deionized water" means water suitable for the individual test. A suitable grade of water for some tests may be selected from the types of reagent waters specified in ASTM D 1193. Special grades of reagent water are also available for different methods of instrumental analysis from suppliers of reagent chemicals.

5.5 Drying.

5.5.1 Desiccants. In methods requiring desiccants, any suitable desiccant may be used although an indicating type is preferred.

5.5.2 Ovens. In methods requiring ovens, the steam heated type is preferred. However, all types should be fitted with temperature limit controls.

5.6 Test data. Use of the metric system and conversion of data to metric units shall be in accordance with ASTM E 380. Use of symbols and abbreviations for metric units of measurement shall also be in accordance with ASTM E 380.

5.7 Material handling. This standard covers sampling and testing of chemical, toxic or explosive materials which are potentially hazardous to personnel. Accordingly, it is emphasized that all applicable safety rules, regulations (including environmental regulations) and procedures shall be followed in handling and processing these materials.

5.8 Testing safety. Laboratories performing test(s) contained in this standard shall review in detail each method for safety practices needed before performing test. Complete procedures (including all safety equipment needed) to perform the test safely shall be documented in a Stnadard Operating Procedure (SOP) written by the laboratory performing the test. The SOP shall be approved by the laboratory performing the test and the local safety department. SOP(s) shall include emergency procedures for malfunctions and unexpected or uncontrolled reactions that might occur.

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 intented use of this standard is, to describe the sampling, examining and testing, for solid propellant.

6.2 Subject term (key word) listing.

Composition Analysis
Indicator Solution
Propellant Testing

6.3 Changes from previous issue. Marginal notations are not used in this revision to identify changes with respect to the previous issue due to the extensiveness of the changes.

METHOD 101.1.2

MOISTURE AND VOLATILES (VACUUM OVEN METHOD)

1. SCOPE

1.1 This method is used for determining the moisture and volatile solvent content of single-base propellants on the basis of loss of weight on heating at 55° C under vacuum. This method is not suitable for large grain propellants.

2. SPECIMEN

2.1 The specimen shall consist of approximately 10 g of the propellant, weighed to within 0.2 mg.

3. APPARATUS

3.1 Weighing dish with tight-fitting cover; diameter, 60 mm; depth, 30 mm, minimum.

3.2 Vacuum oven.

3.3 Desiccator containing an indicating desicant.

4. PROCEDURE

4.1 Place the specimen in a tared weighing dish, and heat it for 6 hours in the vacuum oven at a temperature of 55 ± 2° C and a pressure (absolute) of 80 ± 10 mm of mercury.

4.2 Cool the specimen to room temperature in the desiccator. Cover and reweigh.

4.3 **Calculation.**

$$\text{Percent of moisture and volatiles (by weight)} = \frac{W_1 - W_2}{W_1} \times 100$$

Where:

W_1 = Weight of specimen before drying, g.

W_2 = Weight of specimen after drying, g.

METHOD 101.2.2

MOISTURE AND VOLATILES (OVEN METHOD)

1. SCOPE

1.1 This method is used for determining the moisture and volatile solvent content of propellant on the basis of loss of weight on heating at atmospheric pressure at 100° C. It is particularly applicable to double and triple base propellants and many of their ingredients.

2. SPECIMEN

2.1 The specimen shall consist of 4 to 5 g of propellant, weighed to within 0.2 mg.

NOTE: The specimen shall be either whole grains or cut grains. Ground propellant shall not be used.

3. APPARATUS

3.1 Erlenmeyer flask (with ground glass stopper): base diameter, 40mm; height, 60 mm; neck opening diameter, 15mm; capacity, 25 ml.

3.2 Oven, steam heated. Forced draft type is recommended.

3.3 Desiccator containing an indicating desiccant.

4. PROCEDURE

4.1 Place the specimen in a tared erlenmeyer flask.

4.2 With the stopper removed, heat the flask and contents for two (2) hours in the oven at 100 ± 2° C, and at atmospheric pressure.

4.3 At the end of two (2) hours, place the stopper on the flask, cool in a desiccator and reweigh.

4.4 **Calculation:**

$$\text{Percent of moisture and volatiles (by weight).} = \frac{W_1 - W_2}{W_1} \times 100$$

Where:

W_1 = Weight of specimen before drying, g.

W_2 = Weight of specimen after drying, g.

METHOD 101.3.2

MOISTURE (DESICCATION METHOD)

1. SCOPE

1.1 This method is used for determining the moisture content of solventless propellants on the basis of loss of weight in a desiccated atmosphere.

2. SPECIMEN

2.1 The specimen shall consist of approximately 10g of the propellant, weighed to within 0.2 mg.

NOTE: The specimen shall be either whole grains or cut grains. Ground propellant shall not be used.

3. APPARATUS

3.1 Weighing dish with tight-fitting cover: diameter, 60 mm; depth, 30 mm minimum.

3.2 Desiccator, 250 mm diameter, or equivalent volume, filled nearly to plate with a desiccant.

NOTE: A maximum of 6 weighing dishes may be in the desiccator at any one time.

4. PROCEDURE

4.1 Place the specimen in a tared weighing dish and weigh the dish, contents, and cover.

4.2 Remove the cover and place the dish in the desiccator.

4.3 Weigh the covered dish and contents at 24 hour intervals until the loss in weight between weighings does not exceed one milligram.

NOTE: Constant weight is normally attained within 48 to 72 hours.

4.4 **Calculation:**

$$\text{Percent of moisture (by weight)} = \frac{W_1 - W_2}{W_1} \times 100$$

W_1 = Weight of specimen before drying, g.

W_2 = Weight of specimen after drying, g.

METHOD 101.4

MOISTURE (ELECTROLYTIC HYGROMETER METHOD)

1. SCOPE

1.1 This method is used for determining the moisture content of small grain or flake propellants. Single, double or triple base propellants can be used. The principle of the method is measurement of the current required for electrolysis of water that has been volatilized from the specimen. Volatile compounds such as alcohols, amines and ammonia may also be electrolyzed. Compounds that polymerize may eventually inactivate the cell.

2. SPECIMEN

2.1 The specimen shall consist of 0.2 - 0.6 g of propellant weighed to the nearest 0.2 mg.

3. APPARATUS

3.1 Solids moisture analyzer. (Consolidated Electrodynamics Corporation, 360 Sierra Madre Villa, Pasadena, CA, or equivalent.) See Figure 1.

4. MATERIALS

4.1 Nitrogen, extra-dry grade, in a cylinder with a pressure regulator to supply gas at 5 psig. For calibration of the instrument, use accurately weighed samples of either 0.05 to 0.1g of sodium tartrate dihydrate or 0.3 to 0.5 g of potassium tartrate hemihydrate. Dry at 150° C until the counter indicates that all moisture has been removed. The sodium salt should give a moisture content of 15.66 ± 0.05 percent while the potassium salt should give a moisture content of 3.83 ± 0.02 percent.

5. PROCEDURE

5.1 Prepare the instrument for operation according to the manufacturer's directions.

5.2 Place the weighed specimen in the sample boat, insert into the oven with the aid of tweezers provided with the instrument and close the oven.

CAUTION: These steps must be done as rapidly as possible in order to minimize changes in moisture content.

5.3 Turn the temperature and timer controls to the settings required in the applicable specification. When the test is completed, read the weight of the moisture shown on the dial and convert to grams.

5.4 **Calculation:**

$$\text{Percent of water} = \frac{100A}{W}$$

Where: A = Weight of water shown on dial, g.
W = Weight of specimen, g.

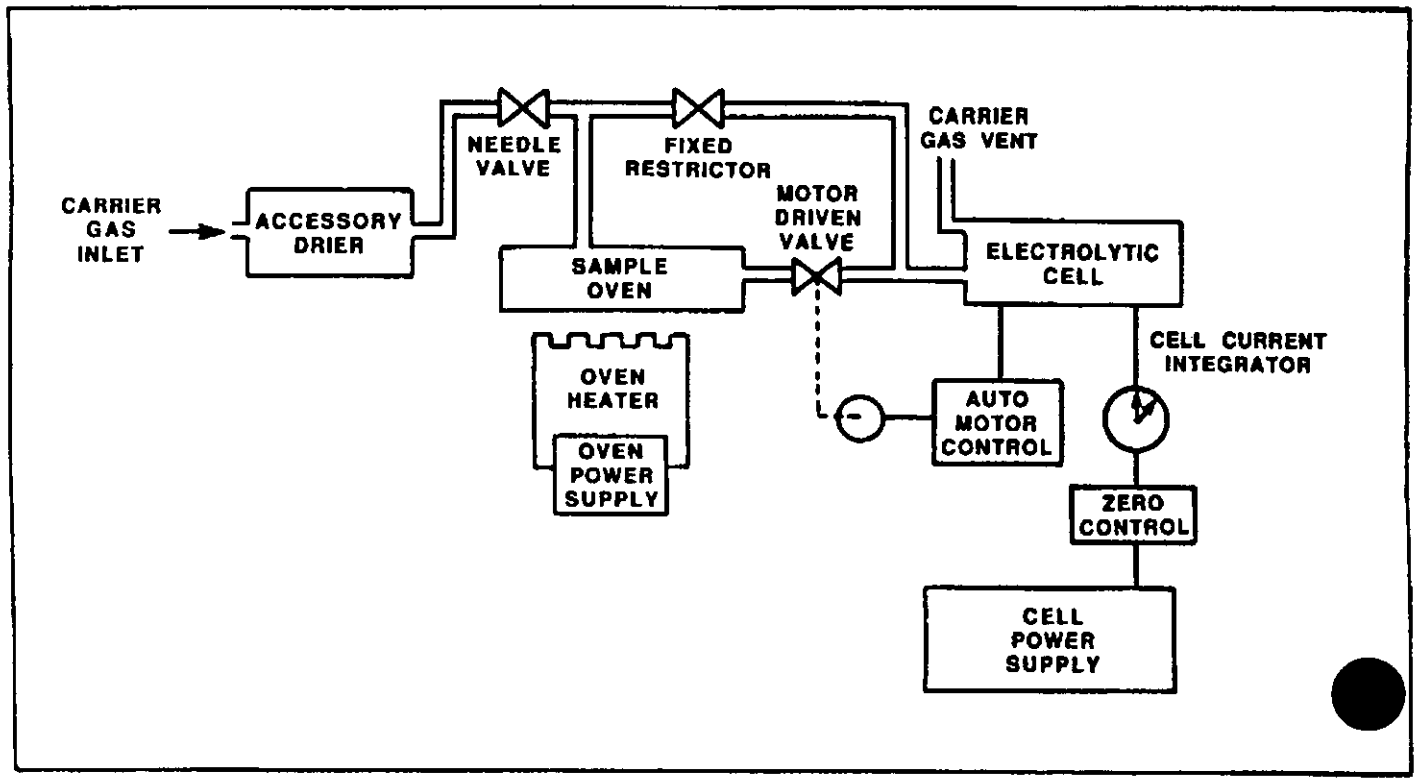


Figure 1. *Block diagram of Electrolytic Hygrometer.*

METHOD 101.5

MOISTURE (KARL FISCHER METHOD)

1. SCOPE

1.1 This method describes the materials, equipment, and procedures for determining the percentage of moisture in casting solvent powder, ingredients, and propellant by the Karl Fischer (KF) method (manual and semi-automatic titrations). This procedure is designed for water contents of less than 1 percent.

Principle. Dry organic solvents are used to dissolve the sample which is then titrated with Karl Fischer reagent.

1.2 Limitations and interferences. The Karl Fischer reagent is composed of pyridine, sulfur dioxide, and iodine dissolved in either methyl alcohol or ethylene glycol monomethyl ether. Substances which react with any of these components will interfere. For example, Karl Fischer reagent will react with aldehydes or ketones in the presence of methyl alcohol. Other examples of interfering substances are oxidizing agents such as peroxides, cupric and ferric salts; reducing agents such as sodium thiosulfate, sodium arsenite, stannous salts and hydrazine; and oxygenated compounds such as metal hydroxides and oxides, bicarbonates and carbonates, and boric acid.

2. SPECIMEN

2.1 Care must be taken that all samples are protected from gain or loss of water before testing. Propellant samples must be reduced in size to about 1/8-inch cubes to readily dissolve in the solvent. The mode in which this is done is left to the discretion of the installation as it is a function of sample stability and general safety.

3. APPARATUS

3.1 Aquameter (Beckman Instruments, Inc., Model KF2 or KF3 or equivalent. Equivalents are described in ASTM E 203).

3.2 Titration Flask, protected from atmosphere with provisions for electrodes and burets.

3.3 Magnetic Stirrer.

3.4 Buret, 20ml capacity, 0.05 ml divisions.

4. MATERIAL

4.1 Karl Fischer Reagent or equivalent, single solution stabilized, methyl cellosolve as solvent (e.g. catalog No. So-K-3 of Fisher Scientific Co.) diluted to about 2 mg/ml titer with methyl cellosolve or a commercial diluent (e.g. catalog No. So-K-5 of Fisher Scientific Co.).

4.2 Solvents. Pyridine-Methanol 1:1; mix equal volumes of reagent quality of each solvent containing less than 0.10 percent water. This must be maintained in a protected system.

4.3 Standards.

a. Sodium Tartrate Dihydrate, ACS grade containing 15.66 percent water.

b. Water - distilled or equivalent.

5. **CALIBRATION AND STANDARDIZATION.**

5.1 The water equivalent (mg H_2O/ml KF reagent) is obtained by titrating weighed amounts of a standard with the KF reagent as follows:

5.1.1 Add about 50-100 ml of the solvent to the titration flask. Maintain a dry nitrogen purge in free volume of container. Using the procedure described in the instrument instruction manual or the routine procedure for the manual titrating assembly, titrate to a potentiometric end point which remains for 30 seconds. By means of a Lunge pipette, syringe, or equivalent, add one drop of water to the titration flask. Record to the tenth of a milligram the weight of water added, fill the burette again, and titrate to a 30 second potentiometric end point. Alternately, 200 mg of sodium tartrate dihydrate may be added instead of water and may be titrated in like manner. Record the volume of reagent used for the titration.

5.1.2 The water equivalent is obtained by dividing the number of milliliters used into the weight of water added. If sodium tartrate dihydrate was added, the calculation is as follows:

$$\text{Water Equivalent (mg } H^2O\text{/ml KF reagent)} = \frac{(\text{mg sodium tartrate dihydrate})(0.1566)}{\text{ml of KF reagent required}}$$

5.1.3 The titer should be about 2 mg/ml. If too high or low adjust concentration and restandardize.

5.1.4 Frequent standardization, is necessary as the reagent is unstable.

6. **PROCEDURE.**

6.1 Accurately weigh a sample large enough to give a minimum titration of 3 ml (5-7 ml is desirable).

6.2 Add 50-100 ml of the solvent used to the titration flask and titrate to a 30 second end point.

6.3 Maintain a dry nitrogen purge over free volume of the flask.

6.4 Add the sample, stir until in solution and titrate to a 30 second potentiometric end point.

NOTE: Some samples require about 1 hour to dissolve. Flasks must be well protected to insure water is not absorbed from atmosphere.

6.5 **Calculation:**

$$\text{Percent water} = \frac{AF}{1000W} \times 100$$

Where:

A = ml Karl Fischer Reagent used to titrate sample.
F = Karl Fischer titer in mg water/ml reagent.
W = Sample weight in grams.

METHOD 101.6.1

MOISTURE (GAS CHROMATOGRAPHY METHOD)

1. SCOPE

1.1 This method may be used for the determination of moisture in single or double base ball powder.

1.2 The moisture is extracted from the propellant with methanol injected into a column, and then the moisture peak is compared with a standard.

2. SPECIMEN

2.1 The sample shall consist of 3.0 grams of propellant.

3. APPARATUS

3.1 Hewlett Packard 3752 with Dual Thermal Conductivity detector or its equivalent interfaced to a PEP-II computer (or other means of peak measurement).

3.2 10 µl syringe.

3.3 Magnetic stirrer and stirring bar.

3.4 60 ml bottle and stopper.

3.5 100 ml volumetric flask.

3.6 Calibration loop.

4. REAGENTS AND STANDARDS

4.1 Methanol - Anhydrous

4.2 Distilled Water

5. CALIBRATION AND STANDARDIZATION

5.1 Gas Chromatograph Conditions: Advisory

Injection Port Temp	-	150° C
Detector Temp	-	150° C
TC Current	-	200 mA
Column Temp	-	125° C
Carrier Gas	-	Helium
Flow Rate	-	40ml/min
Column	-	6 x 1/4 in stainless steel packed with 80/100 mesh Porapak Q or equivalent

5.2 Preparation of Standard.

a. Weigh 0.09 g of water (H_2O) to the nearest 0.1 mg into a 100 ml volumetric flask. Fill to volume with anhydrous methanol.

b. Inject 5 µl into the appropriate column.

c. Identify the water peak (see Figure 1) and measure the area.

d. Run a solvent blank.

6. **PROCEDURE**

6.1 Weigh 3.00 grams to the nearest 0.1 mg of propellant sample and place in 60 ml bottle.

6.2 To this bottle add 20 ml of anhydrous methanol.

6.3 Place 1 magnetic stirrer in the 60 ml bottle and stopper.

6.4 Stir for 30 minutes.

6.5 Inject 5 µl into the appropriate column.

6.6 Identify the water peak (Figure 1) and measure the area.

7. **CALCULATION**

$$\% \text{ Moisture} = \frac{A \times B \times 100}{C \times D} - \text{Blank}$$

Where:

A = grams of distilled water in 20 ml standard

B = area of water peak in sample

C = area of water peak in standard

D = weight of propellant in sample

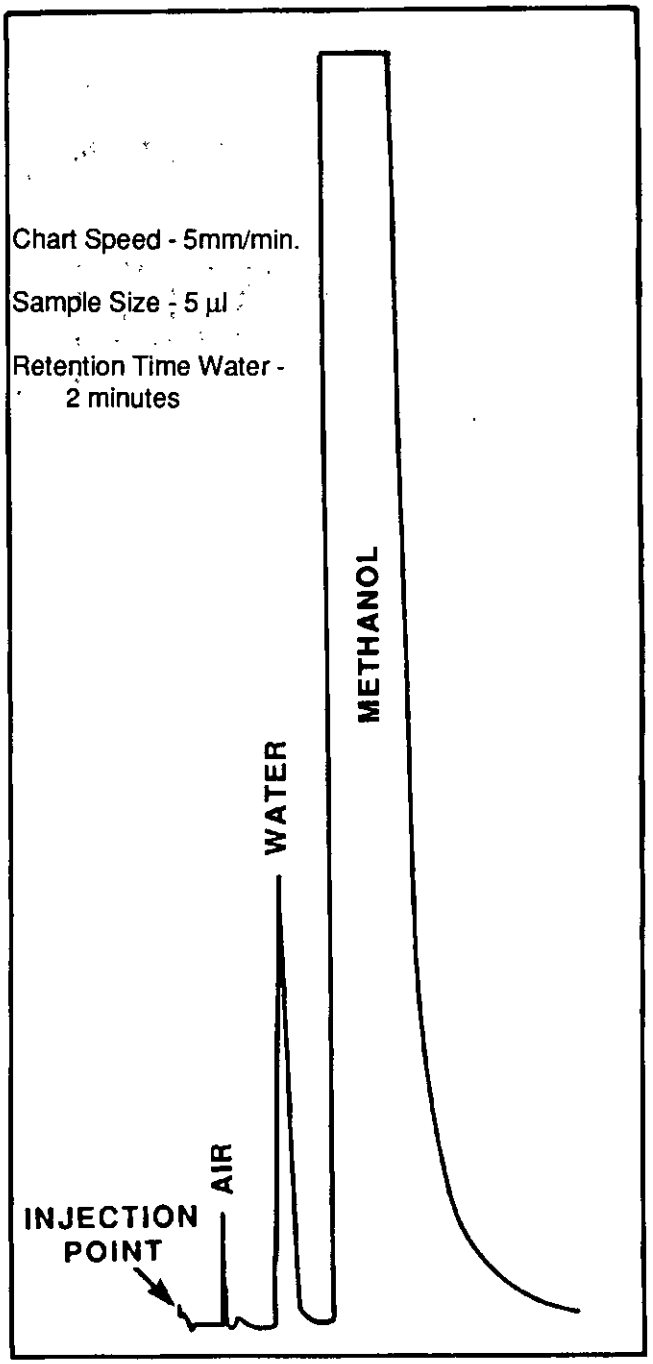


Figure 1. *Chromatogram of Moisture Analysis.*

METHOD 102.1.3

MOISTURE (DISTILLATION METHOD)

1. SCOPE

1.1 This method is used for the determination of moisture content of small grain or cannon propellant. It is based on distillation of the moisture with a solvent that is immiscible with and heavier than water. This method is not suitable for propellants containing less than 0.2 percent moisture. The presence of hydrated compounds may cause high results. The presence of finely divided aluminum may cause a reaction with the chlorinated solvent and, in such cases, tests should be made to demonstrate compatability of propellant and solvent.

2. SPECIMEN

2.1 The specimen shall consist of approximately 100g of the propellant (40-50g for rolled powder paste) preferably as received. Weigh the specimen to within 10 mg.

NOTE: If the size of the propellant as received would unnecessarily prolong the time required for the determination, the specimen may be cut as specified in Method 509.3. The cutting, weighing, and transferring to the stoppered balloon flask must be done rapidly to minimize the change in moisture content through exposure to the atmosphere.

3. APPARATUS

3.1 Boiling flask, round bottom, 500 ml.

3.2 Condenser (Allihn type, or equivalent), 400 mm long (min).

3.3 Drying tube containing indicating calcium sulfate desiccant.

3.4 Moisture tube (Figure 1) (Kontes Glass Co., Cat. NO. K-75500 or equivalent).

CAUTION: If ground glass joints are used, be sure that no propellant is in the joints before making the connection.

3.5 Hot plate (preferably steam or hot water heated.)

4. MATERIALS

4.1 Solvent: Trichloroethylene

5. PROCEDURE

5.1 Place the specimen in the 500 mL boiling flask, and add 200 ml of the solvent.

5.2 Fill the graduated portion of the moisture tube with the solvent, and attach the tube to the flask. Attach the moisture tube to a dry condenser, and connect the drying tube containing the desiccant to the top of the condenser to keep out atmospheric moisture.

5.3 Heat the flask so that the distillate falls from the condenser at the rate of two to three drops per second. Distillation shall be continued for at least the minimum time indicated in Table 1.

5.4 Remove the source of heat, and wash the water from the condenser into the moisture tube with 10 ml portions of the solvent until the volume of the water layer in the measuring tube becomes constant, and no water droplets are observed in the condenser.

NOTE: A total of 30 to 50 ml of the solvent is usually required.

5.5 One milliliter of water may be added to facilitate meniscus separation. If a milliliter of water is added, a corresponding adjustment should be made to the readings.

NOTE: To facilitate the reading of the menisci the surface of moisture tube and the condenser may be made water repellant by treatment with a suitable silicone preparation, such as Desicote (Beckman Instruments Inc.). If water repellant material is used, read the point of contact of the top meniscus with the wall of the tube and the center of the lower meniscus.

5.6 Determine the difference in the readings, and record the difference as the volume of water in the specimen.

5.7 For each lot of solvent run a blank using exactly 2 ml of water and apply any necessary corrections to the sample.

5.8 Considering one milliliter of water as equal to one gram, calculate (by weight) the percentage of moisture in the specimen.

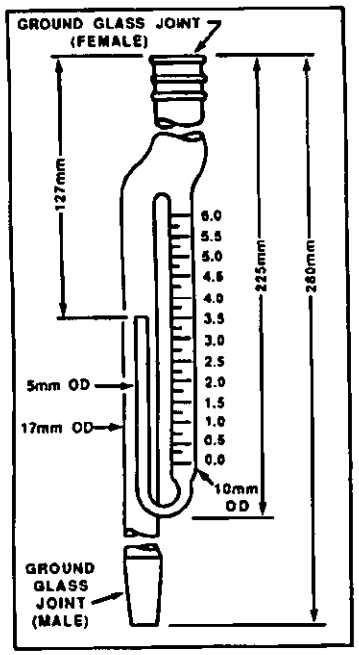


Figure 1. *Moisture tube.*

$$\text{Percent water} = \frac{A - B}{W} \times 100$$

Where: A = Upper meniscus, ml
B = Lower meniscus, ml
W = Weight of specimen, g

Table I. *Distillation times*

Propellant web size, inch	Grain condition	Distillation time, hours
Less than 0.025	Whole	3
0.025 to 0.040	Whole	5
0.041 to 0.060	Whole	10
0.061 to 0.090	Whole	16
	Sliced	6
Over 0.090	Whole	24
	Sliced	8

METHOD 103.1.3

TOTAL VOLATILES (DISH AND CONE METHOD)

1. SCOPE

1.1 This method is used for determining the moisture and volatile solvent content of sheet propellant (such as M-8 propellant) and other propellants where the chief constituent evolved is moisture. The method is generally not applicable to propellants not in sheet form.

NOTE: The cone is intended to prevent loss of nitroglycerin by condensing any that has volatilized.

2. SPECIMEN

2.1 The specimen shall consist of approximately 10g of the propellant, weighed to within 0.2 mg.

3. APPARATUS

3.1 Aluminum dish with glass cone (Figure 1).

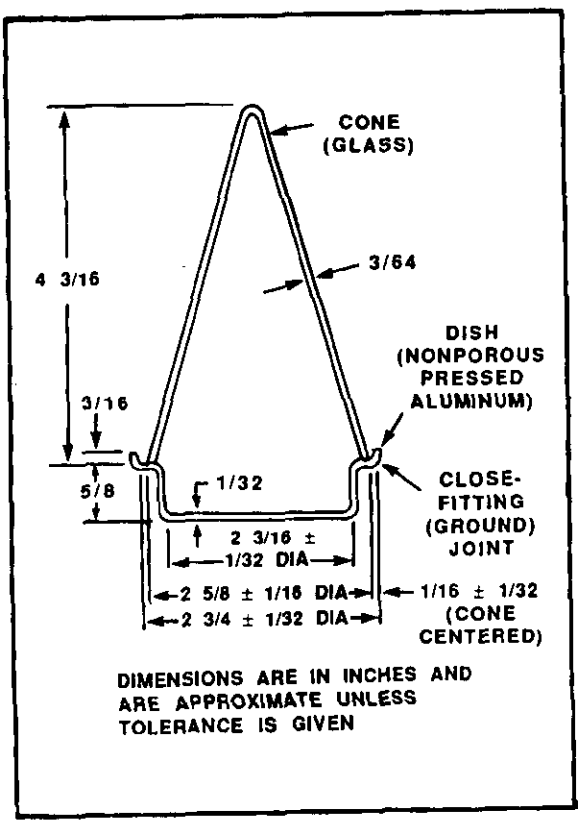


Figure 1. *Dish and Cone.*

3.2 Closed steam plate (surface temperature 90 ± 5° C) or steam heated forced draft type oven maintained at 90 ± 5° C.

3.3 Desiccator containing an indicating calcium sulfate desiccant (Drierite).

4. PROCEDURE

4.1 Prepare the specimen as described in Method 509.3.

4.2 Weigh the dish and cone (para 3.1), place the specimen in the dish, and cover it with the cone. Reweigh the dish, cone and specimen.

4.3 Heat the specimen for 2 hours.

4.4 At the end of 2 hours, place the covered dish in the desiccator, and cool to room temperature.

4.5 Determine the loss in weight, and calculate the loss as the percentage of volatiles in the propellant specimen.

4.6 **Calculation:**

$$\text{Percent of volatiles (by weight)} = \frac{W_1 - W_2}{W_1} \times 100$$

W_1 = Weight of specimen before drying, g.

W_2 = Weight of specimen after drying, g.

METHOD 103.3.3

TOTAL VOLATILES (SOLUTION-EVACUATION METHOD)

1. SCOPE

1.1 This method is used for determining the total volatiles content of either single base, double base, or triple base propellants.

2. SPECIMEN

2.1 The specimen shall consist of approximately 2 g of the propellant prepared with minimum atmospheric exposure in order to reduce loss of volatiles.

3. APPARATUS

3.1 Solution tubes (figure 1).

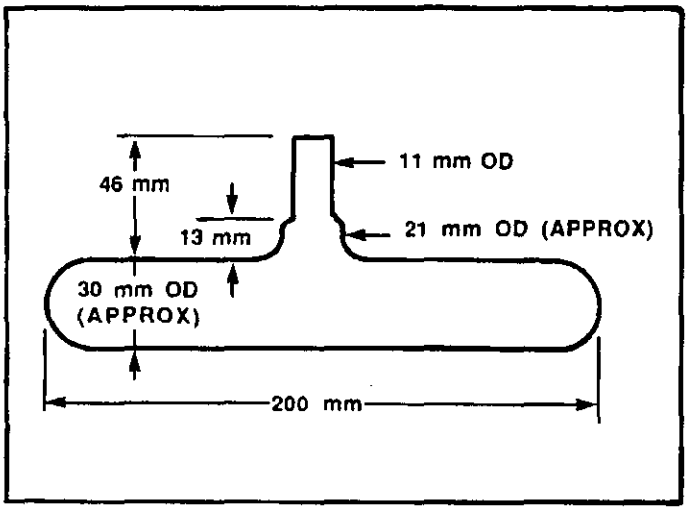


Figure 1. *Solution tube.*

3.2 Steel balls, 5/16-inch diameter.

3.3 Tubing, rubber, 5/16-inch bore, 3/16-inch wall.

3.4 Vacuum line assembly (figure 2).

3.5 Wire screen tray (figure 3).

3.6 Protective drying tubes (figure 4), containing indicating desiccant.

3.7 Vacuum pump capable of maintaining a pressure (absolute) of at least 5 mm of mercury.

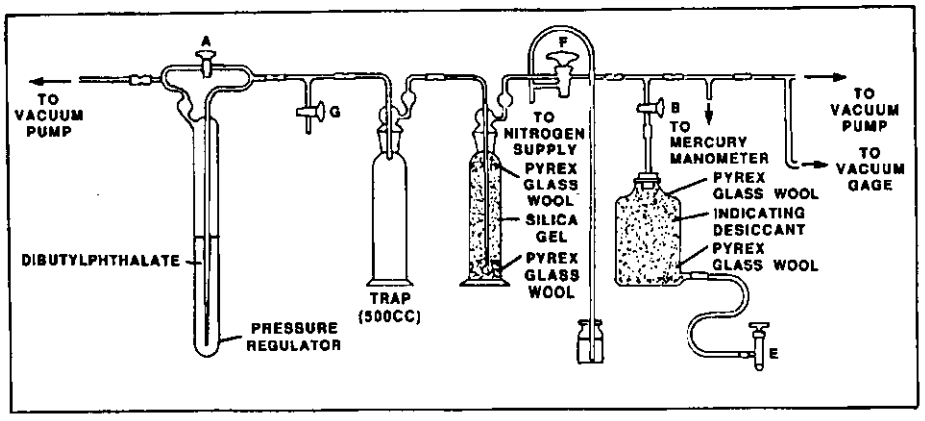


Figure 2. *Vacuum line assembly*

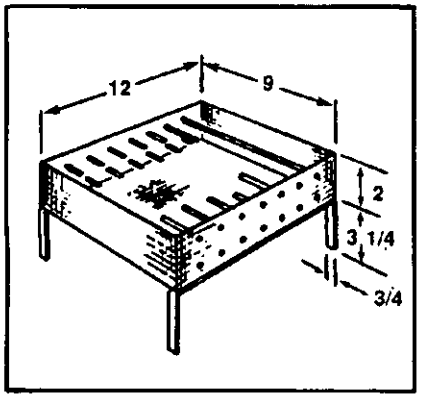


Figure 3. *Wire screen tray.*

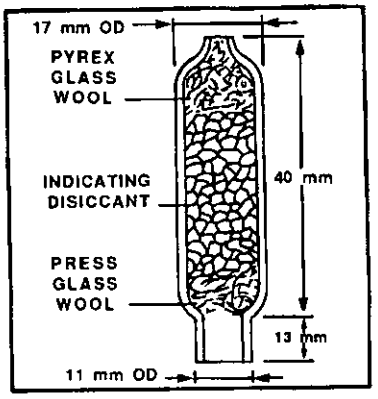


Figure 4. *Protective drying tube.*

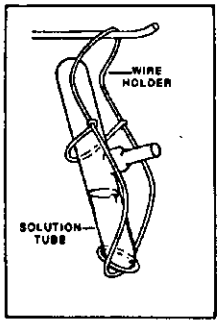


Figure 5. *Solution tube holder.*

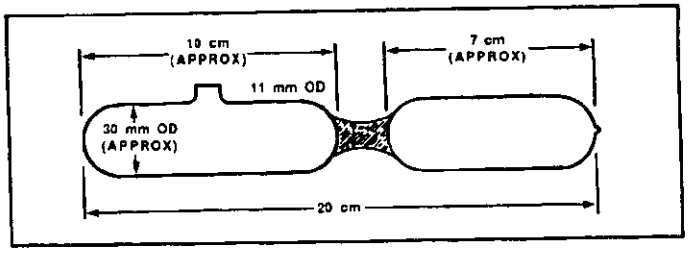


Figure 6. *Counterpoise*

3.8 Wire holders for solution tubes (figure 5).

3.9 Counterpoise (figure 6).

3.10 Pyrex glass wool, or equivalent.

3.11 Oven containing a rocking device with evacuation manifolds (Central Scientific Co., Cat. No. 95105-A modified by addition of a safety latch, or equivalent).

4. **MATERIAL**

4.1 Dibutylphthalate, prepared as follows:

a. Dissolve 1 g of diphenylamine in 100 ml of hot dibutylphthalate.

b. Pour this solution into 500 ml of dibutylphthalate; stir vigorously.

c. Add dibutylphthalate to make 1 liter; stir vigorously.

d. Heat the solution for 2 hours at 145 to 150° C while bubbling dry air through it.

NOTE: The heating ensures that the solution will lose less than 10 mg in 50 ml during the solution-evacuation procedure, and may be omitted if previous tests show that it is unnecessary.

5. **PROCEDURE**

5.1 Prepare at least four solution tubes (two for the specimens, two for blanks) as follows:

a. Place 10 clean, dry steel balls and 50 ml of the dibutylphthalate reagent into each solution tube.

b. Clean the inlet of each solution tube with absorbent cotton held by steel forceps, and insert a wad (approximately 0.2g) of pyrex glass wool, using the forceps.

CAUTION: Position the glass wool at such a point in the tube that it will not fall into the tube and will not touch the cork stopper that is to be inserted subsequently.

5.2 Precondition the solution tubes as follows:

a. Using 5-cm pieces of the rubber tubing, connect the solution tubes to the manifold of the rocking device in the oven placing the tubes containing the blanks at opposite ends of the manifold. Plug or otherwise close unused manifold connections.

NOTE: New connecting tubing should be precleaned by boiling in a 5-percent solution of sodium hydroxide for 10 to 15 minutes, followed by a thorough rinsing and drying at 100° C.

b. Connect the vacuum line assembly (figure 2) to the manifold of the rocking device and to the vacuum pump.

c. On the vacuum line assembly (figure 2) open stopcock A; close stopcocks B, and G and needle valve E; and set stopcock F to connect the manifold to the vacuum pump.

d. Adjust the oven temperature to 85 ± 2° C, start the rocking motor, and turn on the vacuum pump. Evacuate the tubes at a pressure of 5 mm or less for 1 1/2 hours.

e. At the end of 1 1/2 hours, stop the vacuum pump and rocking motor, and slowly open stopcock B. Then slowly admit dry air to the solution tubes by gradually opening needle valve E.

CAUTION: If the air is admitted too rapidly, wads of pyrex wool may be drawn into the solution tubes.

f. Wearing gloves, remove the solution tubes from the oven, leaving the connecting tubing attached to the tubes, and place them in the wire-screen tray (figure 3). Immediately attach a protective drying tube (figure 4) to the inlet of each solution tube to prevent the admission of atmospheric moisture. Allow the tubes to cool to room temperature (approximately 45 minutes).

. When the solution tubes have cooled, remove the protective drying tubes and connecting tubing and insert No. 1 cork stoppers.

CAUTION: The solution tubes must be kept tightly corked hereafter to prevent absorption of atmospheric moisture by the very dry dibutylphthalate, except during evacuation in the oven and while being weighed.

5.3 Clean and remove electrostatic charges from the solution tubes by wiping them with a wet towel and drying them with a clean lint-free cloth (without rubbing). Place the tubes in the wire-screen tray, cover them with a cloth to protect them from dust, and allow them to stand near the balance for at least 30 minutes to attain equilibrium with the moisture content of the air.

CAUTION: After the tubes have been conditioned they should not be touched with the fingers until they have been weighed. When handling the tubes, grip the inlet tube only, after covering the inlet with a tissue paper.

5.4 Cut sheet and large grain propellant as described in Method 509.3 para. 4.1 and 4.3, respectively. Use small grain propellant as received. Take at least two specimens.

5.5 Remove the cork stoppers from two of the prepared solution tubes, and take out the wads of glass wool, using forceps. Add one of the accurately weighed specimens of the propellant to each, using a small metal funnel (9-mm OD outlet) to prevent adherence of the propellant to the walls of the tube. Reinsert the wads of glass wool.

NOTE: Propellants soften and tend to gelantinize when added to dibutylphthalate solution. Therefore, the solution tubes should be rocked as soon as possible after the addition so that the propellant does not adhere to the walls of the tube and prevent the steel balls from moving.

5.6 Support the tubes in wire holders (figure 5), and weigh each solution tube (including blanks) to within 1 mg, using the counterpoise (figure 6) on the right-hand side of the balance.

NOTE: The counterpoise approximates the weight, volume, and exterior surface area of a solution tube containing 10 steel balls and 50 ml of dibutylphthalate. It should be kept standing near the balance, covered with a cloth to protect it from dust. Do not wipe the counterpoise; wiping will disturb its equilibrium with the prevailing temperature, pressure, and humidity.

5.7 Shake the tubes, if necessary to loosen any grains of propellant adhering to the walls of the tubes, and connect the tubes to the manifold of the rocking device in the oven. Plug all unused manifold connections.

5.8 As soon as all the solution tubes have been placed in the oven (maintained at 85 ± 2° C) start the rocking motor.

5.9 On the vacuum line assembly (figure 2), check that stopcock F is turned so that nitrogen does not enter the vacuum line. Then open the valve on the nitrogen cylinder to allow a slow stream of nitrogen to escape through the mercury trap.

5.10 Close stopcocks B and G, and needle valve E, and open stopcock A. Then turn on the vacuum pump, and evacuate the solution tubes to a pressure of 1 mm of mercury or less.

5.11 When the pressure has stabilized at 1 mm of mercury, turn stopcock F to admit nitrogen slowly to the solution tubes.

CAUTION: Admit nitrogen slowly so that the glass wool or other foreign matter from the manifold or tubing is not carried into the solution tubes.

5.12 Evacuate the tubes again, and refill with nitrogen by operating stopcock F.

5.13 Turn stopcock F so that the nitrogen inlet is connected to the oven manifolds, open stopcock G to admit air to the vacuum line, and turn off the vacuum pump. Close stopcock G.

5.14 Allow the solution tubes to rock until sample has completely broken up or a maximum of 15 hours at a temperature of 85 ± 2° C.

5.15 At the end of 15 hours, check that stopcock G is closed and turn stopcock F to connect the oven manifolds to the vacuum pump. Open stopcock B and needle valve E, and start the vacuum pump.

5.16 While observing the solution tubes through the glass door of the oven, gradually close needle valve E to lower the pressure in the vacuum line assembly, being careful not to close the valve so fast that the solution in the tubes boils violently.

CAUTION: Take approximately 10 minutes to lower the pressure to 5 mm of mercury. If the solution boils violently, there is danger of mechanical loss of the solution, and a resulting error in the determination.

5.17 When the pressure reaches 5 mm, or less, close stopcocks A and B, and continue the evacuation for 2 hours at 85 ± 2° C, and at a pressure of 5 mm of mercury or less.

5.18 At the end of two (2) hours, stop the rocking motor, open stopcocks A and B, very slowly open needle valve E to admit dry air, and stop the vacuum pump.

CAUTION: If stopcock A is not open when the pump is shut off, the dibutylphthalate solution will flow out of the pressure regulator.

5.19 Remove the solution tubes from the oven, and cool them, as described in paragraphs 5.2 (f) and 5.2 (g).

5.20 Condition the tubes as described in paragraph 5.3.

5.21 Weigh the tubes, as described in paragraph 5.6 to determine the loss in weight of tube containing the specimen, and the change in weight of the tubes containing the blanks.

5.22 Calculate the percentage of total volatiles in each of the 2 g specimens using the equation given below. The results of calculations must agree to within 0.10 percent with the exception that when the mean TV value is above 1.00 percent the results of calculations must agree to within 10 percent of the mean TV value. If not, repeat the analysis.

5.23 **Calculation:**

$$\text{Percent total volatiles} = \frac{100\,(A + B)}{W}$$

Where:

A = Decrease in weight of specimen tube

B = Change (average) in weight of blank tubes taken algebraically

W = Weight of specimen

NOTE: The change in weight of the blank tubes usually is a decrease and the value substituted for B becomes a negative quantity. However, in some instances it is an increase (possibly as a result of humidity changes) and then the value substituted for B becomes a positive quantity. The blank values must agree to within 2 mg. If not, the analysis must be repeated.

METHOD 103.4.1

RESIDUAL SOLVENT

1. SCOPE

1.1 This method is used for determining percentage of residual solvent in propellants.

2. PROCEDURE

2.1 Determine the percentage of total volatiles in the propellant using Method 103.3.3.

2.2 Determine the percentage of moisture in the propellant using the method prescribed in the applicable specification.

2.3 Subtract percentage of moisture from percent of total volatiles to obtain residual solvent.

METHOD 103.5.2

TOTAL VOLATILES (GAS CHROMATOGRAPHIC METHOD)

1. SCOPE

1.1 This method is used for determining water, ethyl alcohol, and diethyl ether or acetone (total volatiles) in propellant granules (or fine chopped material). It is based on extraction of the solvents from the propellant with a mixture of predried methyl ethyl ketone (MEK) and secondary butyl alcohol. By controlling the ratio of the extracting solvents, propellants containing nitrocellulose of varying nitrogen content can be analyzed by this procedure. For each propellant type, the MEK to sec-butyl alcohol ratio should be adjusted to prevent the granules from completely dissolving.

2. SPECIMEN

2.1 The specimen shall consist of approximately 10 g of the propellant prepared with minimum atmospheric exposure and placed in a suitable sealed container to reduce loss of volatiles or absorption of moisture.

NOTE: If the size of the propellant as received would unnecessarily prolong the time required for extraction, the specimen may be crushed or sliced.

This procedure has been used successfully on the following single-base and multi-base propellants but is applicable to other propellant formulations:

Single-base

M-1 SP, original size
M-1 MP, original size
M-6, crushed
Benite, original size
IMR, original size
CBI, original size

Multi-base

M30, crushed
M26, original size
M-7, crushed
Rolled propellants, cut
Various casting powders, original size

NOTE: Original size refers to material of 0.3 inch or less in diameter.

3. APPARATUS

3.1 Gas chromatograph (GC) equipped with a thermal conductivity detector, a one-millivolt recorder and integrator.

3.2 Columns: 1/4 inch O.D., stainless steel tube containing 80 - 100 mesh Porapak Q and of the following lengths:

a. Eight feet for analysis of water, ethyl alcohol and diethyl ether in single-base propellants.

b. Two feet for analysis of water, ethyl alcohol, and acetone in multi-base propellants.

3.3 Erlenmeyer flasks, 125 ml.

3.4 Rubber stoppers, size 5-1/2, solid.

3.5 Syringe, 50 microliters (µl) or as required.

3.6 Serum bottles, 30 ml capacity.

3.7 Rubber stoppers (or seals) for serum bottles.

3.8 Pipets, 25 and 50 ml volumetric.

3.9 Shaker, horizontal (for flasks).

4. MATERIALS

4.1 Acetone.

4.2 Acetone, dried.

4.3 Methyl ethyl ketone (MEK), certified reagent grade.

4.4 Sec-Butyl alcohol.

4.5 Molecular sieves, type 4A, size 1/16" pellets (or equivalent).

4.6 Ethyl alcohol, absolute, dried.

4.7 Water, distilled.

4.8 Diethyl ether, dried.

4.9 Helium.

4.10 Extraction solution: Mixture of dry methyl ethyl ketone and dry sec-butyl alcohol of the following ratio:

4.10.1 MEK/sec-butyl alcohol 25/75: Primarily used for the analysis of moisture, ethyl alcohol, and diethyl ether in single-base propellants containing nitrocellulose of approximately 13.15% nitrogen.

4.10.2 MEK/sec-butyl alcohol (20/80): Primarily used for the analysis of moisture, ethyl alcohol, and acetone in multi-base propellants containing nitrocellulose of approximately 12.60% nitrogen.

5. PROCEDURE

5.1 Preparation of Extraction Solvents.

5.1.1 Dry solvents for extraction by adding approximately a one-inch layer of molecular sieves directly to gallon containers of methyl ethyl ketone and sec-butyl alcohol prior to mixing in the proper ratio and allow a minimum of two days for the absorption of the moisture in the solvent.

5.1.2 Mix the dry methyl ethyl ketone and dry sec-butyl alcohol in the proper ratio by volume: 25/75 or 20/80 (or as needed).

5.1.3 Add a one-inch layer of molecular sieves to the container of mixed solvents to further dry solvent for a minimum of 2 days and to insure that the solvent remains dry. The container must be kept sealed from atmospheric moisture.

5.2 Preparation of Standard.

5.2.1 With minimum exposure to the atmosphere, pipet 25 ml of the dry extraction solvent into a 30 ml serum bottle.

5.2.2 Immediately stopper the bottle with the appropriate stopper and weigh the bottle to the nearest 0.2 mg.

5.2.3 Using a clean dry syringe, inject through the rubber stopper approximately 0.10 ml each of distilled water, dry ethyl alcohol, and dry diethyl ether or dry acetone, depending on types of process solvents used in the manufacture of the propellant. Reweigh the bottle to the nearest 0.2 mg after each injection to determine the weight of each component added. The syringe should be rinsed with acetone and dried between each injection with dry air.

NOTE: If necessary, the concentration of the standard may be varied depending on the sample concentration.

5.2.4 Record the weight of each component.

5.3. Testing.

5.3.1 Add approximately 10 grams of propellant, weighed to the nearest 0.2 mg, to a 125 ml Erlenmeyer flask and stopper immediately.

5.3.2 Record the sample weight.

5.3.3 Pipet 50 ml of extraction solvent into the flask and immediately stopper.

5.3.4 Place the prepared flask on a horizontal shaker at a low speed for gentle agitation at ambient conditions to extract the process solvents from the propellant. The (MEK) will swell the propellant to facilitate removal of process solvents.

5.3.5 Extraction times will vary with propellant type. Ten hours is usually sufficient for most single-base propellants. Multi-base propellants usually require a 16-hour extraction time.

5.3.6 Remove the flask from the shaker and allow solids to settle 15 minutes.

5.3.7 Check the gas chromatographic operating conditions, make necessary adjustments, and allow the instrument to stabilize (see Table 1).

5.3.8 Inject 20 µl (or as required) of the liquid portion of the sample into the gas chromatograph.

5.3.9 Allow each component to elute from the column and measure its area with an integrator.

5.3.10 The sequence of separation of the components will be as follows:

Condition A: Air, water, ethyl alcohol, impurity from extraction solvent (observed when the gas chromatograph is set at high sensitivity), diethyl ether, and extraction solvent (MEK/sec-butyl alcohol). See Fiqure 1. If acetone is present, it will elute at approximately the same retention time as the impurity from the extraction solvent.

Condition B: Air, water, ethyl alcohol, acetone, impurity from extraction solvent and extraction solvent (MEK/sec-butyl alcohol). See Figure 2. If diethyl ether is present, it will elute immediately before the extraction solvent and will be interfered with by the impurity from the extraction solvent.

NOTE: Acetone and diethyl ether can be analyzed quantitatively using Conditions A and B, respectively, if the area of the impurity is substracted.

TABLE 1

	Condition A	Condition B
Column	8 feet	2 feet
Oven temperature	150° C	125° C
Injection port	170° C	140° C
Detector	180° C	140° C
Bridge current	100 mA	200 mA
Helium (carrier) flow	60 cm^3/min	60 cm^3/min
Helium inlet pressure	50 psig	50 psig

NOTE: 1 psi = 6.9 kPa

Condition A: For analyzing single-base propellants (no nitroglycerin) (or other nitrated esters) present for water, ethyl alcohol, and diethyl ether. See Figure 1.

Condition B: For analyzing multi-base propellants for water, ethyl alcohol and acetone, primarily. See Figure 2.

NOTE: If multi-base propellants are tested using Condition A, nitroglycerin will decompose and interfere with the water peak.

5.3.11 Repeat paragraphs 5.3.8 through 5.3.10 using the standard.

5.3.12 Run a blank by repeating paragraphs 5.3.8 through 5.3.10 using the MEK/sec-butyl alcohol solution to obtain the water correction (if necessary).

5.3.13 **Calculation:**

$$\% H_2O = \frac{(A1 - Ab)(W1)(100)(E)}{(As - Ab)(W2)}$$

$$\% X = \frac{(A1)(W1)(100)(E)}{(As)(W2)}$$

% TV (total volatiles) = the sum of all process solvents [% H_2O+ % alcohol + % ether (or acetone)]

Where:

X = % alcohol, ether, or acetone.

A1 = Area of peak of unknown sample.

As = Area of peak for standard.

Ab = Area of water peak in extraction of solvent.

W1 = Grams of component per 25 ml of standard.

W2 = Sample of weight.

E = Ratio of solvent between sample and standard (equals 2 when 50 ml is used for samples and 25 ml is used for standard).

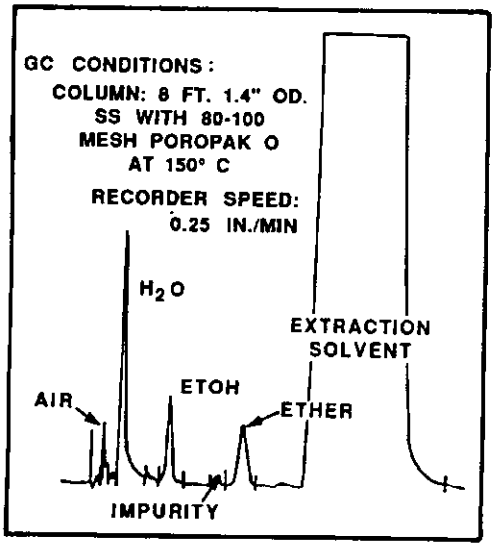


Figure 1. *Condition A, GC Scan of a Typical Single-Base Propellant Extract.*

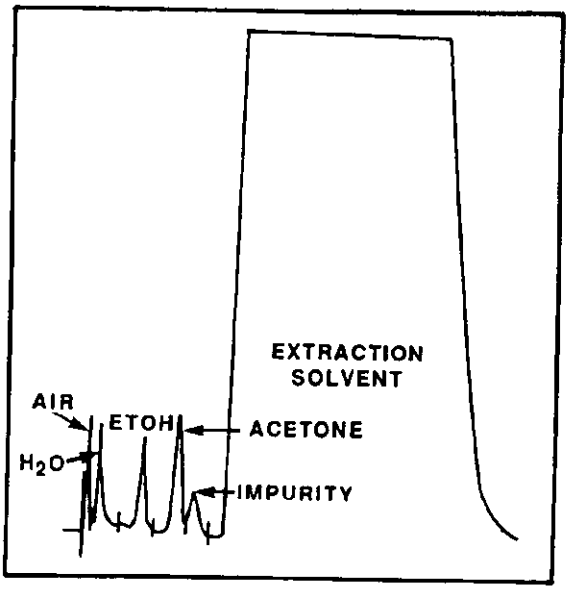


Figure 2. *Condition B, GC Scan of a Typical Multi-Base Propellant Extract.*

METHOD 103.6.1

ISOPROPYL ALCOHOL, ETHYL ACETATE, AND BENZENE (GAS CHROMATOGRAPHY METHOD)

1. SCOPE

1.1 This method may be used for the determination of isopropyl alcohol, ethyl acetate and benzene in single or double base ball powder.

1.2 The solvents are extracted from the propellant with an internal standard solution, injected into a column, and then the solvent peaks are compared with a standard.

2. SPECIMEN

2.1 The sample shall consist of 3.0 grams of the propellant.

3. APPARATUS

3.1 Perkin-Elmer 3920 with flame ionization detector (FID) or its equivalent interfaced to a PEP-II computer (or other means of peak measurement).

3.2 10 µl Syringe.

3.3 Magnetic stirrer and bar.

3.4 60 ml Bottle and stopper.

3.5 1 ml Pipette.

3.6 1 liter volumetric flask

3.7 100 ml volumetric flask.

4. REAGENTS AND STANDARDS

4.1 Methanol - Reagent

4.2 Tert-Butanol - Reagent Grade

4.3 Ethyl Acetate - Reagent Grade

4.4 Benzene - Reagent Grade

NOTE: Benzene is considered a carcinogenic agent.

4.5 2-Propanol - Reagent Grade

4.6 Internal Stock Solution

5. CALIBRATION AND STANDARDIZATION

5.1 Gas Chromatograph Conditions: Advisory

Injection Port temp. - 225 C
Detector Temp. - 225 C
Column Temp. - 165 C
Carrier Gas - Helium
Flow Rate - 40 ml/min
Column - 4 ft x 1/8 in stainless steel tubing containing Porapak Q 80/100 Mesh or equivalent

5.2 Preparation of Internal Standard Solution

1 ml tert-butanol/liter of methanol

5.3 Preparation of Standard

a. Weigh to the nearest 0.1 mg 0.075 g of isopropyl alcohol, 0.075 g of ethyl alcohol, and 0.025 g of benzene into a 100 ml volumetric flask. Fill to volume with internal standard solution.

b. Inject 0.5 µl into the appropriate column.

c. Identify each peak and measure the area for isopropyl alcohol, tert-butanol, ethyl acetate, and benzene. (see Figure 1).

6. PROCEDURE

6.1 Weigh 3.00 grams to nearest 0.1 mg of sample and place in 60 ml bottle.

6.2 To this bottle, add 20 ml of internal standard solution.

6.3 Place magnetic stirrer in bottle and stopper.

6.4 Stir for 30 minutes.

6.5 Inject 0.5 µl into the appropriate column.

6.6 Identify each peak and measure the area for isopropyl alcohol, tert-butanol, ethyl acetate and benzene. (see figure 1).

7. CALCULATION:

$$\% \text{ Isopropyl alcohol} = \frac{B \times C \times 100}{A \times D}$$

$$\% \text{ Ethyl acetate} = \frac{B \times C \times 100}{A \times D}$$

$$\% \text{ Benzene} = \frac{B \times C \times 100}{A \times D}$$

Where:

$$A = \frac{\text{Area of internal standard in sample}}{\text{Area of peak of interest in sample}}$$

$$B = \frac{\text{Area of internal standard in standard}}{\text{Area of peak of interest in standard}}$$

C = Concentration of component in standard grams of component per 20 ml in standard

D = Weight of sample

Chart speed - 5 mm/min

Sample size - 0.5 µl

Component Relative Retention Times (using t-butanol as 1,000)

Isopropyl Alcohol - .629

Ethyl Acetate - 1.532

Benzene - 2.389

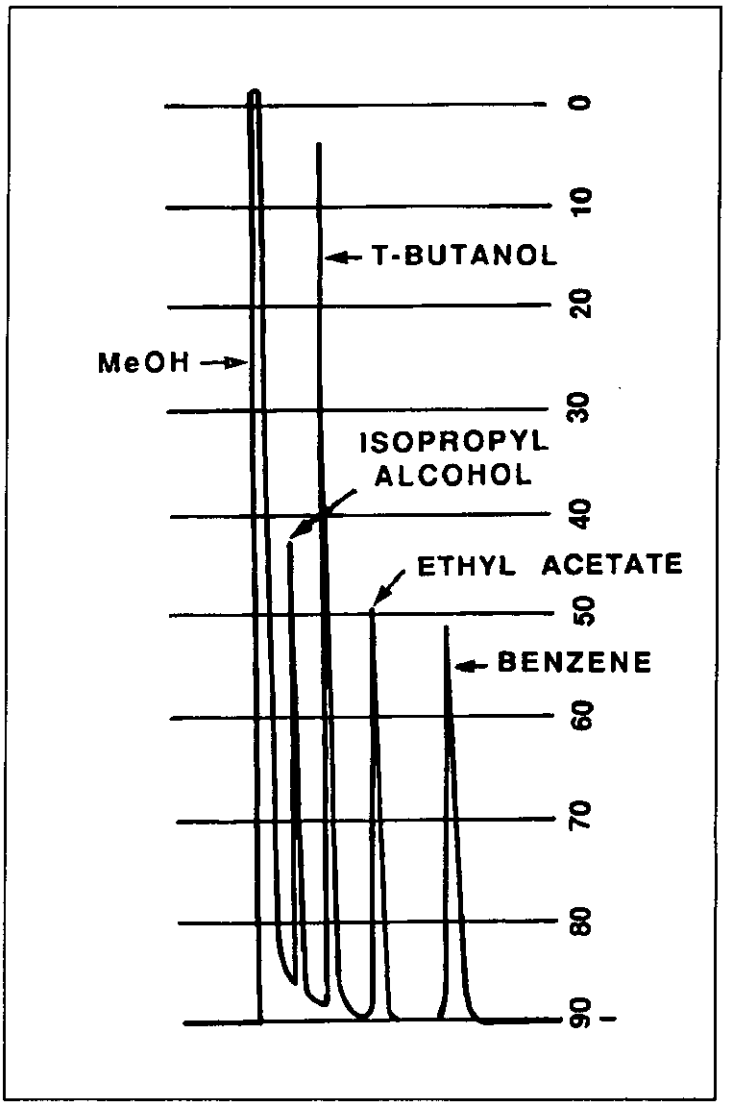


Figure 1. *Chromatogram of Isopropyl Alcohol, t-Butanol, Ethyl Acetate and Benzene*

METHOD 104.1.3

SOLVENT EXTRACTIVE MATTER

1. SCOPE

1.1 This method is used for separating soluble ingredients from propellants by selective extraction for use in subsequent determinations. The extraction time will depend on the apparatus, the solvent and the propellant but usually requires between 6 and 20 hours. In general the Roweg extractor is two to three times faster than the Soxhlet.

NOTE: This method is applicable to a variety of extraction conditions, and is not intended to restrict or limit such factors as the solvent or apparatus used, or the time of extraction. For specific instructions, refer to the applicable propellant specification.

2. SPECIMEN

2.1 The specimen shall consist of an accurately weighed portion of the propellant as specified in the applicable method or specification. For large grains it is often necessary to slice, chop or grind the propellant.

3. APPARATUS

3.1 Extraction flask (tared, if the weight of the solvent extractive matter is to be determined).

3.2 Extractor (Roweg, Soxhlet, or equivalent).

3.3 Extraction thimble.

3.4 Condenser (Allihn type or equivalent).

3.5 Hotplate (steam or hotwater heated).

3.6 Vacuum desiccator maintained at a pressure (absolute) of approximately 25 mm of mercury over desiccant. (The desiccator is used only if the weight of the solvent extractive matter is required).

4. MATERIALS

4.1 Extracting solvent, such as diethyl ether, or anhydrous methylene chloride, as specified in the applicable method or propellant specification.

NOTE: Unless otherwise specified, use methylene chloride for extraction. Do not use chlorinated solvents on propellants containing aluminum.

5. PROCEDURE

5.1 Transfer the accurately weighed specimen to the extraction thimble, and the prescribed solvent to the extraction flask. In highly plasticized propellants, it is desirable to add the solvent through the condenser after the apparatus has been assembled.

5.2 Assemble the extraction apparatus on the hotplate, and adjust the temperature so that the solvent drips from the condenser at the rate of two to three drops per second.

CAUTION: The heat source should be dependent upon the continuation of flow of water to the condenser and should be automatically cut off if the flow is discontinued.

5.3 Extract for a time which experience or preliminary work has shown to be adequate for the type of sample and kind of determination to be made on the extract or residue. The preliminary work utilizes a suitable qualitative test to estimate completion of extraction and estimates the minimum time required. The extraction time is then established as some excess of this minimum. One simple test is to evaporate a portion of the extract in a tared container and determine the weight of the residue. A number of colorimetric tests are also suitable for determining completeness of extraction.

5.4 When the extraction is complete, evaporate the solvent, using a stream of dry air, and retain the dry residue for the required determination.

5.5 If percent extractables is desired, place flask in a vacuum desiccator and leave overnight. Remove flask and weigh to the nearest 0.1 mg and return to vacuum desiccator for two additional hours. Reweigh and if the second weight is within 0.0025 g of the first, the lower of these two weights is used in the calculation; however, if the variation between weights is more than 0.0025 g, the flask must be redesiccated until two successive weights are within limits. Use the "dried" extract for subsequent procedures.

5.6 **Calculation:**

$$\text{Percent extractables} = \frac{A - B}{W} \times 100$$

$$\text{Percent of solvent insolubles} = 100 - \text{Percent extractables}$$

Where:

A = Weight of flask and extract, g.

B = Weight of flask, g.

W = Weight of specimen, corrected for total volatiles, g.

METHOD 106.1.2

ASH (NO INORGANIC ADDITIVES PRESENT)

1. SCOPE

1.1 This method is used for determining the ash content of propellants where no inorganic additives are present.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5 g of the propellant, weighed to within 0.2 mg.

3. APPARATUS

3.1 Evaporating dish, 90 mm Silica or chemical porcelain.

3.2 Steam bath in a well-ventilated hood.

3.3 Muffle furnace.

3.4 Desiccator containing an indicating desiccant.

4. MATERIALS

4.1 Nitric acid, 70-percent solution.

5. PROCEDURE

5.1 Place the specmen in a tared evaporating dish that has been previously ignited and cooled.

5.2 Add 10-15 ml of the 70 percent nitric acid solution, and place the evaporating dish on the steam bath until the propellant is completely disintegrated, and no liquid remains.

5.3 Ignite the dish and contents, heating it gently at first until fumes are no longer evolved, then heating it in the muffle furnace (or over a gas flame) at 500 to 600°C for 30 minutes.

5.4 Cool the dish and contents to room temperature in the desiccator, and weigh.

5.5 Repeat the heating, cooling, and weighing until the change in weight between weighings does not exceed 0.2 mg.

5.6 Determine the weight of the residue (ash) and calculate the percentage.

METHOD 106.2.3

ASH (POTASSIUM SALTS PRESENT)

1. SCOPE

1.1 This method is used for determining the ash content of propellant containing potassium salts but no other inorganic additives.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5 g of the propellant, weighed to within 0.2 mg.

3. APPARATUS

3.1 Evaporating dish, 90 mm silica or chemical porcelain.

3.2 Steam bath in a well-ventilated hood.

3.3 Muffle furnace.

3.4 Desiccator containing an indicating desiccant.

3.5 Watchglass.

3.6 Filter paper (ashless), fine porosity.

3.7 Crucible, porcelain.

4. MATERIALS

4.1 Nitric acid, 70-percent solution.

4.2 Hydrochloric acid, 38 percent solution.

4.3 Methyl red indicator solution as described in Method 702.1.

4.4 Ammonium hydroxide, 5 percent solution.

5. PROCEDURE

5.1 Convert the specimen into ash as described in Method 106.1.

5.2 After the dish has cooled, rinse down the sides of the dish with 5 to 10 ml of distilled water, and add 5 ml of the hydrochloric acid solution. Cover the dish with a watch-glass and place it on the steam bath for 5 minutes.

5.3 Remove the dish from the steam bath, and dilute the contents to approximately 25 ml with distilled water.

5.4 Add one drop of the methyl red indicator, and sufficient 5-percent ammonium hydroxide to make the solution slightly alkaline.

5.5 Filter the solution through ashless filter paper, washing the dish and filter paper with distilled water to remove all soluble constituents.

5.6 Transfer the filter paper to a previouslv ignited and weighed crucible, and dry the filter paper for 30 minutes at approximately l00°C.

5.7 Char the paper by means of a burner, and ignite the crucible in a muffle furnace for 30 minutes at 600°C.

5.8 Cool the crucible and contents to room temperature in the desiccator, and weigh.

5.9 Repeat the heating, cooling, and weighing until the change in weight between weighings does not exceed 0.2 mg.

5.10 Determine the weight of the residue (ash), and calculate the percentage.

METHOD 106.3.2

ASH (POTASSIUM SALTS AND TIN PRESENT)

1. SCOPE

1.1 This method is used for determining the ash content of propellant containing potassium salts and tin.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5 g of the propellant, weighed to within 0.2 mg.

3. APPARATUS

3.1 Crucible, porcelain (with lid), 50-ml.

3.2 Steam bath in a well-ventilated hood.

3.3 Hotplate.

3.4 Muffle furnace.

3.5 Desiccator containing an indicating desiccant.

4. MATERIALS

4.1 Nitric acid, 70-percent solution.

4.2 Sulfuric acid, concentrated.

5. PROCEDURE

5.1 Ignite two 50 ml porcelain crucibles and lids, and cool in a desiccator. Weigh one of the crucibles, using the other as a counterpoise.

5.2 Transfer the specimen to the weighed crucible, and add 10 ml of 70-percent nitric acid. Also add 10 ml of the nitric acid to the counterpoise.

5.3 Place both crucibles and lids on the steam bath, adjust the lids to permit the escape of volatile matter, and heat the crucibles until the propellant has been converted into a gummy mass.

5.4 Transfer the crucibles to a hotplate (at approximately 250°C), and drive off the volatile matter.

5.5 Ignite the crucibles in muffle furnace at 600°C, for approximately 2 hours to remove carbonaceous matter.

5.6 Cool the crucibles, and add five drops of concentrated sulfuric acid to each.

5.7 Return the crucibles to the hotplate, and heat them until the fuming ceases.

5.8 Ignite the crucibles in the muffle furnace for 15 minutes at 600°C., then cool to room temperature in the desiccator.

5.9 Reweigh the crucible containing the ash, using the other as a counterpoise.

5.10 Calculate the percentage of ash as follows:

$$\text{Percent}_{\text{ash}} = \frac{100A}{W} - \left(\frac{87B}{D} + 1.27E\right)$$

Where:

A = Weight of propellant ash, g.

B = Potassium salt in propellant, percent.

D = Equivalent weight of potassium salt in propellant.

E = Tin in propellant, percent.

W = Weight of specimen,g.

METHOD 106.4.2

ASH (LEAD SALTS WITH OR WITHOUT POTASSIUM SALTS PRESENT)

1. SCOPE

1.1 This method is used for determining the ash content of propellant containing a lead salt. It can be used whether potassium salts are present or not.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5 g of the propellant, weighed to within 0.2 mg.

3. APPARATUS

3.1 Crucible, porcelain.

3.2 Steam bath in a well-ventilated hood.

3.3 Hotplate.

3.4 Watchglass.

3.5 Filter paper (ashless), fine porosity.

3.6 Muffle furnace.

3.7 Desiccator containing an indicating desiccant.

4. MATERIALS

4.1 Nitric acid, 70-percent solution.

4.2 Sulfuric acid, concentrated.

5. PROCEDURE

5.1 Place the specimen in a tared porcelain crucible, and 10 ml of nitric acid solution, and place the crucible on the steam bath.

5.2 When the reaction starts, remove the crucible from the steam bath, and allow it to stand in the hood until the evolution of the fumes has ceased. Then reheat the crucible until the residue consists of a gummy mass.

5.3 Cautiously add 5 ml of the concentrated sulfuric acid and 10 ml of nitric acid solution. Cover the crucible with a watchglass, and heat it on a hotplate until the fumes of sulfur trioxide are evolved.

5.4 Cool the crucible for approximately 1 minute, add 5 ml of the nitric acid solution, and reheat until the fumes of sulfur trioxide are evolved.

5.5 Repeat step 5.4 until all organic matter is destroyed, and the sulfuric acid solution is practically colorless.

5.6 Remove the watchglass, wipe it off with ashless filter paper, and place the filter paper in the crucible. Reheat the crucible until sulfur trioxide fumes are no longer evolved.

5.7 Ignite the crucible in a muffle furnace for approximately 2 hours at 600°C (or to a dull red heat over a gas flame).

5.8 Cool the crucible to room temperature in a desiccator.

5.9 Weigh the crucible and contents at 2-hour intervals until the change in weight between weighings does not exceed 0.2 mg.

5.10 Determine the gain in weight of the crucible, and calculate the gain as the percentage of ash in the specimen, as follows:

5.11 **Calculation:**

$$\text{Percent ash} = \frac{100A}{W} - \left(\frac{152C}{D} + \frac{87F}{G}\right)$$

Where:

A = Weight of ash, g.

C = Lead salt in specimen, percent.

D = Equivalent weight of lead salt in specimen.

F = Potassium salt in specimen, percent.

G = Equivalent weight of potassium salt in specimen.

W = Weight of specimen, corrected for total volatiles, g.

METHOD 107.1

ACIDITY OR ALKALINITY OF NITROGLYCERIN OR CASTING SOLVENT

1. SCOPE

1.1 This method is applicable to the determination of acidity as sulfuric acid (H_2S0_4) or alkalinity as sodium carbonate (Na_2CO_3) in casting solvents primarily in the range of 1-100 parts per million (ppm). The sample of casting solvent is dissolved in toluene and washed in water to dissolve out the acid or alkaline material. The water washings are then titrated with a standardized base or acid. The standard deviation is 1 ppm.

2. SPECIMEN

2.1 The specimen shall consist of approximately 10 ± 0.1 ml (about 16 grams) of nitroglycerin or casting solvent.

3. APPARATUS

3.1 Beakers, 150 ml and 250 ml, plastic (compatible with all materials to be used in this beaker).

3.2 Separatory funnel, 250 ml preferably with Teflon stopcock and rubber stopper, plastic (compatible with all materials to be used in this funnel).

3.3 Pipet, 10 ml, plastic (compatible with all materials to be used in this pipet).

3.4 Buret, 10 ml, plastic.

4. MATERIALS

4.1 Sodium hydroxide, 0.01N.

4.2 Sulfuric acid, 0.01N.

4.3 Bromthymol blue indicator prepared as specified in Method 709.1.

4.4 Toluene

5. PROCEDURES

5.1 Pipet the specimen into a 250 ml separatory funnel which already contains 100 ml of toluene and mix thoroughly.

5.2 Wash twice by shaking with 50 ml portions of water.

5.3 Separate and combine the water washings in a 250 ml beaker and add several drops of indicator.

5.4 If the indicator turns yellow, titrate with the 0.01N sodium hydroxide (NaOH). If the indicator turns blue, titrate with 0.01N sulfuric acid.

5.5 Run a blank determination using 100 ml of toluene and two 50 ml portions of water, and titrating in the same manner as for the sample.

5.6 Calculate the ppm acidity or alkalinity in the original sample as follows:

5.7 **Calculation:**

$$\text{ppm } H_2SO_4 \text{ or ppm } Na_2CO_3 = \frac{(A - B)(N)(C)(100)}{W} \times 10{,}000$$

Where:

A = H_2SO_4 or NaOH required for sample, ml.

B = H_2SO_4 or NaOH required for blank, ml.

N = Normality of H_2SO_4 or NaOH.

W = Weight of sample, mg.

C = Equivalent weight of sulfuric acid (49.0) or sodium carbonate (53.0).

10,000 = ppm factor.

METHOD 201.1.4

DIPHENYLAMINE (SOLVENT EXTRACTION - BROMINATION METHOD)

1. SCOPE

1.1 This method is used for determining the diphenylamine content of newly manufactured single, double, and triple-base propellants containing no other brominatable material (such as salicylates, phenols, or centralites).

NOTE: Aged propellants or propellants containing brominatable material other than diphenylamine should be analyzed for diphenylamine by Method 201.4 or 217.3.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5 g of propellant, weighed to within 0.2 mg.

3. APPARATUS

3.1 Iodine titration flask (with stopper), 250 ml.

3.2 Volumetric flask, 100 ml (required if specimen contains 0.5 percent or more diphenylamine).

4. MATERIALS

4.1 Glacial acetic acid.

4.2 Potassium iodide, 15-percent solution.

4.3 Hydrochloric acid, 38-percent solution.

4.4 Potassium bromate - bromide solution, 0.2N Standard Solution as specified in Method 605.1.

4.5 Sodium Thiosulfate, 0.2N Standard Solution as specified in Method 602.1.

4.6 Starch indicator solution as specified in Method 701.1.

5. PROCEDURE

5.1 Prepare the specimen as described in Method 509.3.

5.2 Extract the specimen as described in Method 104.1.

5.3 Dissolve the dried residue of the extraction in 10 to 15 ml of glacial acetic acid.

5.4 If the nominal content of the diphenylamine in the propellant is 1 percent, or less, transfer the solution to the 250 ml iodine titration flask; rinse the extraction flask with several 10 ml portions of glacial acetic acid; and transfer the rinsings to the titration flask, using a total of 50 ml.

NOTE: If the nominal diphenylamine content of the propellant is greater than 1 percent, transfer the solution (para 5.3) to the 100 ml volumetric flask and make to volume with glacial acetic acid. Transfer a 50 ml aliquot of this solution to the titration flask.

5.5 To the 50 ml solution in the iodine titration flask, and 25 ml of the potassium bromate-bromide solution accurately measured to within 0.01 ml.

5.6 Moisten the stopper of the flask with a drop of 15-percent potassium iodide solution, and add 5 ml of 38-percent hydrochloric acid to the flask, noting the time. Stopper the flask immediately, swirl the contents for a few seconds, and allow the bromination to proceed for 1.0 plus or minus 0.25 minutes from the time of addition of the hydrochloric acid.

5.7 At the end of the brominating time, add 10 ml of 15-percent potassium iodide solution, and swirl the contents of the flask.

NOTE: If an oil separates, add 25 ml of methylene chloride.

5.8 Wash down the gutter and walls of the flask with distilled water, and titrate the resulting solution immediately with 0.2N sodium thiosulfate until the solution assumes a light yellow color.

5.9 Add 5 ml of the starch indicator solution, and continue the titration carefully until the blue color of the solution disappears.

5.10 Make a blank determination, using 50 ml of glacial acid and exactly the same volume of the potassium bromate-bromide solution (para 5.5).

5.11 Calculate the percentage of diphenylamine in the specimen.

5.12 **Calculation:**

$$\text{Percent Diphenylamine} = \frac{2.115\,(A - B)\,N}{W}$$

Where:

A = Sodium thiosulfate required for the blank, ml.

B = Sodium thiosulfate required to titrate the liberated iodine in the solution containing the brominated specimen, ml.

N = Normality of the sodium thiosulfate solution.

W = Weight of the specimen, corrected for total volatiles, g.

METHOD 201.2.3

DIPHENYLAMINE (GRAVIMETRIC METHOD)

1. SCOPE

1.1 This method is used for determining the diphenylamine content of newly manufactured propellants where the solvent extract contains no other brominatable constituents.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5 g of the propellant, weighed to within 0.2 mg.

3. APPARATUS

3.1 Pipet, 10-ml.

3.2 Beaker, 50-ml.

3.3 Beaker, 250-ml.

3.4 White spot plate.

3.5 Steam bath in a well-ventilated hood (maintained at approximately 75°C on the surface.)

3.6 Filtering crucible with mat that will permit rapid filtration.

3.7 Desiccator containing an indicating desiccant.

4. MATERIALS

4.1 Acetone.

4.2 Sodium nitrite solution (1-percent in sulfuric acid).

4.3 Diethyl ether, anhydrous.

4.4 Bromine.

4.5 Ethyl alcohol, 95-percent.

4.6 Ethyl alcohol, 47.5 percent (by volume).

5. PROCEDURE

5.1 Prepare the specimen as described in Method 509.3

5.2 Extract the specimen as specified in Method 104.1.

NOTE: If anhydrous ether is used for the extraction, it need not be evaporated unless the percentage of total solvent extract is to be determined.

5.3 Check for completeness of extraction as follows if the propellant contains no nitroglycerin.

a. Disassemble the extraction apparatus just before the solvent siphons out of the extractor. Transfer 10 ml of the solvent from the extractor to a 50 ml beaker, using a 10-ml pipet.

b. Evaporate the 10 ml of solvent, using a stream of dry air.

c. Add 2 to 5 drops of acetone to the beaker to dissolve any residue, and place this solution in the indenture of a white spot plate.

d. Add 2 or 3 drops of the solution of sodium nitrate. The immediate appearance of a deep blue color indicates the presence of diphenylamine, and therefore incomplete extraction.

5.4 When the extraction is complete dissolve the residue in the extraction flask in approximately 50-ml of diethyl ether; quantitatively transfer the ether solution to a 250-ml beaker.

5.5 Place the beaker on the steam bath, and add enough bromine (0.6-ml for each percent of diphenylamine), drop by drop, to assure a slight excess over the amount necessary to convert all the diphenylamine to tetrabrom-diphenylamine.

NOTE: A slight excess of bromine is indicated by the persistence of a reddish light-brown color.

5.6 Swirl the contents of the beaker, place on the steam bath, and allow the solution to come to a boil.

5.7 When the solution boils, remove the beaker from the steam bath, and evaporate the ether and the excess bromine under a current of dry air until the odor of ether is no longer detectable.

CAUTION: Prolonged evaporation after reaching dryness will yield low results.

5.8 To the residue in the beaker, add 40-ml of 95-percent ethyl alcohol, and heat to boiling.

5.9 Note the time, and add 40 ml of distilled water at room temperature. Allow the beaker to remain on the steam bath for exactly 10 minutes.

5.10 At the end of 10 minutes, filter the hot liquid through the tared filtering crucible. Wash the retained precipitate of tetrabrom-diphenylamine, first with approximately 80-ml of boiling 47.5-percent ethyl alcohol, and then with hot distilled water.

5.11 Heat the crucible for 1 hour at $105^{\circ} \pm 2^{\circ}C$, and cool in a desiccator until the change in weight between weighings at 2-hour intervals is less than 0.5 mg.

5.12 Determine the increase in weight of the crucible to within 0.2 mg.

5.13 Calculate the percentage of diphenylamine.

5.14 **Calculation:**

Where:

$$\text{Percent Diphenylamine} = \frac{34.90A}{W}$$

A = Weight of tetrabromdiphenylamine (increase in weight of crucible).

W = Weight of specimen, corrected for total volatiles.

METHOD 201.4.2

DIPHENYLAMINE AND ETHYL CENTRALITE IN ADMIXTURE OR SEPARATELY (STEAM DISTILLATION-SPECTROPHOTOMETRIC METHOD)

1. SCOPE

1.1 This method is suitable for nitroxy-base propellant composition containing nitro-compounds and saponifiable esters, in either aged or newly manufactured propellants. Other propellant ingredients (such as DNT and phthalate esters) that steam distill an absorb light in the spectrophotometric regions used for analysis will interfere. The coefficient of variation (standard deviation/average) of this method should not exceed 0.01.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5 g of the propellant (1 g if the nominal content of either stabilizer is 2 percent or more) weighed to within 0.2 mg.

3. APPARATUS

3.1 Steam distillation apparatus (fiqure 1). A stopper should be placed in a steam outlet of the 3-necked flask if only one distillation is being conducted.

3.2 Spectrophotometer capable of measuring absorbance of liquid between 230 and 300 nanometers (nm).

4. MATERIALS

4.1 Spectrophotometric standards

a. Diphenylamine (DPA), melting range

$53.5 \pm 0.5^{\circ}C$

If necessary, recrystallize from propanol and then from absolute ethanol. Make each crystallization from a solution that has been saturated at room temperature and cooled to $5^{\circ}C$. Filter with suction through a Buchner funnel and press dry with a rubber diaphragm. Finally, dry to constant weight in a vacuum desiccator protected from light.

b. Ethyl Centralite (EC), melting range

$72.5 \pm 0.5^{\circ}C$

If necessary, recrystallize twice from absolute ethanol and dry in the same manner as for DPA.

4.2 Ethanol - 95 percent (benzene free); same lot to be used for calibration and analysis of the propellant.

4.3 Sodium hydroxide solution - aqueous 50 per cent, (weight/weight).

5. PROCEDURE

5.1 Determination of inverse absorptivity.

a. Place approximately 100 mg (weighed to 0.2 mg) of the DPA spectrophotometric standard in a 250ml volumetric flask; dissolve in and dilute to volume with ethanol. From the solution transfer 15 ml to a 200 ml volumetric flask and dilute to the mark with alcohol. Transfer 5, 10, 15 and 25 ml aliquots to separate 100 ml volumetric flasks and dilute to volume with ethanol.

b. Place approximately 100 mg (weighed to 0.2 mg) of the EC spectrophotometric standard in a 250 ml volumetric flask; dissolve in and dilute to volume with ethanol. Transfer a 25 ml portion of this solution to a 100 ml volumetric flask and dilute to the volume with alcohol. Transfer 5, 10, 15, and 20 ml aliquots to separate 100 ml volumetric flasks and dilute to volume with ethanol.

c. Determine the absorbances of the four stabilizer solutions at 247 nm for EC and absorbances of the four solutions of DPA at 285 nm using 95% ethanol in the reference cell of the spectrometer. Plot the absorbance value against the concentration of each solution and draw the best straight line from the origin through the four data points. Reject the data if the four points do not fall substantially along the line. Calculate the spectrophotometric factor in the followinq manner:

$$D = \frac{\Sigma\ (C^2)}{\Sigma\ (AC)}$$

Where:

A = Absorbance of standard solution at 285 nm or 247 nm

C = Concentration of standard solution.

$\Sigma\ (C^2)$ = Sum of squared concentrations of the standard solutions, mg per 100 ml.

Σ (AC) = Sum of products of absorbance and concentration of the standard solutions, mg per 100 ml.

D = Spectrophotometric factor in ethanol, milligrams per 100 ml per unit absorbance.

5.2 Determination of Available Diphenylamine. Weigh accurately a sample of the propellant not greater than 5 grams and corresponding nominally to 20 milligrams of DPA and place it in the distillation flask (figure 1). Add 50 ml of 50 percent NaOH and 100 ml of 95 percent ethanol. Fit the flask with a reflux condenser, heat the mixture to boiling and continue refluxing for 30 minutes. After the heating period rinse the condenser into the flask with 20-30 ml of alcohol. Remove the condenser, add 50 ml of ethanol to the receiver and assemble the distillation apparatus (figure 1) so that the tip of the adapter is just below the surface of the added ethanol. Introduce live steam and distill at the rate of 7-9 ml per minute until 500 $\pm$ 25 ml of distillate have been collected. When the distillation is complete, rinse the condenser and adapter with alcohol, collecting the washings in the receiver. Transfer the contents of the receiver to a 1,000 ml volumetric flask with the aid of ethanol. Allow to attain room temperature and dilute to volume with this solvent. Take a 20 ml portion of this solution and transfer to a 100 ml volumetric flask and dilute to volume with ethanol. Determine the absorbance at 285 nm using 95 percent ethanol in the reference cell. Calculate the percentage of available DPA as follows:

$$\text{Available DPA (\%)} = \frac{100\,A_1D_1}{C_1}$$

Where:

A_1 = Absorbance of the solution at 285 nm

C_1 = Weight of the original propellant sample represented in the 20 ml aliquot in mg

D_1 = Spectrophotometric factor for DPA

5.3 Determination of Available Ethyl Centralite

NOTE: This determination must be completed on the day it is started.

Weigh accurately a sample of propellant not greater than 5 g and corresponding nominally to 80 mg of ethyl centralite and place it in the distillation flask (figure 1). Add 50 ml of 50 percent NaOH and 100 ml of 95 percent ethanol. Fit the flask with a reflux condenser, heat the mixture to boiling and continue refluxing for 30 minutes. After the heating period, rinse the condenser into the flask with 20-30 ml of ethanol. Remove the condenser, add 50 ml of 95 percent ethanol to the receiver and assemble the distillation apparatus (figure 1) so that the tip of the adapter is just below the surface of the added ethanol. Introduce live steam and distill at the rate of 7-9 ml per minute until 500 ± 25 ml of distillate have been collected. When the distillation is complete, rinse the condenser and adapter with ethanol, collecting the washings in the receiver. Transfer the contents of the receiver to a 1,000 ml volumetric flask with the aid of ethanol. Allow to attain room temperature and dilute to volume with this solvent. Take a 20 ml portion of this solution and transfer to a 100 ml volumetric flask and dilute to volume with 95 percent ethanol. Determine the absorbance at 247 nm using 95 percent ethanol in the reference cell of the spectrophotometer. Calculate the percentage of available ethyl centralite as follows:

$$\text{Available EC (\%)} = \frac{100\,A_2D_2}{C_2}$$

Where:

A_2 = Absorbance of the solution at 247nm

C_2 = Weight of the original propellant sample represented in the 20 ml aliquot in mg

D_2 = Spectrophotometric factor for EC

5.4 Propellants with both Diphenylamine and Ethyl Centralite Stabilizers: Determination of Available Diphenylamine.

5.4.1 Determination of Spectrophotometric Factors (Inverse Absorptivity) for DPA and EC. Prepare standard solutions of DPA and EC, measure their absorbances, and plot absorbance against concentration and measure the absorbance of the solutions of each substance at both 285 and 247 nm. Calculate the spectrophotometric factor for each substance at each wavelength. Designate the spectrophotometric factors as follows:

	DPA	EC
285nm	D_{1a}	D_{2a}
247nm	D_{1b}	D_{2b}

5.4.2 Determination of Available Diphenylamine. Weigh accurately a sample of the propellant not greater than 5 g and corresponding nominally to neither more than 30 mg of DPA nor more than 100 mg of EC. Reflux the sample with alkali, steam distill, and measure the absorbance of the distillate at both 285 and 247 nm. Calculate the percentages of available stabilizer.

5.4.3 **Calculation:**

$$\text{Available as DPA(\%)} = \frac{100\, D_{1a}\, D_{1b}}{KC_1} \times (A_a D_{2a} - A_b D_{2b})$$

Where:

A_a, A_b = Absorbance of solution at 285 nm and 247 nm respectively

C_1 = Weight of the original propellant sample represented in the 20 ml aliquot, mg

$D_{1a}, D_{2a}, D_{1b}, D_{2b}$ = Spectrophotometric factors

$K = D_{1b}D_{2a} - D_{1a}D_{2b}$

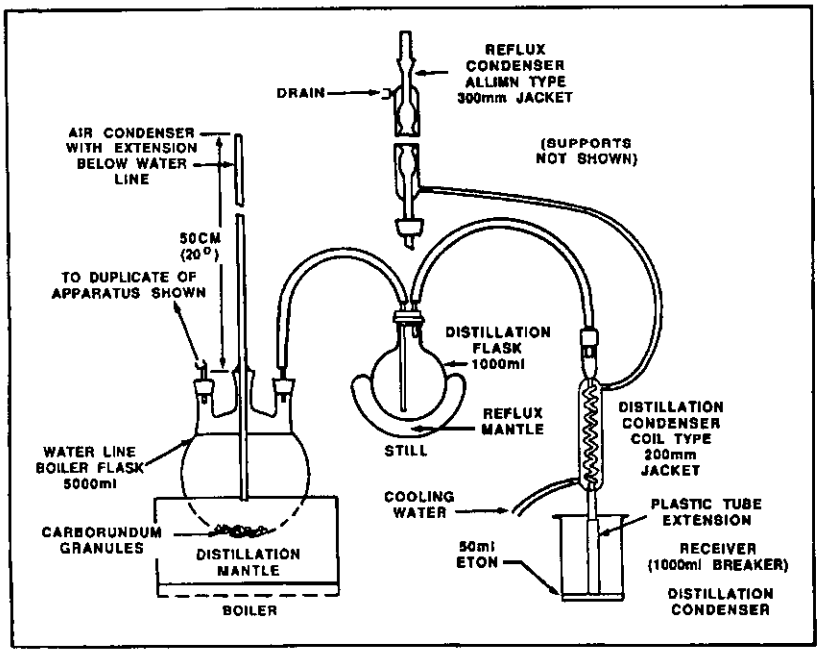


Figure 1. *Steam Distillation Apparatus.*

METHOD 202.2.3

ETHYL CENTRALITE (VOLUMETRIC BROMINATION METHOD)

1. SCOPE

1.1 This method is used for determining the ethyl centralite content of newly manufactured propellants containing no other brominatable material, such as diphenylamine, phenols, and salicylates.

NOTE: Aged propellants, or propellants containinq brominatable material other than ethyl centralite should he analyzed for ethyl centralite by Method 201.4.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5 g of the propellant, weighed to within 0.2 mg.

3. APPARATUS

3.1 Iodine titration flask (with stopper), 250 ml.

3.2 Volumetric flask, 100 ml.

3.3 Pipet, 25 ml.

4. MATERIALS

4.1 Glacial acetic acid.

4.2 Potassium iodide, 15-percent solution.

4.3 Hydrochloric acid, 38-percent solution.

4.4 Potassium bromate - bromide, 0.2N standard solution as specified in Method 605.1.

4.5 Sodium thiosulfate, 0.2N standard solution as specified in Method 602.1.

4.6 Starch indicator solution as specified in Method 701.1.

5. PROCEDURE

5.1 Prepare the specimen as described in Method 509.3.

5.2 Extract the specimen as described in Method 104.1.

5.3 Dissolve the dried residue of the extraction in 10 ml of glacial acetic acid.

5.4 If the nominal content of the ethyl centralite in the propellant is less than 4 percent, transfer the solution to the 250 ml iodine titration flask; rinse the extraction flask with several 10 ml portions of glacial acetic acid; and transfer the rinsings to the titration flask, using a total of 50 ml.

NOTE: If the ethyl centralite content of the propellant is between 4 and 6 percent, transfer the solution (par 5.3) to a 100 ml volumetric flask and make up to volume with glacial acetic acid. Measure a 50-ml aliquot of this solution, and transfer it to the titration flask. However, if the ethyl centralite content is over 6 percent, measure a 25ml aliquot of the 100 ml in the volumetric flask, transfer it to the titration flask, and add 25 ml of glacial acetic acid.

5.5 To the 50 ml solution, cooled to 20 to 25°C in the iodine titration flask, add 25 ml of the potassium bromate-bromide solution accurately measured to within 0.03 ml.

5.6 Moisten the stopper of the flask with a drop of 15 percent potassium iodide solution, and add 5 ml of 38-percent hydrochloric acid to the flask, noting the time. Stopper the flask immediately, swirl the contents for a few seconds, and allow the bromination to proceed for 1.0 ± 0.25 minutes from the time of addition of the hydrochloric acid.

5.7 At the end of the brominating time, add 10 ml of 15 percent potassium iodide solution, and swirl the contents of the flask.

NOTE: If an oil separates, add 25 ml of methylene chloride.

5.8 Wash down the gutter and walls of the flask with distilled water, and titrate the resulting solution immediately with 0.2N sodium thiosulfate solution until the solution assumes a light yellow color.

5.9 Add 5 ml of the starch indicator solution, and continue the titration carefully until the blue color of the solution disappears.

5.10 Make a blank determination, using 50 ml of glacial acetic acid and exactly the same volume of the potassium bromate-bromide solution (par 5.5).

5.11 Calculate the percentage of ethyl centralite in the specimen on a volatiles-free basis.

5.12 **Calculation:**

$$\text{Percent ethyl centralite} = \frac{6.71(A - B)\,N}{W}$$

Where:

A = Sodium thiosulfate required for the blank, ml.

B = Sodium thiosulfate required to titrate the liberated iodine in the solution containing the brominated specimen, ml.

N = Normality of the sodium thiosulfate solution.

W = Weight of the specimen corrected for total volatiles, g.

METHOD 203.5

DIETHYLPHTHALATE OR DIBUTYLPHTHALATE (ZINC REDUCTION-VOLUMETRIC METHOD)

1. SCOPE

1.1 This method is used for determining the diethylphthalate or dibutylphthalate content of propellants that do not contain interfering esters such as other phthalates, dimethyl sebacate, triacetin, or sucrose octaacetate.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5 g of the propellant weighed to within 0.2 mg.

3. APPARATUS

3.1 Filter paper, Whatman No. 41 or equivalent.

3.2 Erlenmeyer flask, 250-ml, with 24/40 ground glass joint, borosilicate glass.

3.3 Erlenmeyer flask, 300-ml, with 24/40 ground glass joint, alkali-resistant glass.

3.4 Watchglass.

3.5 Separatory funnel, 500 ml.

3.6 Beaker, 400 ml.

3.7 Medicine dropper.

3.8 Delivery pipets.

3.9 Reflux condenser water cooled.

3.10 Buret, 50 ml.

3.11 Steam bath in well-ventilated hood.

3.12 Hotplate.

4. MATERIALS

4.1 Diethyl ether, anhydrous

4.2 Zinc dust.

4.3 Glacial acetic acid

4.4 Petroleum ether, boiling point 30 to 60°C.

4.5 Ethyl alcohol, 95 percent.

4.6 Phenolphthalein indicator solution as specified in Method 703.1.

4.7 Potassium hydroxide, approximately 0.45 N alcoholic solution, prepared by dissolving 30 g of potassium hydroxide (85 percent) pellets in a mixture of 600 ml of ethyl alcohol and 50 ml of water, filtering through a Whatman No. 41 filter paper, diluting to 1 liter with ethyl alcohol in a borosilicate glass flask (alkali-resistant) sealing with a tight fitting rubber or plastic stopper.

4.8 Hydrochloric acid, 0.1N standard solution.

4.9 Hydrochloric acid, 1:1 by volume.

4.10 Hydrofluoric acid, 1:3 by volume.

5. **PROCEDURE**

5.1 Prepare the specimen as described in Method 509.3.

5.2 Extract the specimen as described in Method 104.1 using diethyl ether as the solvent and the 250 ml Erlenmeyer flask for receiving the extract.

5.3 Evaporate the extract to dryness as described in Method 104.1.

5.4 Add 6 g of zinc dust.

5.5 Add 20 ml of glacial acetic acid around the sides of the flask containing the dried residue and swirl to dissolve. Add 15 ml of water while swirling. Cover with a watch glass and heat to an incipient boil at moderate heat.

5.6 Remove the flask from the hotplate (remove and put aside the watchglass), swirl, and add a small portion of zinc dust. Swirl again and continue adding the zinc until 6 g have been added.

5.7 Cover the flask with the same watchglass, return to a cooler part of the hotplate, and heat for 5 minutes so that the solution effervesces strongly. Swirl the flask frequently during this period. Be sure that the solution effervesces strongly during the 5 minute period, but do not heat at more than gentle to moderate heat.

5.8 Remove the flask from the hotplate and cool to room temperature.

5.9 Wash down the watchglass and direct a stream of water from a wash bottle so as to wash down any loose zinc.

5.10 Add 200 ml of water, swirl, allow to settle, and decant into the 500 ml separatory funnel, leaving the zinc in the flask (a little zinc in the separatory funnel will do no harm).

5.11 Add 50 ml of water to the flask, swirl, allow to settle, and decant into the separatory funnel. Repeat with another 50 ml of water.

5.12 Add 60 ml of petroleum ether to the flask, swirl, allow to settle, and decant into the separatory funnel. Repeat with 60 ml of petroleum ether.

5.13 Shake the separatory funnel for a minute and allow the layers to separate.

5.14 Drain the aqueous solution into the 400 ml beaker while swirling the separatory funnel occasionally. Allow about 0.5 ml of the petroleum ether to drain off with the acqueous solution.

5.15 Decant the petroleum ether layer through the top of the separatory funnel into the alkali-resistant dry 300 ml Erlenmeyer flask while leaving about 0.5 ml of solution in the separatory funnel.

NOTE: A borosilicate glass Erlenmeyer flask can be used, but the result will be somewhat less accurate, because there is always some attack of the glass by the alkali used in the saponification.

5.16 Wash the contents of the 400 ml beaker back into the separatory funnel. Add 60 ml of petroleum ether to the original flask containing the zinc and decant into the separatory funnel. Extract as before and then make a third extraction with another 60 ml portion of petroleum ether.

5.17 Evaporate the petroleum ether as specified in Method 104.1

5.18 Add 10 ml of ethyl alcohol around the sides of the flask and swirl.

5.19 Add 3 or 4 drops of phenolphthalein indicator solution and cool.

5.20 Add alcoholic potassium hydroxide solution dropwise with a medicine dropper until the solution is just pink, and then add 0.1N hydrochloric acid dropwise with a medicine dropper until the pink color just disappears.

5.21 Add by means of a delivery pipet, a volume of alcoholic potassium hydroxide solution calculated to be a least twice that required to saponify the phthalate ester present.

5.22 Reflux for 30 minutes under a water condenser. If salts precipitate during the refluxing, add a small amount of water through the top of the condenser.

5.23 Add 50 ml of water through the top of the condenser and remove the flask.

5.24 Cover with a watchglass and cool to room temperature.

5.25 Add 3 or 4 drops of phenolphthalein indicator solution and titrate fairly rapidly with 0.1N hydrochloric acid until the disappearance of the pink color.

5.26 Conduct a blank titration, after neutralizing 10 ml of alcohol as described above, adding the same volume of alcolholic potassium hydroxide solution as was used for the sample, and refluxing for 30 minutes. Perform the calculation of 5.28.

5.27 Remove the zinc that adheres to the flask by rinsing with 1:1 hydrochloric acid. If a borosilicate glass is used for the saponification, allow it to soak for a few minutes occasionally in 1:3 hydrofluoric acid to remove the superficial etching produced by the alkali.

5.28 **Calculations:**

$$\text{Percent diethylphthalate} = \frac{11.11\,(A - B)\,N}{W}$$

or

$$\text{Percent dibutylphthalate} = \frac{13.92\,(A - B)\,N}{W}$$

Where:

A = ml of hydrochloric acid for blank titration.

B = ml of hydrochloric acid for titration of sample.

N = Normality of hydrochloric acid.

W = Weight of specimen (g), corrected for total volatiles.

METHOD 204.1.2

DIBUTYLPHTHALATE (DIFFERENCE METHOD)

1. SCOPE

1.1 This method is used for determining the percentage of dibutylphthalate in propellants.

2. PROCEDURE

2.1 Extract the specimen of propellant in accordance with Method 104.1.

2.2 Determine the total percentage of methylene chloride extractive matter in the propellant on a volatiles-free basis.

2.3 Determine the percentages of all methylene chloride extractive components in the propellant (except dibutylphthalate), using appropriate methods.

2.4 Subtract the sum of the determined percentages of all extractable matter (par. 2.3) from the total percentage of extraction matter (para. 2.2) to determine the percentaqe of dibutylphthalate.

METHOD 204.2.1

DIMETHYL, DIETHYL, AND DIBUTYL PHTHALATES (GAS CHROMATOGRAPHIC METHOD)

1. SCOPE

1.1 This method is used for determining the dimethyl, diethyl, or dibutyl phthalate content of double-base propellants containing less than 1% dinitrotoluene.

2. SPECIMEN

2.1 The specimen shall consist of approximately 10 g of the propellant weighed within 0.2 mg.

3. APPARATUS

3.1 Gas chromatograph equipped with a thermal conductivity cell.

3.1.1 Gas chromatographic column, 20% silicone SE-30 on acid-washed Chromosorb W (60/80 mesh). Column dimensions, 1/4 inch O.D. x 6 ft.

3.2 Volumetric flasks, 100 ml and 25 ml.

3.3 Syringe, 10-microliters.

4. MATERIALS

4.1 Methylene chloride.

4.2 Dimethyl phthalate.

4.3 Diethyl phthalate.

4.4 Dibutyl phthalate.

4.5 Triacetin.

4.6 Dimethyl sebacate.

4.7 Standard dimethyl phthalate solution (4%). Dissolve 4.000 g of dimethyl phthalate in methylene chloride and dilute to 100 ml with methylene chloride.

4.8 Standard diethyl phthalate solution (4%). Dissolve 4.000 g of diethyl phthalate in methylene chloride and dilute to 100 ml in a volumetric flask with methylene chloride.

4.9 Standard dibutyl phthalate solution (4%). Dissolve 4.000 g of dibutyl phthalate in methylene chloride and dilute to 100 ml in a volumtric flask with methylene chloride.

4.10 Standard triacetin solution (4%). Dissolve 4.000 g of triacetin in methylene chloride and dilute to 100 ml in a volumetric flask with methylene chloride.

4.11 Standard dimethyl sebacate solution (5%). Dissolve 5.000 g of dimethyl sebacate in methylene chloride and dilute to 100 ml in a volumetric flask with methylene chloride.

4.12 Helium.

5. PROCEDURE

5.1 Instrument conditions.

a. Column temperature, 200°C for dimethyl and/or diethyl phthalate and 230°C for dibutyl phthalate

b. Injection port temperature, 275°C.

c. Detector temperature, 275°C.

d. Carrier gas, helium at 35 ml per minute.

NOTE: The above conditions are suitable for the Aerograph Model 90 gas chromatograph. The conditions may vary with other instruments.

5.2 Preparation of calibration curves.

a. Dimethyl phthalate. Add 5.00 ml of standard triacetin solution (4%) to six 25 ml volumetric flasks. Add 2.50, 7.50, 10.00, 12.50, and 15.00 ml of standard dimethyl phthalate solution (4%) and dilute to the mark with methylene chloride. Adjust the chromatograph to the proper operating conditions and inject 10 microliters. The peaks for the triacetin and dimethyl phthalate emerge in about 2-1/2 and 4 minutes, respectively. Plot mg of dimethyl phthalate against the ratio of the peak areas of dimethyl phthalate and triacetin.

b. Diethyl phthalate. Proceed as described for dimethyl phthalate 5:2 (a) but use standard diethyl phthalate solution (4%). The peaks for triacetin and diethyl phthalate emerge in about 2-1/2 and 6-1/2 minutes, respectively.

c. Dibutyl phthalate. Proceed as described for dimethyl phthalate 5.2 (a) but use 5.00 ml of standard dimethyl sebacate solution (5%) (instead of the standard triacetin solution) and standard dibutyl phthalate solution (4%). The peaks for dimethyl sebacate and dibutyl phthalate emerge in about 4 and 10-1/4 minutes, respectively.

5.3 Analysis of samples.

a. Dimethyl phthalate. Extract a 10 g sample of the propellant overnight with approximately 90 ml of methylene chloride, using a Soxhelt extractor and 125 ml extraction flask as described in Method 104.1. Evaporate the extract to 5 to 10 ml by aeration. Transfer to a 25-ml volumetric flask with 5 to 8 ml of methylene chloride. Add 5.00 ml of standard triacetin solution (4%) and dilute to the mark with methylene chloride. Adjust the chromatograph to the proper operating conditions and inject 10 microliters. Calculate the ratio of the peak areas of dimethyl phthalate to triacetin, determine the mg of dimethyl phthalate by referring to the calibration curve, and calculate the present dimethyl phthalate.

b. Diethyl phthalate. Proceed as described for dimethyl phthalate 5.3 (a) but use the calibration curve for diethyl phthalate.

c. Dibutyl phthalate. Proceed as described for dimethyl phthaate 5.3 (a) but use 5.00 ml of standard dimethyl sebacate solution (5%) (instead of the standard triacetin solution). Use the calibration curve for dibutyl phthalate.

d. Dimethyl phthalate and diethyl phthalate in the presence of each other. Proceed as described for dimethyl phthalate 5.3 (a) but calculate the ratios of the peak areas of the dimethyl phthalate to the triacetin and use the appropriate calibration curve.

METHOD 205.1.2

DINITROTOLUENE (NITRATE ESTERS ABSENT)

1. SCOPE

1.1 This method is used for determining the dinitrotoluene content of propellants containing no nitrate esters.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5 g of the propellant, weighed to within 0.2 mg.

3. APPARATUS

3.1 Volumetric flask, 250 ml.

3.2 Titration flask (figure 1).

3.3 Pipet, 25 ml.

3.4 Reflux condenser.

3.5 Hotplate.

3.6 Buret, class A.

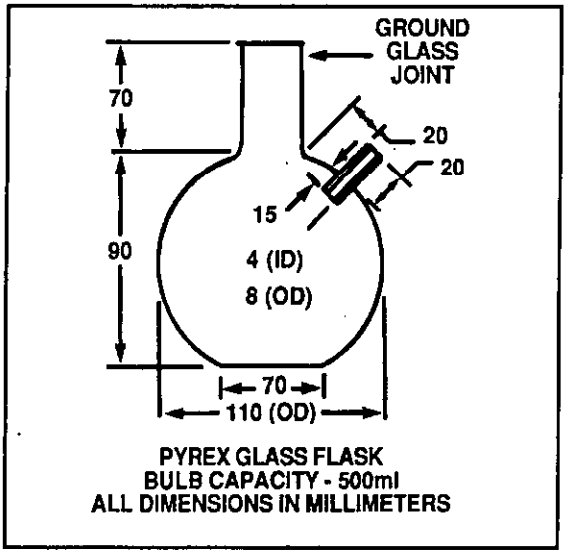


Figure 1. *Titration Flask.*

4. MATERIALS

4.1 Glacial acetic acid.

4.2 Inert gas (carbon dioxide or nitrogen)

4.3 Titanous chloride, 0.2N standard solution as specified in Method 601.1.

4.4 Ammonium thiocyanate, 20-percent solution as specified in Method 706.1.

4.5 Ferric ammonium sulfate, 0.15N standard solution as specified in Method 603.1.

4.6 Hydrochloric acid, 15-percent solution.

5. PROCEDURE

5.1 Prepare the specimen as specified in Method 509.3.

5.2 Extract the specimen and dry the extract as specified in Method 104.1.

5.3 Dissolve the dried residue in glacial acetic acid, and transfer the solution to a 250 ml volumetric flask. Dilute the flask to the mark with acetic acid.

CAUTION: Glacial acetic acid has a high coefficient of expansion. Therefore, to assure accuracy in measuring an aliquot of a solution containing glacial acetic acid, the solution must be maintained at a constant temperature until after the aliquot has been taken.

5.4 Attach a source of inert gas to the titration flask; allow the gas to flow gently for 5 minutes to displace the air in the flask. Continue the flow of gas through the flask throughout the remainder of the determination.

NOTE: After the solution has been added, the flow of gas should be adjusted so that it just ripples the surface of the solution.

5.5 After the inert gas has flowed for 5 minutes, rinse the pipet with the propellant extract solution, and transfer an accurately measured 25-ml portion of the solution to the titration flask.

5.6 From the detailed specification, ascertain the nominal percentage of dinitrotoluene present in the propellant. Add an accurately measured portion of the 0.2N titanous chloride solution (4 ml for each 1 percent of dinitrotoluene in the propellant) to the flask.

5.7 Add 25 ml of 15-percent hydrochloric acid and a few glass beads (to prevent bumping), and connect the flask to a reflux condenser.

5.8 Place the flask and condenser on a hot-plate, and boil the solution gently for 5 minutes. Without disconnecting the condenser, remove the flask from the hotplate.

5.9 Increase the current of inert gas (to keep air from entering the flask during cooling), and cool the solution to room temperature in a cold-water bath. Disconnect the condenser.

5.10 Add 5 ml of 20 percent ammonium thiocyanate solution, and titrate with the 0.15 N ferric ammonium sulfate solution to the end point, as indicated by the first permanent red color.

5.11 Conduct a blank determination, using 25 ml of glacial acetic acid, 25 ml of 15 percent hydrochloric acid, and exactly the same quantity of 0.2N titanous chloride solution added to the propellant extract solution. Titrate the blank solution with 0.15N ferric ammonium sulfate until near the end point. Then add 5 ml of 20-percent ammonium thiocyanate and titrate to the end point.

5.12 Calculate the percentage of dinitrotoluene in the propellant.

5.13 **Calculation:**

$$\text{Percent dinitrotoluene} = \frac{1.518\,(A - B)\,N}{W}$$

Where: A = Volume of ferric ammonium sulfate solution used for blank, ml.

B = Volume of ferric ammonium sulfate solution used for propellant, ml.

N = Normality of ferric ammonium sulfate solution.

W = Weight of specimen represented by aliquot taken, corrected for total volatiles, g.

METHOD 205.2.3

DINITROTOLUENE (NITRATE ESTERS PRESENT)

1. SCOPE

1.1 This method is used for determining the dinitrotoluene content of propellants containing a nitrate ester in admixture. Other reducible materials must be absent.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5 g of propellant, weighed to within 0.2 mg.

3. APPARATUS

3.1 The needed apparatus are described in Method 208.1.

4. MATERIALS

4.1 Ferric ammonium sulfate, 0.15N standard solution as specified in Method 603.1

4.2 Other needed materials are described in Method 208.1.

5. PROCEDURE

5.1 Determine the nitrate ester content of the specimen according to Method 208.1. Save the titrated solution for the determination of dinitrotoluene as follows:

a. Add to the titrated solution an accurately measured volume of 4 ml of titanous chloride solution for each percent (nominal) of dinitrotoluene in the propellant.

b. Connect the titration flask to the reflux condenser, and boil gently for 5 minutes. Cool to room temperature in cold water.

CAUTION: Toxic fumes may evolve during refluxing. A trap or hood should be provided.

c. Disconnect the condenser, and titrate the solution with 0.15N ferric ammonium sulfate solution until a permanent red color appears.

d. Run a blank determination using 25 ml of glacial acetic acid, 25 mL of 15 percent hydrochloric acid, and exactly the same quantity of 0.2N titanous chloride solution added to the solution in paragraph 5.1 (a). Titrate with 0.15N ferric ammonium sulfate solution until near the end point. Then add 5 ml of 20 percent ammonium thiocyanate solution and titrate to the end point.

e. Calculate the percentage of dinitrotoluene in the propellant.

f. **Calculation:**

$$\text{Percent dinitrotoluene} = \frac{1.518\ (A - B)\ N}{W}$$

Where:

A = Ferric ammonium sulfate solution required for the blank, ml.

B = Ferric ammonium sulfate required for the propellant extract solution, ml.

N = Normality of ferric ammonium sulfate solution.

W = Weight of the specimen represented by the aliquot taken, corrected for total volatiles, g.

METHOD 205.3.1

DINITROTOLUENE (INFRARED METHOD)

1. SCOPE

1.1 This method may be used for determining the dinitrotoluene content of propellants in which dinitrotoluene is the only extractable ingredients having strong infrared absorbance at 7.4 micrometers (1350 cm^{-1}).

2. SPECIMEN

2.1 The specimen shall consist of sufficient propellant to give an extract having absorbance of approximately 0.2 to 0.8 in the chosen cell under the conditions described in paragraph 5. A specimen of 5 g is satisfactory at the level of 5 to 15 percent dinitrotoluene, with dilution to 100 ml and cell path length of 0.2 mm. The specimen shall be weighed to within 0.2 mg.

3. APPARATUS

3.1 Extraction apparatus, Soxhlet or equivalent.

3.2 Volumetric flask, l00 ml or as required.

3.3 Double-beam infrared spectrophotometer.

3.4 Infrared spectrophotometer cells (two), matched, preferably with calcium fluoride or barium fluoride windows, suggested path length 0.2mm.

4. MATERIALS

4.1 Extraction solvent: methylene chloride.

NOTE: Diethyl ether should not be used because of its strong absorbance at 7.4 micrometers.

4.2 Infrared solvent, one of the following:

a. Methylene chloride.

b. 1, 2 Dichloroethane.

4.3 Dinitrotulene - MIL-D-204.

5. PROCEDURE

5.1 Prepare a calibration curve as follows:

a. Select a solvent from paragraph 4.2 and prepare solutions of known concentrations of dinitrotoluene in that solvent at the applicable concentration range. For 0.2 mm cells a suitable range is from 0.2 to 0.8 g per 100 ml.

b. Set the zero and 100% lines of the infrafred spectrophotometer at 7.4 micrometers (1350 cm^{-1}).

c. Fill the reference cell with solvent and place it in the reference beam.

d. Fill the sample cell with solvent and note the absorbance at 7.4 micrometers, not scanning. Record as solvent absorbance.

e. Taking each of the dinitrotoluene solutions in turn, scan the region approaching and including the peak of the absorbance band that occurs at about 7.4 micrometers. Record absorbance at the peak of the band. Subtract solvent absorbance to obtain net absorbance.

f. Prepare a graph of net absorbance vs dinitrotoluene concentration.

5.2 Determine correction for other ingredients as follows:

a. Prepare separate solutions of the extractable ingredients at known concentrations of about 0.2 and 0.4 g per 100 ml in the same solvent as in 5.1.

b. Determine the absorbance of each solution at 7.4 micrometers, not scanning. Subtract solvent absorbance to obtain net absorbance.

c. For each solution calculate:

$$A = \frac{B}{C}$$

Where:

A = Correction per g per 100 ml.

B = Net absorbance.

C = Concentration in g per 100 ml.

d. Calculate the average value of A for each ingredient.

e. For each ingredient in a particular propellant calculate the correction (in absorbance units) as follows:

Correction = A x D x E x 0.01

Where:

D = Grams of propellant per 100 ml of solution.

E = Nominal percent of the ingredient in the propellant.

5.3 Determine the dinitrotoluene in the propellant as follows:

a. Extract the specimen with methylene chloride.

b. Evaporate the methylene chloride if it was not the solvent chosen in paragraph 5.1 (a).

c. Dilute to 100 ml (or as required) with the solvent chosen in paragraph 5.1 (d).

d. Determine the solvent absorbance as in 5.1 (d).

e. Determine the absorbance of the propellant extracts as in 5.1 (e).

f. Subtract solvent absorbance to obtain net absorbance.

g. Subtract correction for each of the other extractable ingredients.

h. Determine the concentration of dinitrotoluene from the graph.

i. **Calculation:**

$$\% \text{ dinitrotoluene in propellant} = \frac{F \times G}{H}$$

Where:

F = Concentration in g per 100 ml from graph.

G = Volume of solution, ml.

H = Weight of specimen represented, g.

METHOD 206.1.2

TRINITROTOLUENE (NITRATE ESTERS ABSENT)

1. SCOPE

1.1 This method is used for determining the trinitrotoluene content of propellants containing no nitrate esters.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5 g of the propellant, weighed to within 0.2 mg.

3. APPARATUS

3.1 The apparatus used in this method is identical with that used in Method 205.1.

4. MATERIALS

4.1 The materials used in this method are identical with those used in Method 205.1

5. PROCEDURE

5.1 Follow the procedure described in Method 205.1 for the determination of dinitrotoluene in the propellant. However, in the determination of trinitrotoluene, add an accurately measured excess of 5 ml of 0.2N titanous chloride solution to the propellant extract solution of each 1 percent (nominal) of trinitrotoluene present (instead of the 4 ml of titanous chloride used for the determination of dinitrotoluene).

5.2 Calculate the percentage of trinitrotoluene in the propellant.

5.3 **Calculation:**

$$\text{Percent trinitrotoluene} = \frac{1.262\,(A - B)\,N}{W}$$

Where:

A = Ferric ammonium sulfate solution required for the blank, ml.

B = Ferric ammonium sulfate solution required for propellant extract solution, ml.

N = Normality of ferric ammonium sulfate solution.

W = Weight of the specimen represented by the aliquot taken, corrected for total volatiles, g.

METHOD 206.3.3

TRINITROTOLUENE (NITRATE ESTERS PRESENT)

1. SCOPE

1.1 This method is used for determining the nitrate ester and trinitrotoluene contents of propellants. Other reducible materials must be absent.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5 g of the propellant, weighed to within 0.2 mg.

3. APPARATUS

3.1 The apparatus used in this method is identical with that used in Method 205.2

4. MATERIALS

4.1 The materials used in this method are identical with those used in Method 205.2.

5 PROCEDURE

5.1 Follow the procedure described in Method 205.2. However, in the determination of trinitrotoluene, add an accurately measured excess of 5 ml of the 0.2N titanous chloride solution to the propellant extract solution for each 1 percent (nominal) of trinitrotoluene present (instead of the 4 ml of titanous chloride used for the determination of dinitrotoluene).

CAUTION: Toxic fumes may evolve during refluxing. A trap or hood should be provided.

5.2 Calculate the percentage of trinitrotoluene in the propellant.

5.3 **Calculation:**

$$\% \text{ trinitrotoluene} = \frac{1.262\,(A - B)\,N}{W}$$

Where:

A = Ferric ammonium sulfate solution required for the blank, ml.

B = Ferric ammonium sulfate solution required for the propellant extract solution, ml.

N = Normality of ferric ammonium sulfate solution.

W = Weight of the specimen represented by the aliquot taken, corrected for total volatiles, g.

METHOD 208.1.3

NITRATE ESTERS

1. SCOPE

1.1 This method is used for determining nitrate esters, such as nitroglycerin, in propellants containing no other component in admixture which can be reduced by ferrous ion.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5 g of the propellant, weighed to within 0.2 mg.

3. APPARATUS

3.1 Volumetric flask, 250 ml.

3.2 Titration flask (figure 1).

3.3 Pipet, 25 ml.

3.4 Reflux condenser.

3.5 Hotplate.

4. MATERIALS

4.1 Glacial acetic acid.

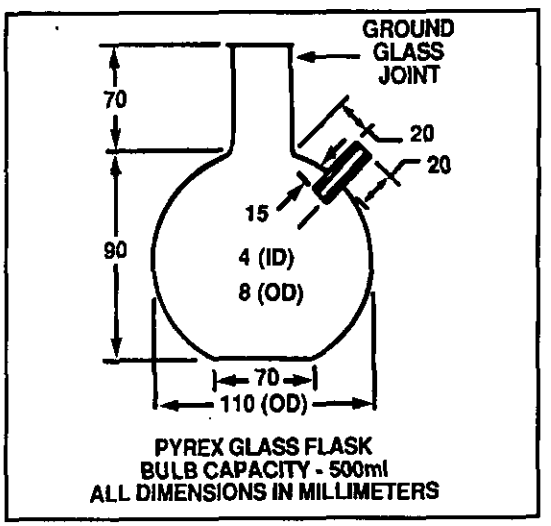


Figure 1. *Titration Flask.*

4.2 Titanous chloride, 0.2N standard solution as specified in Method 601.1.

4.3 Ferrous ammonium sulfate, 0.7N standard solution as specified in Method 604.1.

4.4 Ammonium thiocyanate, 20 percent solution as specified in Method 706.1

4.5 Hydrochloric acid, 15 percent solution.

4.6 Inert gas (carbon dioxide or nitrogen).

5. PROCEDURE

5.1 Prepare the specimen as specified in Method 509.3.

5.2 Extract the specimen and dry the extract as specified in Method 104.1.

5.3 Dissolve the dried residue in glacial acetic acid, and transfer the solution to a 250 ml volumetric flask. Dilute to the mark with glacial acetic acid. If the nitrate ester content is less than 5 percent transfer directly to a titration flask with 50 ml of glacial acetic acid.

CAUTION: Glacial acetic acid has a high coefficient of expansion. Therefore, to assure accuracy in measuring an aliquot of a solution containing glacial acetic acid, the solution must be maintained at a constant temperature until after the aliquot has been taken.

5.4 Attach a source of inert gas to the titration flask; allow the gas to flow gently for 5 minutes to displace the air in the flask. Continue the flow of gas through the flask throughout the remainder of the determination.

5.5 After the inert gas has flowed for 5 minutes, rinse the pipet with the propellant extract solution, and transfer an accurately measured portion of the solution to the titration flask so that it contains 0.1 to 0.2 g of nitroglycerin or the equivalent thereof.

5.6 Add 15 ml of 0.7 N ferrous ammonium sulfate and 25 ml of 15-percent hydrochloric acid solution to the flask.

5.7 Add a few glass beads to the flask (to prevent bumping), and connect the flask to the reflux condenser.

5.8 Place the flask on the hotplate and reflux the solution until the reduction is complete as indicated by the color change. Then without disconnecting the condenser, remove the flask from the hotplate.

NOTE: The color of the solution will change from yellow to dark green to reddish-brown or golden yellow as the reaction proceeds. Usually 5 minutes of refluxing is required, after the color change.

5.9 Increase the current of inert gas (to keep air from entering the flask during cooling), and cool the solution to room temperature by immersing the flask in cold water. Then disconnect the condenser.

5.10 Titrate the contents of the flask with 0.2N titanous chloride solution until near the end point, as indicated by the fading of the reddish-brown color of the ferric ion.

5.11 Add 5 ml of 20 percent ammonium thiocyanate solution to the flask to produce a deep red color.

5.12 Continue the titration until the deep red color of the ferric thiocyanate complex disappears. Record the total amount of titanous chloride used.

5.13 Conduct a blank determination following the procedure described in paragraph 5.3 through 5.12 substituting pure glacial acetic acid for the solution of the propellant extract in acetic acid. The blank titration should not exceed 0.5 ml.

5.14 ***Calculation:***

$$\text{Percent nitrate ester} = \frac{F\,(V - v)\,N}{W}$$

Where:

V = Titanous chloride solution required for propellant extract solution, ml.

v = Titanous chloride solution required for blank solution, ml.

N = Normality of titanous chloride solution.

W = *Weight of specimen represented by the aliquot taken, corrected for total volatiles.*

$$F = \text{Factor for nitrate ester} = \frac{A}{3n}$$

A = Molecular weight of nitrate ester.

n = Number of nitrate groups in ester compound.

NOTE: Commonly used factors are:

$$\text{Nitroglycerin} = \frac{227.11}{3(3)} = 25.23$$

$$\text{Triethyleneglycoldinitrate} = \frac{240.20}{3(2)} = 40.03$$

$$\textit{Diethyleneglycoldinitrate} = \frac{196.14}{3(2)} = 32.69$$

METHOD 208.2.2

NITROGLYCERIN (ACETIC ACID EXTRACTION METHOD)

1. SCOPE

1.1 This method is used for determining the nitroglycerin content of propellants manufactured from nitrocellulose containing not less than 12.2 percent nitrogen. If other reducible compounds, such as inorganic nitrates, are extracted the calculations must be corrected. Propellants containing nitrocellulose having a lower nitrogen content may yield high results. The method is inapplicable in the presence of reactive metals such as aluminum.

2. SPECIMEN

2.1 The specimen shall consist of approximately 3 g of the propellant, weighed to within 0.2 mg.

3. APPARATUS

3.1 Erlenmeyer flask, 500 ml.

3.2 Reflux condenser.

3.3 Filter paper, Whatman No. 4, or equivalent.

3.4 Volumetric flask, 250 ml.

3.5 Titration flask (figure 1).

3.6 Pipet, 50 ml.

3.7 Hotplate.

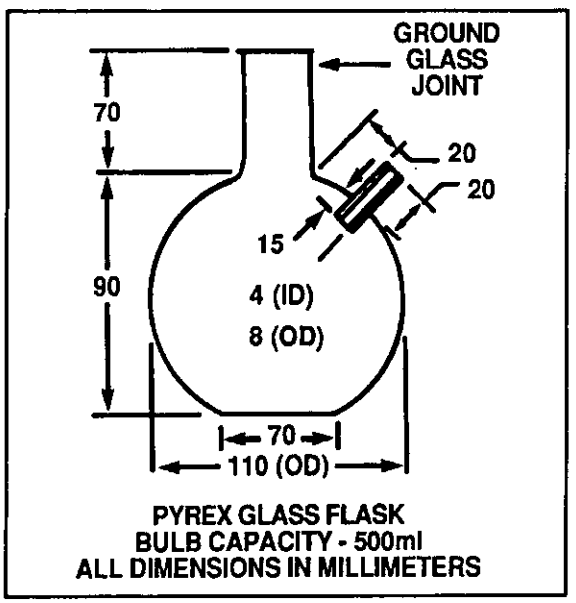


Figure 1. *Titration Flask.*

4. MATERIALS

4.1 Acetic acid solution, containing not less than 65 percent nor more than 70 percent acetic acid by weight. (Check by titrating with standard alkali).

4.2 Titanous chloride, 0.2N standard solution as specified in Method 601.1.

4.3 Ferrous ammonium sulfate, 0.7N solution as specified in Method 604.1

4.4 Ammonium thiocyanate, 20 percent solution as specified in Method 706.1.

4.5 Hydrochloric acid, 1:1 solution.

4.6 Inert gas (carbon dioxide or nitrogen).

5. PROCEDURE

5.1 Prepare the specimen as specified in Method 509.3.

5.2 Extract the specimen as follows:

a. Place the specimen in the Erlenmeyer flask, and add 100 ml of the acetic acid solution (para 4.1).

b. Connect the flask to a reflux condenser, and gently boil the contents of the flask on a hotplate for 30 minutes.

NOTE: The boiling should be vigorous enough to provide some agitation of the propellant particles, but not to cause bumping. If boiling does not appear to produce sufficient stirring, swirl the flask occasionally by hand.

c. After 30 minutes, remove the flask and condenser from the hotplate, and cool to room temperature in a cold-water bath.

d. When the flask is cool, remove the reflux condenser and rinse into the flask with acetic acid.

NOTE: As an alternative to steps (b), (c), and (d), loosely place a glass stopper on the Erlenmeyer flask and heat on a steam bath for at least 3 hours.

5.3 Filter the extract into a 250 ml volumetric flask. Rinse the Erlenmeyer flask and filter thoroughly with a little less than 100 ml of acetic acid solution, and dilute the filtrate to the mark with acetic acid. Mix thoroughly.

5.4 Attach a source of inert gas to the titration flask and allow the gas to flow gently for 5 minutes to displace the air in the flask. Continue the flow of gas through the flask throughout the remainder of the determination.

5.5 After the inert gas has flowed for 5 minutes, rinse the pipet with the propellant extract solution, and transfer an accurately measured aliquot to the titration flask. The aliquot should contain approximately 0.18 g of nitroglycerin.

5.6 Add accurately measured portions of 25 ml of 0.7N ferrous ammonium sulfate and 15 ml of the 1:1 hydrochloric acid solution to the flask.

5.7 Add a few glass beads to the flask (to prevent bumping), and connect the flask to the reflux condenser.

5.8 Place the flask and condenser on a hotplate, and boil the solution gently for 5 minutes. Then, without disconnecting the condenser, remove the flask from the hotplate.

NOTE: The color of the solution will turn from yellow to dark green to reddish-brown or golden yellow as the reaction proceeds.

5.9 Increase the current of inert gas (to keep air from entering the flask during cooling)and cool the solution to room temperature by immersing the flask in a cold-water bath.

5.10 Disconnect the flask from the condenser, and wash down the condenser and the joint rapidly with 30 ml of the acetic acid solution. Then reconnect the flask to the condenser, and allow the condenser to drain for a few minutes. Disconnect the flask.

5.11 Titrate the contents of the flask with 0.2N titanous chloride solution until near the end point, as indicated by the fading of the reddish-brown (or golden yellow) color of the ferric ion.

5.12 Add 5 ml of 20 percent ammonium thiocyanate solution to the flask.

5.13 Continue the titration until the deep red color of ferric thiocyanate complex disappears. Record the total amount of titanous chloride used.

5.14 Conduct a blank determination using 250ml of the acetic acid solution, 15 ml of the 1:1 hydrochloric acid, and exactly the same quantity of O.7N ferrous ammonium sulfate solution (para. 5.6).

5.15 Calculate the nitroglycerin content of the propellant.

5.16 **Calculation:**

$$\text{Percent nitroglycerin} = \frac{2.523\,(V - v)\,N}{W}$$

V = Volume of titanous chloride solution used for sample, ml.

v = Volume of titanous chloride used for blank, ml.

N = Normality of titanous chloride solution.

W = Weight of specimen represented by the aliquot taken, corrected for total volatiles, g.

METHOD 208.3.1

NITROGLYCERIN, PLASTICIZERS, AND STABILIZERS (LIQUID CHROMATOGRAPHY METHOD)

1. SCOPE

1.1 This method is used for determination of nitroglycerin, plasticizers, (such as phthalate esters), and stabilizers (such as ethyl centralite and 2-nitrodiphenylamine) in nitrocellulose-base propellants. Other formulated ingredients, impurities and degradation products having the same retention time as the desired components will interfere.

1.2 The ingredients are extracted from the propellant with methylene chloride. The solvent, methylene chloride is evaporated so that the extract can be transferred to a volumetric flask. The contents of the flask are diluted to the mark with methylene chloride. A 10 microliter sample is injected into the column and then the peaks are compared with standards.

2. SPECIMEN

2.1 The specimen shall consist of approximately 3 to 4 grams of the propellant weighed to within 0.5 mg.

3. APPARATUS

3.1 Liquid chromatograph equipped with constant mobile phase flow system, constant temperature heated column oven, a 254nm ultraviolet detector, and a fixed volume sample injector valve.

3.2 Sample injection valve (Rheodyne Model 7120 or equivalent), 10 microliters (or as required).

3.3 Integrator, electronic digital (Hewlett-Packard Model 3370B or equivalent) - Optional, See Note 7.1.

3.4 Recorder, 10-in, 1 mV, analytical

3.5 Column, 0.46 x 25 cm, reverse phase ODS-Sil-X-1 (Perkin Elmer No. 890-0707) or equivalent.

3.6 Flask, 100 ml, volumetric (or as required).

3.7 Flask, 250 ml, extraction.

4. MATERIALS

4.1 Methylene Chloride, Reagent Grade

4.2 Methanol, Reagent Grade

4.3 Water, Purified

4.4 Nitroglycerin (NG), MIL-N-246.

NOTE: Nitroglycerin is a highly explosive material and must be handled with extreme care.

4.5 Ethyl Centralite, MIL-E-255.

4.6 2-Nitrodiphenylamine (2 NDPA), MIL-N-3399.

4.7 Diethylphthalate, MIL-D-218.

4.8 Other stabilizers, highest available purity.

4.9 Other plasticizers, highest available purity.

5. CALIBRATION AND STANDARDIZATION

5.1 Prepare three or more standards, containing known weights of the components to be analyzed, in 100 ml volumetric flasks. (The concentration of the standards should cover the ranges expected for the samples). Weigh to an accuracy of ± 0.2 mg.

5.2 Dilute each standard to volume with reagent grade methylene chloride.

5.3 Test each standard per paragraph 6.3 and 6.4. The order of elution is shown in Figures 1 and 2.

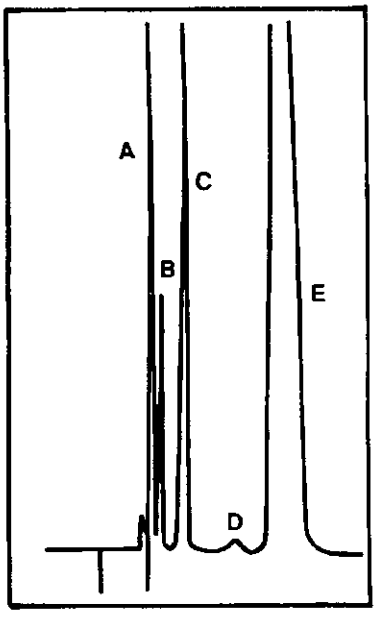


Figure 1
A - Extraction Solvent
B - Nitroglycerin
C - Diethylphthalate
D - Nitration Product of Ethyl Centralite
E - Ethyl Centralite

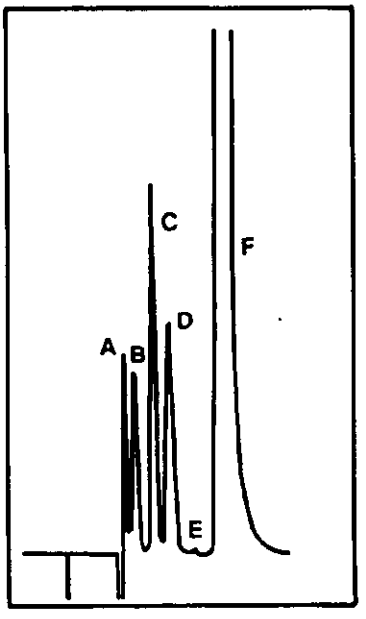


Figure 2
A - Extraction Solvent
B - Nitroglycerin
C - Impurity in 2-NDPA
D - Impurity in 2-NDPA
E - Impurity in 2-NDPA
F - 2-NDPA

5.4 Prepare a calibration cure for each component by plotting peak areas (or peak heights) vs concentrations of standards. Plots should be linear to assure sample weight, sample dilution, and size of injected sample are suitable for concentration of components in sample and for the liquid chromatograph employed. Once standardization linearity is established only two standards, representing concentration range of samples, are needed for future calibration.

5.5 Using peak areas (or peak heights), obtain the slope of each calibration curve as follows:

$$\text{Slope } (K_i) = \frac{Y_2 - Y_1}{X_2 - X_1}$$

Where:
Y = Peak areas of peak height
X = Corresponding concentration of standards

5.6 Determine the Y-axis intercept for calibration curve.

$$b = Y_2 - K_i X_2$$

Where:
b = Y axis intercept
Y = Peak area or peak height
X = Corresponding concentration of standard
K_i = Slope of calibration curve

5.7 Use the slopes and Y-axis intercepts to obtain a simplified equation for each ingredient to be calculated.

$$\text{Percent of ingredients in propellant (\% } C_i) = \frac{(A_1 + b)\,(100)}{(K_i)\,(Wg)}$$

Where:

A_1 = peak area (or peak height) of ingredient in test sample.

K_i = slope of calibration curve.

b = Y-axis intercept value.

Wg = grams of sample extracted.

6. PROCEDURE

6.1 Specimen. The specimen shall normally consist of approximately 3 to 4 g of propellant weighed to within 0.5 mg. The sample weight may be adjusted based on concentrations of components in the propellants.

6.2 Sample preparation.

a. Prepare the specimen as described in Method 509.3 of MIL-STD-286.

b. Extract the specimen as described in Method 104.1 of MIL-STD-286 with reagent grade methylene chloride.

c. Using a steam chest, evaporate enough extraction solvent from the extraction flask so that the extract can be quantitavely transferred to a 100 ml volumetric flask (or as required).

d. Dilute the contents of the flask to volume with reagent grade methylene chloride.

e. Sample is ready to be tested once the instrument has stabilized.

6.3 Instrument Conditions.

a. Wavelength of detector: 254nm.

b. Column temperature: 50°C.

c. Mobile phase: Degassed methanol/water (50/50 by volume).

NOTE: Solvent ratio may be varied to aid in separation of components.

d. Mobile phase flow rate : 1.3 ml/min (approximately 700 psig).

NOTE: 1 psi = 6.9 kPa

e. Sample size: 10.0 microliters (or as required).

f. Recorder speed: 0.2 in/min (or as required).

6.4 Sample testing.

a. Once the liquid chromatograph has stabilized, inject 10.0 microliters of the prepared sample into the liquid chromatograph and monitor peak areas with the electric digital inctegrator or peak heights with the recorder.

b. Components will elute from the column through the detector as shown in Figures 1 and 2. For other components not shown in these figures, identify their retention times prior to testing.

c. Using the integrated peak area (or peak heights), calculate the percentage of ingredients by the simplified equations obtained during calibration.

7. NOTES

7.1 Liquid chromatograph ultraviolet detectors are concentration detectors and constant mobile phase flow rate is a necessity to obtain reproducible peak areas.

7.2 If additional precision is necessary for product evaluation or control, an internal standard may be employed and the ratio of component to internal standard peak areas (or peak heights) may be used in the equations in place of peak areas (or peak heights). The internal standard can be any component that does not interfere with the chromatographic separation and is compatible with the propellant components. Diethylphthalate may be used in the testing of M30 and M26 propellant extracts for NG and ethyl centralite.

METHOD 208.4.1

NITRATE ESTERS, STABILIZERS, AND PLASTICIZERS (GAS-LIQUID CHROMATOGRAPHIC METHOD)

1. SCOPE

1.1 This method is used for qualitatively and quantitatively determining combination of nitrate esters, stabilizers, and plasticizers in nitrocellulose-base propellants. Specific components that have been determined are listed in Table I.

2. SPECIMEN

2.1 The specimen shall consist of a 5 to 10 gram representative propellant sample ground to pass a US No. 20 sieve accordin method 509.3 The ground specimen shall be immediately placed in a sealed glass container. Small samples of this specimen are used for propellant testing.

3. APPARATUS

3.1 Gas chromatograph (Hewlett-Packard Model 5711A or equivalent) with "on-column" injection port, a linear temperature programmer, a dual flame-ionization detector, and dual flow controllers.

3.2 Integrator, electronic digital (Hewlett-Packard Model 3370 B or equivalent).

3.3 Tubing, chromatographic grade type 304 stainless steel, 3.2 mm OD, solvent washed (Hewlett-Packard or equivalent).

3.4 Columns, 3.2 mm x 91.4 cm stainless steel, packed with 5 wt % OV-101 on 80 to 100 mesh GAS-CHROM Q.

3.5 Columns, 3.2 mm x 45.7 cm stainless steel, packed with 1.0 to 1.5 wt % OV-225 on 80 to 100 mesh GAS-CHROM Q.

3.6 Recorder, gas chromatographic, 1-mv fullscale (Hewlett-Packard Model 7127A or equivalent).

3.7 SONIFIER, cell disruptor with standard microtip (Heat Systems - Ultrasonics, Inc., Model W185 or equivalent).

3.8 Centrifuge.

3.9 Mixer/mill (Spex Industries, Inc., Model 5100 or equivalent).

3.10 Syringe, 10 µl (Hamilton type 701-N or equivalent).

3.11 Balance, micro (Perkin Elmer Model AD-2 or equivalent).

3.12 Fluidizer (Applied Science Laboratories, Inc., Model HI-EFF or equivalent).

3.13 Pans, sample, aluminum (Perkin Elmer differential scanning calorimeter or equivalent).

3.14 Tubes, test, 13 x 100 mm.

3.15 Vials, glass, 1 dram (Laboratory Apparatus Company "Titeseal" or equivalent).

3.16 Pipets, Pasteur type, disposable, 14.6 cm length.

4. MATERIALS

4.1 1, 2-Dichloroethane, chromatographic grade.

4.2 Powder, 10% nitroglycerin-B-lactose.

4.3 Nitrate esters, highest available purity.

4.4 Stabilizers, highest available purity.

4.5 Plasticizers, highest available purity.

4.6 Acetone.

4.7 Diethyl phthalate.

4.8 Hydrocarbons, saturated aliphatic, C_{12} -C_{34}, highest available purity.

4.9 N, 0-bis (trimethylsilyl) acetamide (BSA).

4.10 Stationary phase, OV-101.

4.11 Stationary phase, OV-225.

4.12 Solid support, GAS-CHROM Q, 80 to 100 mesh.

4.13 Hydrogen, ultra pure.

4.14 Helium, high purity.

4.15 Air, breathing, water pumped, high purity.

5. PROCEDURE

5.1 Column Preparation.

5.1.1 Prepare a 20 g batch of each packing using a filtration-fluidization method according to the instructions supplied with the fluidizer. Dry the filtered, damp packing with the fluidizer.

5.1.2 Clean the correct lengths of stainless steel 3.2 mm OD tubing with 200 ml of acetone each, and remove the residual acetone by passing dry air through the tubing.

5.1.3 Fill dual columns with each packing material (OV-101 and OV-225) by incremental addition while tapping the tubing. Each filled column should contain a minimum of 450 mg of packing per foot.

5.1.4 Coil the dual columns of each type to the proper configuration, and condition them in the chromatograph oven overnight at the following temperatures while maintaining a helium carrier gas flow of 10 to 15 ml/min: OV-101: 275°C, OV-225: 225°C.

5.1.5 Before using the conditioned columns for nitrate ester determinations, check the linearity of the nitroglycerin response as a function of nitroglycerin amount analyzed as follows:

5.1.5.1 Prepare a nitroglycerin standard solution comprised of 0.1 to 0.15 g ± 0.1 mg of 10% nitroglycerin-B-lactose powder, and 2 to 3 mg ± 2 ug of diethyl phthalate internal standard in 1 ml of 1,2-dichloroethane according to the procedure of paragraph 5.3.1.3. Analyze four replicates each of 1-µl and 3-µl aliquots according to paragraph 5.3.3, and calculate the calibration factors for each series of aliquots.

5.1.5.2 Determine by a "t"-test whether there is a significant difference between the averages of the two aliquot sizes at the 5% significance level. If there is no significant difference, the columns are suitable for the precise and accurate determination of nitrate esters. Otherwise, a higher quality batch of packing must be made by the procedure of paragraph 5.1.1. This procedure consistently produces suitable, high quality packings. Other procedures are generally not suitable.

5.1.6 After extended use a column may become unsatisfactory for determining nitrate esters because of contamination or decomposition at the injection end. If this occurs, rejuvinate the column by removing 3 to 5 cm of the packing from the injection end, replacing it with unused packing, and reconditioning the column for 4 hours at the original conditioning temperature.

5.2 Instrument Conditions.

5.2.1 Set the flame ionization detector temperature at 250°C, and the initial column oven temperature at 70°C. These temperatures must be fully equilibrated before proceeding with the analysis of samples. Set the electrometer range to give a minimum sensitivity of 5×10^{-10} amperes fullscale (AFS) on the 1-mV recorder. However, insure that all signals are within the linear dynamic ranges of both the electrometer and the detector.

5.2.2 Pass all gases through molecular sieve type driers before they enter the chromatograph. Adjust the helium carrier gas flow to 40 ml/min on both columns with the dual flow-controllers. Adjust the flame detector hydrogen and air flows to the values recommended by the manufacturer or, if these are not available, to obtain maximum sensitivity. The correct adjustments for the 5711A chromatograph are 40 ml/min for hydrogen, and 240 ml/min for air.

5.3 Calibration

5.3.1 Assay of Nominal 10% Nitroglycerin-B-Lactose Powder.

5.3.1.1 This assay is performed only when a new lot of 10% nitroglycerin-B-Lactose powder is received, to verify the manufacturer's nominal percentage of nitroglycerin. Thereafter the assayed powder is used instead of more hazardous neat nitroglycerin for all nitroglycerin calibrations.

5.3.1.2 Prepare four calibration mixtures for assay of the powder as follows: Weigh 10 to 15 mg ± 10 µg of pure, neat nitroglycerin, and 2 to 3 mg ± 2 µg of diethyl phthalate internal standard into a 1-dram glass vial for each mixture using the aluminum sample pans and the microbalance. Add 1 ml of 1,2-dichloroethane to each vial, and shake the sealed vials on the mixer/mill for 1 minute. Analyze a 1-µl aliquot from each mixture according to paragraph 5.3.3, and calculate the average nitroglycerin calibration factor.

WARNING: Neat nitroglycerin and other nitrate esters are explosive materials, and must be handled with extreme care.

5.3.1.3 Prepare four 10% nitroglycerin-B-lactose powder samples for nitroglycerin assay as follows:

Weigh 0.1 to 0.15 g ± 0.1 mg of the powder, and 2 to 3 mg ± 2 µg of diethyl phthalate internal standard into a 1-dram glass vial for each sample, using the aluminum sample pans and the microbalance for the internal standard weighings. Add 1 ml of 1,2-dichloroethane to each vial, and shake the sealed vials on the mixer/mill for 5 minutes to extract the nitroglycerin. Centrifuge the vials for 10 minutes. Then analyze a 1-µl aliquot from each sample vial according to the procedure in paragraph 5.3.3. Calculate the average percentage of nitroglycerin in the powder as shown in paragraph 5.5.2.

5.3.2 Preparation of Calibration Mixture.

5.3.2.1 Select the appropriate column(s) and internal standard for the components to be determined based on the retention data in Table I. The internal standard can be any saturated aliphatic hydrocarbon, stabilizer, or plasticizer that does not interfere with separation of the propellant components.

5.3.2.2 Prepare duplicate calibration mixtures of components to be analyzed as follows:

Weigh 0.1 to 0.15 g ± 0.1 mg of 10% nitroglycerin-B-lactose powder, 4 to 6 mg ± 4 µg of each additional nitrate ester, 2 to 3 mg ± 2 µg of the internal standard, and 2 to 3 mg ± 2 µg of each stabilizer and plasticizer for each mixture into a 1-dram glass vial. Use the aluminum sample pans and the microbalance for weighing all components except the 10% nitroglycerin-B-lactose powder, and transfer the pans to the vials with the components. Add 1 ml of 1,2-dichloroethane to each vial, shake the sealed vials on the mixer/mill for 5 minutes, then centrifuge them for 10 minutes.

5.3.2.3 For the determination of resorcinol or other components containing active hydrogen, prepare the calibration mixtures or the chromatographic columns by one of the following methods.

5.3.2.3.1 Method 1: Transfer the supernatant liquid from each calibration mixture in paragraph 5.3.2.2 to a dry 1-dram glass vial with a disposable pipet. Add 0.5 ml of BSA to each vial, shake the solutions by hand, and allow them to stand for 10 minutes to form the trimethylsilyl (TMS) derivatives. Analyze 1-µl aliquots of these mixtures on either the OV-101 or OV-225 column.

5.3.2.3.2 Method 2: Pretreat the OV-225 column before each series of component (resorcinol) determinations by analyzing a 2-µl aliquot of a 5-mg/ml solution of the component (resorcinol) in 1,2 dichloroethane. Perform the analysis in the same manner as for the calibration mixture. Then analyze the calibration mixtures of paragraph 5.3.2.2 without silylation.

5.3.3 Inject, with the 10-µl syringe, a 1-µl aliquot of each of the calibration mixtures "on-column" at 70°C. Immediately program the column oven temperature at the rate of 8°C/min until the last

component elutes. Do not exceed a temperature of 240°C, or the column conditioning temperature. Measure the area of each component peak with the electronic digital integrator, and calculate the calibration factor of each component from:

$$Fc = \frac{A_s W_c}{A_c W_s}$$

Where:

F_c = component calibration factor

A_s = internal standard peak area

A_c = component peak area

W_s = milligrams of internal standard

W_c = milligrams of component

5.3.4 Re-establish the nitrate ester calibration factors at the beginning of each day's analyses or anytime the detector temperature is changed. Re-establish the stabilizer and plasticizer calibration factors less frequently, based on individual experience.

5.4 Sample Preparation.

5.4.1 Weigh duplicate 0.1 to 0.15 g ± 0.1 mg propellant samples (20 mesh) into 13 x 100 mm test tubes. Weigh 2 to 3 mg ± 2 µg of the same internal standard used in the calibration mixtures into aluminum pans on the microbalance. Add the internal standard and pan, and 2 ml of 1,2 dichloroethane to each tube.

5.4.2 Suspend each sample test tube in a water-filled container, which acts as a heat sink. Then position the microtip of the SONIFIER in the 1, 2-dichloroethane, adjust the ultrasonic power to given maximum cavitation, and extract the propellant components for 15 minutes. Cover the tubes with aluminum foil, and centrifuge them for 10 minutes.

5.4.3 For the determination of resorcinol or other components containing active hydrogen, treat 1-ml of the extract or the OV-225 column as described in paragraph 5.3.2.3.1 or 5.3.2.3.2 for the calibration mixture before performing the sample testing.

5.5 Sample Testing.

5.5.1 Using the same column(s) selected for the calibration mixture analysis, inject a 1-µl aliquot of each sample extract "on column" at 70°C. Immediately program the column oven temperature at the rate of 8°C/min until the last component elutes, then return the temperature to 70°C. Do not exceed an oven temperature of 240°C or the column conditioning temperature. If the sample contains extraneous high boiling compounds having significant peak areas, hold the column temperature at 240°C until these elute before returning to the initial temperature.

5.5.2 Measure the area of each component peak with the electronic digital integrator, and calculate the percentage of each component in the propellant samples from the expression.

$$W_C\ \% = \frac{A_C F_C W_S}{A_S W_P} (100)$$

Where:

W_C% = component weight percent.

W_P = milligrams of propellant sample.

5.5.3 Typical gas chromatograms for the testing of a double-base propellant are given in Figure 1.

5.5.4 The estimated relative standard deviations of individual aliquot determinations within samples are 0.4 to 1.5% for nitrate esters, depending mainly on column quality, and 0.2 to 0.7% for stabilizers and plasticizers.

5.5.5 Qualitatively determine components in unknown propellants by establishing their relative retention times, or Kovats indices on both columns, and comparing them with the data in Table I.

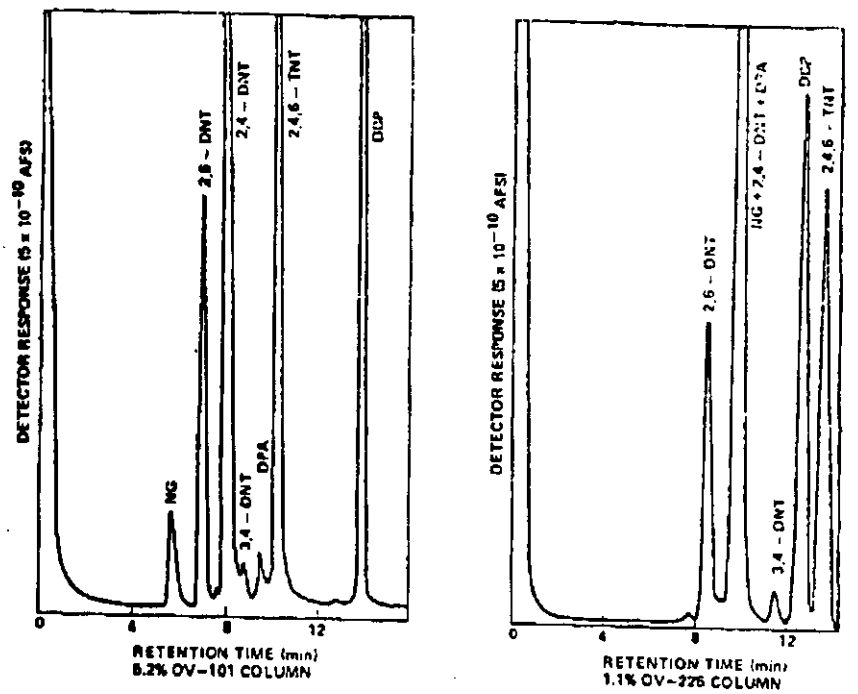


Figure 1. Typical gas chromatograms for double-base propellant testing showing separation of nitroglycerin (NG); 2,6-dinitrotoluene (2,6-DNT); 2,4-dinitrotoluene (2,4-DNT); 3,4-dinitrotoluene (3,4-dnt); diphenylamine (DPA); 2,4,6-trinitrotoluene (2,4,6-TNT); and di-n-butyl phthalate (DBP).

TABLE I. GAS-LIQUID CHROMATOGRAPHIC RETENTION DATA FOR NITROCELLULOSE-BASE PROPELLANT COMPONENTS

	Adjusted Retention Time		Relative Retention Time		Kovats Index		Retention Temperature (°C)	
Component	OV-101[a]	OV-225[b]	OV-101	OV-225	OV-101	OV-225	OV-101	OV-225
Resorcinol	5.30	10.60	0.57	1.20	1277	2273	114	156
Diethylene glycol dinitrate	5.49	7.60	0.60	0.86	1290	1989	115	132
Nitroglycerin	5.70	9.53	0.62	1.08	1305	2169	117	147
Triacetin	5.88	6.11	0.64	0.69	1317	1856	118	120
TMS-Resorcinol	6.81	2.91	0.74	0.33	1380	1563	126	94
2,6 Dinitrotoluene	6.96	8.42	0.75	0.95	1390	2065	127	139
Dimethyl phthalate	7.21	7.45	0.78	0.84	1408	1975	129	131
2,4 Dinitrotoluene	8.04	9.79	0.87	1.10	1466	2193	135	149
Trimethylolethane trinitrate	8.54	11.33	0.92	1.28	1501	2346	139	162
1,2,4 Butanetriol trinitrate	8.63	11.91	0.94	1.35	1507	2404	140	166
3,4 Dinitrotoluene	8.79	11.61	0.95	1.31	1518	2374	141	164
Di-n-propyl adipate	9.19	7.21	1.00	0.82	1546	1954	145	129
Diethyl phthalate	9.23	8.83	1.00	1.00	1549	2103	145	142
Triethylene glycol dinitrate	9.36	11.08	1.01	1.25	1558	2321	146	160
Diphenylamine	9.56	9.55	1.04	1.08	1572	2171	148	148
Dimethyl sebacate	10.17	8.38	1.10	0.95	1616	2061	152	138
2, 4, 6-Trinitrotoluene	10.34	13.65	1.12	1.55	1628	2591	154	180
N-methyl-p-nitroaniline	10.45	13.91	1.13	1.58	1637	2621	155	182
Diethanolnitramine dinitrate	10.54	15.53	1.14	1.76	1644	2807	155	195
TMS-Phloroglucinol	10.76	6.04	1.17	0.68	1660	1850	157	120
2,4,5-Trinitrotoluene	11.47	15.58	1.24	1.76	1714	2814	163	196
Methyl Centralite	12.30	11.43	1.33	1.29	1777	2356	170	163
Diphenylurethane	12.48	11.65	1.35	1.32	1790	2378	171	164
Ethyl centralite	13.12	11.14	1.42	1.26	1842	2327	176	160
2-Nitrodiphenylamine	13.77	13.47	1.49	1.52	1895	2572	181	179
Di-n-butyl phthalate	13.97	12.61	1.51	1.43	1912	2480	183	172
Phloroglucinol	14.39	18.03	1.56	2.04	1947	3124	186	215
TMS-Akardit-I	14.52	13.14	1.57	1.49	1957	2537	187	176
Akardit-II	14.82	15.74	1.61	1.78	1982	2833	190	197
Akardit-I	15.66	17.10	1.70	1.94	2056	3001	196	208
Di-n-butyl sebacate	16.56	13.44	1.79	1.52	2137	2569	204	179
Di(2-ethylhexyl)adipate	18.93	15.18	2.05	1.72	2362	2767	223	193
Di(2-ethylhexyl) phthalate	20.07	17.28	2.18	1.96	2479	3025	232	209

a. 5.2% stationary phase loading.

b. 1.1% stationary phase loading.

METHOD 208.5.1

NITROGLYCERIN, 2-4 DINITROTOLUENE DIPHENYLAMINE AND DIBUTYLPHTHALATE (LIQUID CHROMATOGRAPHY METHOD)

1. SCOPE

1.1 This method may be used for the determination of Nitroglycerin (NG), 2-4 Dinitrotoluene (DNT), Diphenylamine (DPA) and Dibutylphthalate (DBP) in spherical powder.

1.2 The ingredients of the propellant are extracted with methanol and an internal standard solution and injected into a column and then the peaks are compared with a standard.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5.0 g of the propellant weighed to within ± 0.5 g.

3. APPARATUS

3.1 Perkin-Elmer Model 601 Liquid Chromatograph or equivalent with column oven (temperature controlled) and a 3 µl fixed loop injector.

3.2 Perkin-Elmer Model LC55 Variable Wavelength UV Detector or its equivalent, interfaced to a PEP-II computer or equivalent.

3.3 Magnetic stirrer and bar.

3.4 60 ml bottle and stopper.

3.5 1-liter Volumetric flask.

4. REAGENTS AND STANDARDS

4.1 Methanol - Reagent

4.2 Acetone - Reagent Grade

4.3 Methyl Centralite - Reagent Grade

4.4 Hexane, UV Grade

4.5 Isopropyl Alcohol (IPA) - Reagent Grade.

5. CALIBRATION AND STANDARDIZATION

5.1 Liquid Chromatograph Advisory Conditions:

Solvents - 1% by volume IPA in Hexane
Flow Rate - 1.0 ml/min
Injection Volume - 3 µl loop
Column Oven Temperature - 55°C
Pressure - 300 to 500 psig
Column - 25 cm x 2.5 mm Cyano-Sil-X-I

NOTE: 1 psi = 6.9kPA

5.2 Variable Wavelength UV Detector Conditions:

Wavelength - 208 nm
Filter Setting - 0
Readout Mode - Absorbance

5.3 Preparation of Internal Standard

6.0 grams ± 0.1 mg of Methyl Centralite/liter of acetone.

5.4 Preparation of standard.

a. DPA, DBP, DNT Standard solution

Weigh 0.12 g DPA, 0.65 g DBP, and 0.05 g DNT (to nearest 0.1 mg) into a 100 ml volumetric flask. Add 5 ml of internal standard, fill to volume with absolute methanol.

b. Calculate percent as $\%\text{ in 10 ml} = \frac{(\text{Wt. of compound})\ (100)}{10}$

c. Dissolve by inverting bottle

d. Fill loop with sample and inject into liquid chromatograph.

e. Identify each peak and measure area for DNT, DPA, DBP, NG, and Methyl Centralite (see figure 1 for chromatogram and relative retention times).

6. PROCEDURE

6.1 Add 5 ml of Internal Standard solution and 20 ml of methanol to a 60 ml bottle.

6.2 To this, add 1.00 gram of spherical powder (to the nearest 0.1 mg).

6.3 Place magnetic stirrer in bottle and stopper.

6.4 Stir for 30 minutes.

6.5 Fill loop injector with sample (solvent) and inject into the liquid chromatograph.

6.6 Identify each peak and measure the area for DNT, DPA, DBP, NG and Methyl Centralite.

6.7 **Calculation:**

$$\% \text{ Diphenylamine} = \frac{B \times C \times 100}{A \times D}$$

$$\% \text{ Dinitrotoluene} = \frac{B \times C \times 100}{A \times D}$$

$$\% \text{ Nitroglycerin} = \frac{B \times C \times 100}{A \times D}$$

$$\% \text{ Dibutylphthalate} = \frac{B \times C \times 100}{A \times D}$$

Where:

$A = \frac{\text{area of internal standard in sample}}{\text{area of peak of interest in sample}}$

$B = \frac{\text{area of internal standard in standard}}{\text{area of peak of interest in standard}}$

C = Weight of component in standard

D = Weight of sample

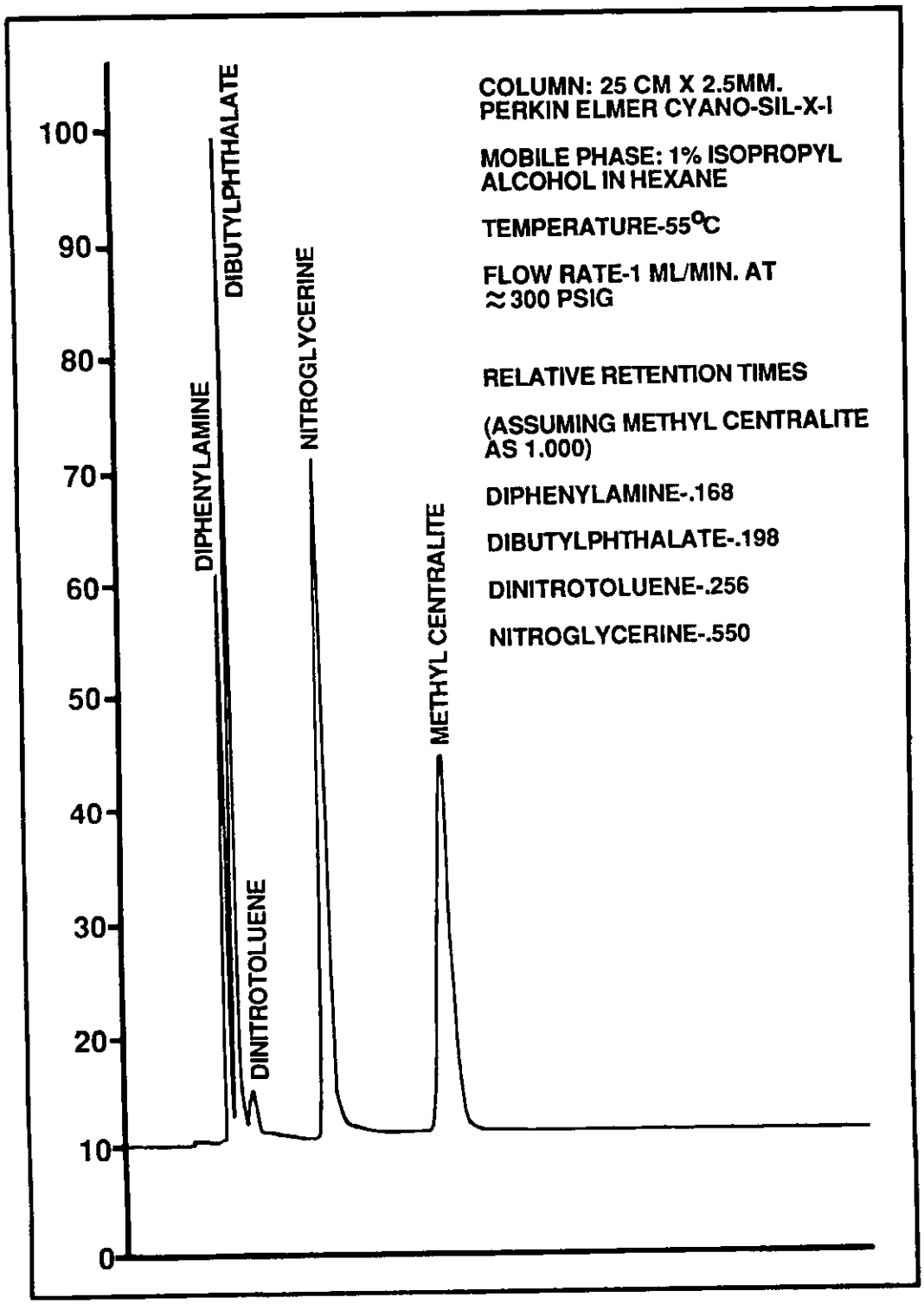


Figure 1. *Separation of Diphenylamine, Dibutylphthalate, Dinitrotoluene & Nitroglycerin*

METHOD 209.2.1

NITROCELLULOSE (DIFFERENCE METHOD)

1. SCOPE

1.1 This method is used for determining the nitrocellulose content of propellants.

2. PROCEDURE

2.1 Determine the percentages of all other ingredients in the propellant, using appropriate methods.

2.2 Subtract from 100 percent the sum of the percentages of the other ingredients.

METHOD 209.3.2

NITROCELLULOSE (NITROMETER METHOD)

1. SCOPE

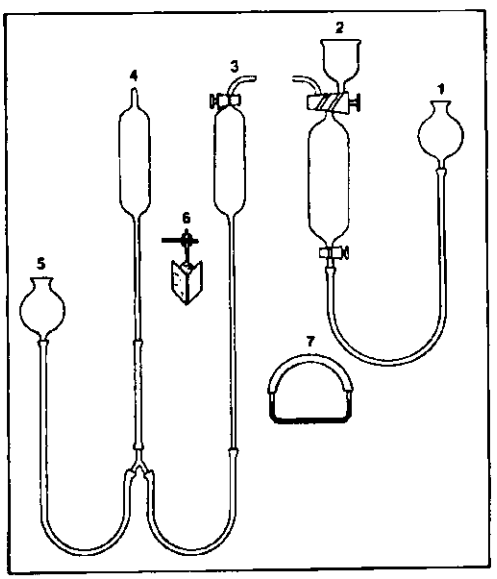
1.1 This method is used for determining the nitrogen content of nitrocellulose.

2. SPECIMEN

2.1 A portion of the nitrocellulose shall be air-dried at a temperature not above 46°C. A specimen of about 1 g shall be transferred to a tared weighing bottle dried for 1.5 hours at 100 ± 2°C, cooled in a desiccator and weighed to within 0.2 mg.

3. APPARATUS

3.1 Nitrometer, duPont (5-part), or equivalent (figure 1).



Key

1. Mercury Reservoir
2. Gas Generating Bulb
3. Measuring Tube
4. Compensating Tube
5. Mercury Reservoir
6. Reading Mirror
7. U-Tube Leveling Device

Figure 1. *Dupont Nitrometer*

3.2 Levelling device. Either the U tube or the reading mirror shown in figure 1 may be used.

3.3 Weighing bottles, ground glass stoppered, 50 mm high by 25 mm diameter.

3.4 Desiccator containing an indicating desiccant (Drierite or equivalent).

4. MATERIALS

4.1 Potassium nitrate.

4.2 Sulfuric acid, stet-diluted to 94.5 ± 0.5 percent (nitrogen-free).

5. PROCEDURE

Note: Technician should wear a full face shield in addition to safety glasses and acid resistant lab coats during the initial shaking of the reaction vessel for both standard and sample analysis.

Note: Gas vented from the measuring tube after the test is complete should be removed in such a manner as to prevent release within the operators breathing zone. The gas contains toxic nitric oxides.

5.1 Assemble the nitrometer as follows:

a. Clean and dry all parts of nitrometer, and assemble them on the rack.

b. Completely fill all parts except the reservoirs with mercury.

c. Either dry air or nitrogen may be used for standardization. The latter is preferable since air slowly reacts with the mercury to form a scum that obscures the surface. If air is used, it should be dried as described in 5.1 (d) and (e).

d. Place 25 mL of concentrated, sulfuric acid in the cup of the generating bulb, and open both stopcocks on the generating bulb. Draw the sulfuric acid, together with air, into the bulb by lowering the mercury reservoir until the mercury in the bulb is at the level of the lower shoulder of the bulb.

e. Close both stopcocks and shake the generating bulb vigorously for 3 minutes, replace the bulb on the rack and allow to stand for at least 15 minutes.

f. Connect the (unsealed) upper end of the compensating tube to the generating bulb, making sure that the connecting, compensating and measuring tubes are completely filled with mercury.

g. Open the upper stopcock and, by regulating the heights of the two mercury reservoirs, transfer sufficient dry air or nitrogen from the generating bulb to fill the compensating tube to a level about 14 inches below the bulb.

h. Adjust the columns of mercury in the compensating and measuring tubes to the same level (about 14 inches on the compensating tube and 12.5 mark on the measuring tube. The stopcocks on the generating bulb and measuring tube should be open.

i. Seal the compensating tube with a blowpipe flame.

j. Raise the levels of the mercury in the measuring tube and the generating bulb until the capillary tubes are completely filled with mercury. Close the ends of the capillaries with stoppers.

NOTE: Convenient stoppers are made from short lengths of nitrometer tubing closed at one end with glass rod.

5.2 Standardize the nitrometer as follows:

a. Weigh exactly 1.000 gm of the potassium nitrate (pa 4.1) in a small weighing bottle. Transfer the potassium nitrate to the cup of the generating bulb.

b. With the upper stopcock of the generating bulb closed and the lower stopcock open, lower the mercury reservoir to create a slightly reduced pressure in the generating bulb.

c. Pour a small amount of sulfuric acid (para 4.2) into the cup; open the upper stopcock and allow the sulfuric acid and potassium nitrate to be drawn into the bulb. Rinse the cup with further portions of the sulfuric acid, using 25 ml in all.

d. Force out any air drawn into the bulb, and close the upper stopcock. With the mercury reservoir low enough to maintain a slightly reduced pressure in the generating bulb, shake the bulb until most of the gas has been generated.

e. Replace the generating bulb on the rack and lower the mercury reservoir so that the mercury in the bulb drops nearly to the level of the lower shoulder.

f. Close the lower stopcock and shake the bulb vigorously for an additional 3 minutes.

g. Replace the bulb on the rack, and open the lower stopcock. Adjust the mercury in the generating bulb and the reservoir to approximately the same level, and allow the generating bulb to stand for 5 minutes.

h. Close lower stopcock and shake the generating bulb for an additional minute. Replace the bulb on the rack.

i. Adjust the height of the measuring tube on the rack so that its capillary exactly meets the top capillary of the generating bulb. Remove the stoppers, and make an airtight connection between the two capillaries with a piece of rubber nitrometer tubing.

j. Transfer the gas from the generating bulb to the measuring tube, and close the stopcock on the measuring tube. Disconnect the measuring tube and the generating bulb; adjust the levels of the mercury in the measuring and compensating tubes to approximately the same height, and allow the gas in the measuring tube to stand for approximately 20 minutes to permit equalization of the temperature.

k. Using a leveling device to check the mercury levels, adjust the measuring tube and the mercury reservoir so that the mercury in the measuring tube is at the 13.855 mark, and the mercury in the compensating tube is at exactly the same level.

NOTE: The figure 13.855 represents the percentage of nitrogen in potassium nitrate.

l. Mark the compensating tube with a strip of gummed tape to show the level of the mercury in step (k). This is the standard reference mark used in the determinations.

m. Refill the measuring tube and generating bulb and their capillaries with mercury, and seal the capillaries with stoppers.

5.3 Wash the cup of the generating bulb with sulfuric acid and draw the acid through the upper stopcock. When the washing is completed, turn the stopcock and expel the acid from the generating bulb through the capillary tube. A small beaker may be used to catch the acid plus any small quantity of mercury that may come over.

5.4 Transfer the weighed specimen from the weighing bottle to the nitrometer cup. Measure out approximately 25 ml of sulfuric acid and use about 10 ml to rinse the weighing bottle. Transfer the rinsing to the cup of the generating bulb and mix with the specimen with the aid of a small, thin stirring rod to form a slurry.

a. Open the lower stopcock of the generating bulb. Lower the mercury reservoir to cause reduced pressure in the generating bulb. Open the upper stopcock to allow the mixture of sulfuric acid and nitrocellulose to be drawn into the bulb.

b. Use the remaining sulfuric acid in 5 portions (about 3 ml each) to rinse the weighing bottle and cup of the generating bulb. Draw the acid into the bulb after each rinsing.

c. When 25 ml of sulfuric acid have been drawn into the generating bulb, force out any air that might have been drawn into the bulb, and close the upper stopcock. Lower the mercury reservoir until its mercury level in the reservoir is 15 to 20 inches below the mercury level of the generating bulb.

d. Shake the generating bulb gently, until most of the gas has been generated. Then replace the bulb on the rack.

CAUTION: Do not raise the generating bulb so that its mercury level is more than 20 inches above that in the reservoir.

e. Adjust the mercury reservoir so that the mercury level in the generating bulb drops nearly to the lower shoulder. Then close the lower stopcock, and shake the generating bulb vigorously for 3 minutes. Replace the bulb on the rack.

f. Open the lower stopcock, and bring the pressure inside the generating bulb to approximately one atmosphere by bringing the mercury in the reservoir to a level with the mercury in the bulb.

NOTE: This insures that the solubility of the nitric oxide gas in the sulfuric acid will be normal. The normal solubility of the nitric oxide in sulfuric acid is negligibe.

g. Close the lower stopcock and shake the generating bulb vigorously for 3 minutes. Then replace the bulb on the rack.

h. Adjust the height of the measuring tube so that its capillary exactly meets the top capillary of the generating bulb. Remove the stoppers, and make a connection between the two capillaries with a piece of rubber tubing so that air is excluded.

i. Open the stopcock on the measuring tube and the lower stopcock on the generating bulb. Then open the upper stopcock on the generating bulb, and slowly draw the gas from the generating bulb into the measuring tube by manipulating the mercury reservoirs. Close the stopcock of the measuring tube when the acid just reaches it.

5.5 Close the upper stopcock on the generating bulb, and disconnect the measuring tube from the generating bulb.

5.6 Adjust the position of the measuring tube so that the mercury in it is at approximately the same level as the mercury in the compensating tube, and allow it to stand for 20 minutes to permit equalization of the temperature.

5.7 Using a U-tube or mirror leveling device, adjust the measuring tube and the mercury reservoir so that the mercury in the compensating tube is at the standard reference mark, and the mercury in the measuring tube is at exactly the same level.

5.8 Calculate the percentage of nitrogen in the nitrocellulose.

5.9 **Calculation:**

$$\text{Percent nitrogen} = \frac{A}{W}$$

Where:

A = Reading of the measuring tube.

W = Weight of specimen, gm.

METHOD 209.6.2

NITROCELLULOSE (ACETIC ACID EXTRACTION METHOD)

1. SCOPE

1.1 This method is used for determining the nitrocellulose content of propellants manufactured from nitrocellulose having a nitrogen content of not less than 12.2 percent.

NOTE: Propellants containing nitrocellulose having a lower nitrogen content may yield high results. The method is inapplicable in the presence of reactive metals, such as aluminum.

2. SPECIMEN

2.1 The specimen shall consist of 3 to 5 g of the propellant, weighed to within 0.2 mg.

3. APPARATUS

3.1 Erlenmeyer flask (with stopper), 250 ml.

3.2 Steam bath.

3.3 Filtering crucible, medium porosity sintered glass.

3.4 Suction filtration apparatus.

3.5 Oven.

4. MATERIALS

4.1 Acetic acid solution, containing not less than 65 percent nor more than 70 percent acetic acid by weight. (Check by titrating with standard alkali).

5. PROCEDURE

5.1 Prepare the specimen as described in Method 509.3.

5.2 Extract the specimen as follows:

a. Place the specimen in the Erlenmeyer flask, and add 100 ml of the acetic acid solution (para 4.1).

b. Loosely stopper the flask and place it on a steam bath. Heat the flask for at least 3 hours (or overnight if convenient).

NOTE: As an alternative method of extraction, attach a reflux condenser to the flask, and reflux gently for 30 minutes on hotplate.

c. Decant the hot supernatant liquid through the tared filtering crucible, with the aid of suction.

d. Repeat steps (b) and (c) three times, twice using 50 ml portions of acetic acid, and finally using one 50 ml portion of distilled water.

5.3 Quantitatively transfer the residue in the flask to the filtering crucible, using a stream of hot distilled water.

5.4 Wash the contents of the crucible with two 40 ml portions of hot water.

5.5 Dry the crucible in an oven at $100 \pm 5^{\circ}C$ until loss of weight between two weighings 1 hour apart does not exceed 3 mg.

5.6 Calculate the percentage of nitrocellulose in the propellant.

5.7 **Calculation:**

$$\text{Percent nitrocellulose} = \frac{100A}{W} - B$$

Where:

A = Gain in weight of crucible, g.

B = Correction for acetic acid and water insoluble material (such as carbon black or graphite present in the propellant) as determined by the appropriate methods, percent.

W = Weight of specimen, corrected for total volatiles, g.

METHOD 209.7

NITROGEN IN NITROCELLULOSE OR NITROCELLULOSE IN PROPELLANT (FERROUS TITANOUS CHLORIDE METHOD)

1. SCOPE

1.1 This method is used for determining the nitrogen content of nitrocellulose or the nitrocellulose content of propellants. Other reducible elements or compounds must be absent. Typical standard deviation for the nitrogen content of nitrocellulose is 0.019 percent, and relative standard deviation (for 13.4 percent N samples) is 0.14 percent. Typical standard deviation for the nitrocellulose content of propellant is 0.112 percent, and relative standard deviation (for 48 percent nitrocellulose content) is 0.23 percent.

2. SPECIMEN

2.1 Nitrocellulose. Dry the nitrocellulose sample to constant weight in a shallow weighing botttle in a vacuum oven at 50 to 70°C and an absolute pressure of 2 to 5 cm of mercury. Before weighing, cool in a desiccator containing fresh indicating calcium sulfate, such as Drierite, either with a cover on the bottle or under vacuum. Use a specimen of 0.20 to 0.25 g of the dried sample for the analysis. Weigh the specimen to within 0.2 mg.

2.2 Propellant. Extract the weighed propellant sample (ground to pass 20 mesh or otherwise suitably comminuted) with a suitable solvent (e.g. methylene chloride or 68 - 70 percent by weight of acetic acid) to remove nitroglycerin or other soluble nitrate esters.

Dry the extracted residue to constant weight in the manner described above for nitrocellulose. Use a specimen of 0.20 to 0.25 g of the dried sample for the analysis. Weigh the specimen to within 0.2 mg.

3. APPARATUS

3.1 Reflux condenser, Graham or Roweg type, 50 cm jacket length (figure 1).

3.2 Titration apparatus (figure 2).

3.3 Electric hot plate.

3.4 A system for providing carbon dioxide protection for titration flasks, solutions in storage, and in burets. Both the titanous chloride and ferrous ammonium sulfate solutions should be protected by carbon dioxide at all times, and the titanous chloride solution in storage should be shielded from light. The carbon dioxide system should have an automatic pressure relief control to prevent excessive pressure in solutions, and the system should be arranged so that pressure on burets and on storage containers will be approximately equal. Each outlet leading to a reflux condenser should have a small bubbler to indicate the rate of gas flow.

3.5 Vacuum oven which can be maintained at 50 to 70°C and an absolute pressure of 2 to 5 mm of mercury.

4. MATERIALS

4.1 Extraction solvent. Methylene chloride or 68-70 percent acetic acid.

4.2 Glacial acetic acid.

4.3 Titanous Chloride, 0.2N standard solution as specified in Method 601.1.

4.4 Ferrous ammonium sulfate, 0.7N standard solution as specified in Method 604.1.

4.5 Ammonium thiocyanate, 20 percent, weight to volume, solution as specified in Method 706.1.

4.6 n-Butyl acetate.

4.7 n-Pentane.

4.8 n-Hexane.

4.9 Hydrochloric acid, concentrated.

4.10 Inert gas (carbon dioxide or nitrogen).

5. **PROCEDURE**

5.1 Transfer the dried specimen of nitrocellulose from the tared weighing bottle or the propellant residue from the filtration crucible to a dry titration flask by means of a powder funnel and a stream of n-pentane n-hexane solvent (about 3 to 1 ration) from an all-glass or polyethylene wash bottle. Wash the funnel by pouring 45 ml of glacial acetic through it into the titration flask.

5.2 Add a few glass beads or carborundum chips to the titration flask.

5.3 Remove most of the pentane-hexane solvent by heating the flask for a few minutes on a steam bath.

5.4 Connect the inert gas supply tube to the flask and start a gentle flow of the gas. Maintain the gas flow throughout the remainder of the determination.

5.5 Add 25 ml of n-butyl acetate to the flask and connect it to the reflux condenser.

5.6 Gently boil the solution for 5-10 minutes.

5.7 From a graduate add 25 ml of the 0.7N ferrous ammonium sulfate solution through the top of the condenser.

5.8 From a graduate add 8 to 10 ml of concentrated hydrochloric acid through the top of the condenser.

5.9 Boil until the solution becomes a clear yellow color, and then for 10 minutes longer. (Usually, 30 to 40 minutes are required). Throughout the boiling period agitate the flask contents by hand shaking at about 5 minute intervals to insure washing down any particles which might adhere to the flask above the liquid level.

5.10 Increase the flow of inert gas slightly and cool the flask and contents in a water bath to approximately room temperature.

5.11 Loosen the condenser joint slightly and wash down the condenser and joint with 30 ml of oxygen free 68 - 70 percent acetic acid.

5.12 Tighten the flask and condenser connection and allow a few minutes for draining.

5.13 Disconnect the flask and titrate its contents with 0.2N titanous chloride solution, adding 5 ml of ammonium thiocyanate solution near the end point. Allow at least 10 seconds with good agitation for the color to reach equilibrium between drops and titrate until the red coloration is discharged.

5.14 Make a blank determination on the reagents in the same amounts and include all steps used for the nitrogen determinations.

5.15 Calculate the nitrogen content of nitrocellulose and/or the nitrocellulose content in the propellant.

5.16 **Calculations:**

$$\text{Percent nitrogen} = \frac{0.4669\,(V - B)\,N}{W}$$

$$\text{Percent nitrocellulose} = \frac{F\,(V - B)\,N}{W}$$

Where:

V = Volume of titanous chloride solution used for the sample, ml.

B = Volume of titanous chloride solution used for the blank, ml.

N = Normality of titanous chloride solution.

W = Weight of specimen titrated, g.

F = A factor depending on the nominal or known nitrogen content of nitrocellulose used in manufacturing the propellant. $= \frac{46.69}{\%\text{ nitrogen in nitrocellulose}}$

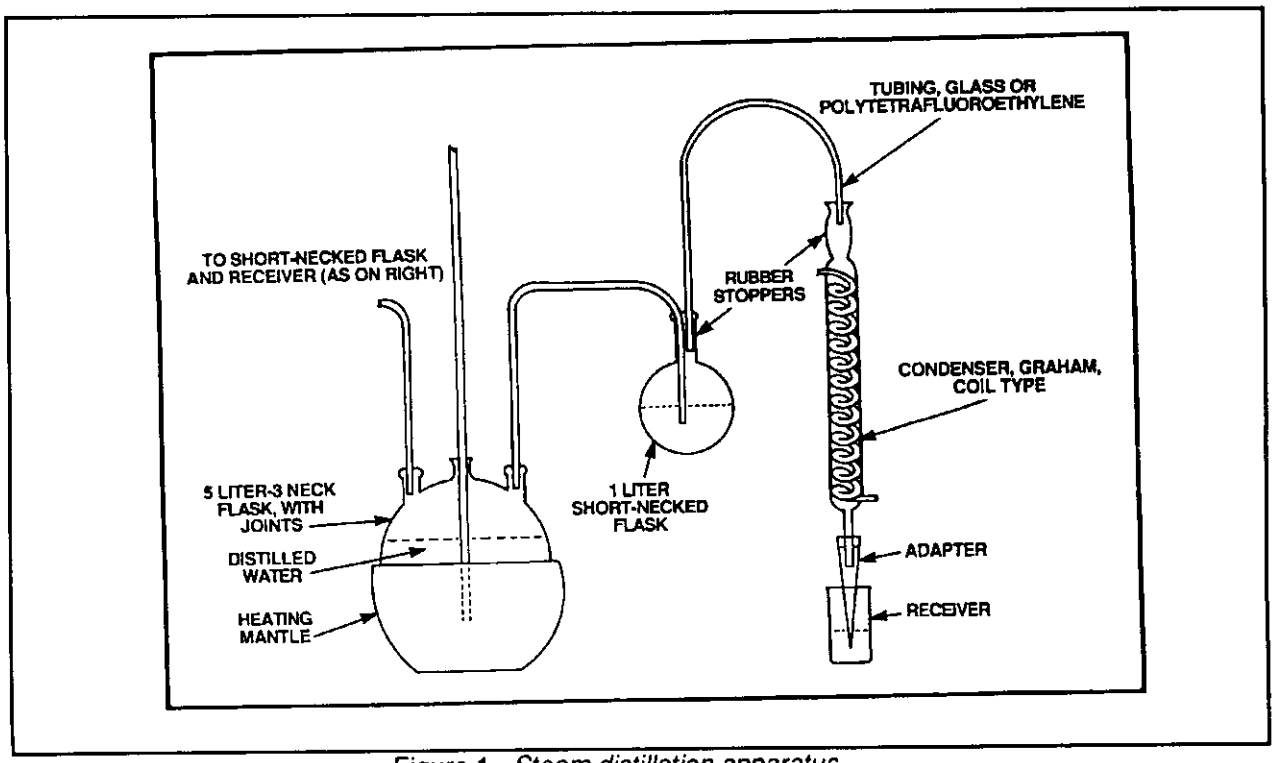


Figure 1. *Steam distillation apparatus.*

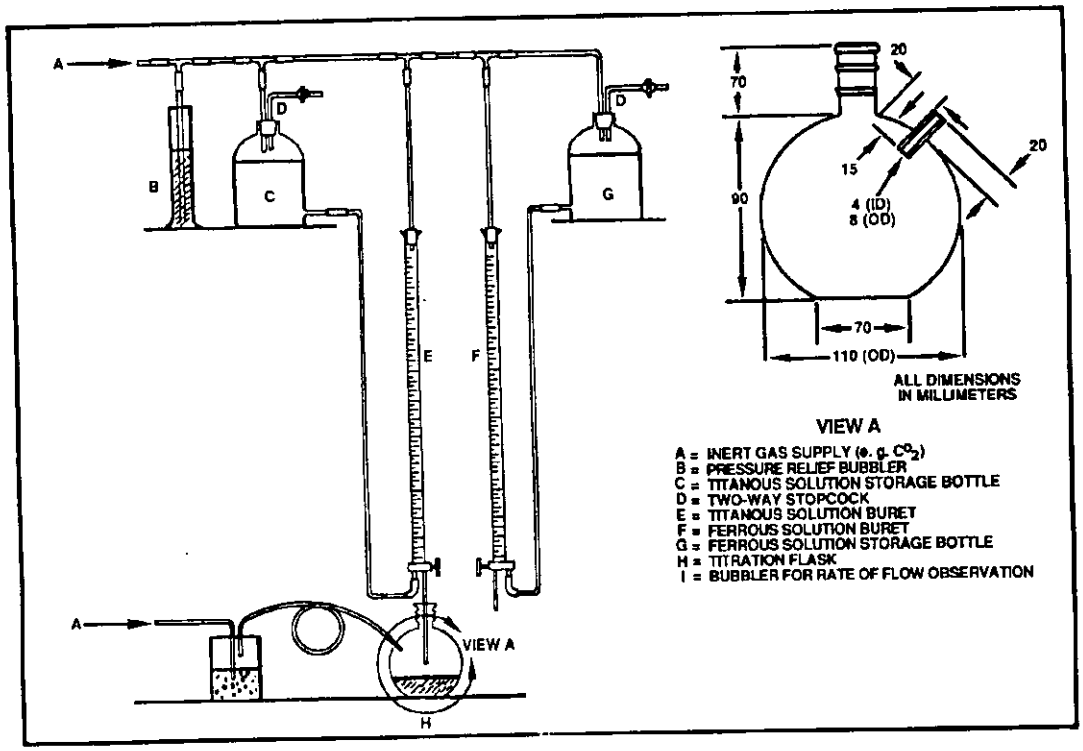


Figure 2. *Ferrous-titanous titration apparatus.*

METHOD 209.8.1

NITROGEN IN NITROCELLULOSE ON A MACRO AND SEMIMICRO SCALE (INFRARED METHOD)

1. SCOPE

1.1 This method is used for determining the nitrogen content of nitrocellulose on a macro or semimicro scale.

2. SPECIMEN

2.1 The specimen shall consist of 0.3000 g of nitrocellulose (exact weight) weighed to within 0.1 mg for the macro method and 30.0 mg of sample (exact weight) weighed to 0.1 mg for the semi-micro method.

3. APPARATUS

3.1 Vacuum oven.

3.2 Infrared Spectrophotometer, Perkin-Elmer Model 621 or equivalent.

3.3 Sodium Chloride cell, 0.2 mm.

3.4 Syringe, 1 ml, Luer slip, B-D Yale or equivalent.

3.5 Beakers, 5 ml and 50 ml.

3.6 Volumetric flasks, 5 ml and 50 ml.

3.7 Aluminum foil.

3.8 Rubber bands.

4. MATERIALS.

4.1 Tetrahydrofuran. Store in a constant temperature room. Keep covered.

4.2 Methylene chloride.

4.3 Nitrocellulose, MIL-N-244.

5. PROCEDURE

5.1 Preparation of calibration curve. Air dry 3 or 4 samples of nitrocellulose, whose nitrogen content has been accurately determined by the nitrometer method, then dry in a vacuum oven at 2 to 5 cm of mercury at 65°C for 4 hours, and cool in a desiccator. Weigh 0.3000 g of the samples into tared 50 ml beakers. Add 35 ml of tetrahydrofuran and immediately cover with aluminum foil, which is held in place by rubber bands. Carry along a blank. Allow to stand overnight in the room containing the infrared instrument at constant temperature. After the overnight standing period, stir with small stirring rod, wash down stirring rod with tetrahydrofuran, wash into a 50 ml volumetric flask, and dilute to the mark with tetrahydrofuran. Stopper and shake. Work with only one sample at a time, from

point of stirring to stoppering of volumetric flask. Rinse and fill a 0.2 mm sodium chloride cell with the solution, using a 1 ml syringe. Obtain the spectrum from 5.80 to 6.05 micrometer (1724 to 1653 cm^{-1}) at a speed of 25 cm^{-1} per minute. Gain, response, and resolution settings should be normal. Suppression setting should be zero. Observe I_A and I (figure 1) and calculate absorbance from the expression absorbance = log (I_A/I). Deduct the blank. Plot absorbance against percent nitrogen in the nitrocellulose. The calibration curve should be re-checked occassionally, and redrawn if a new lot of tetrahydrofuran is used.

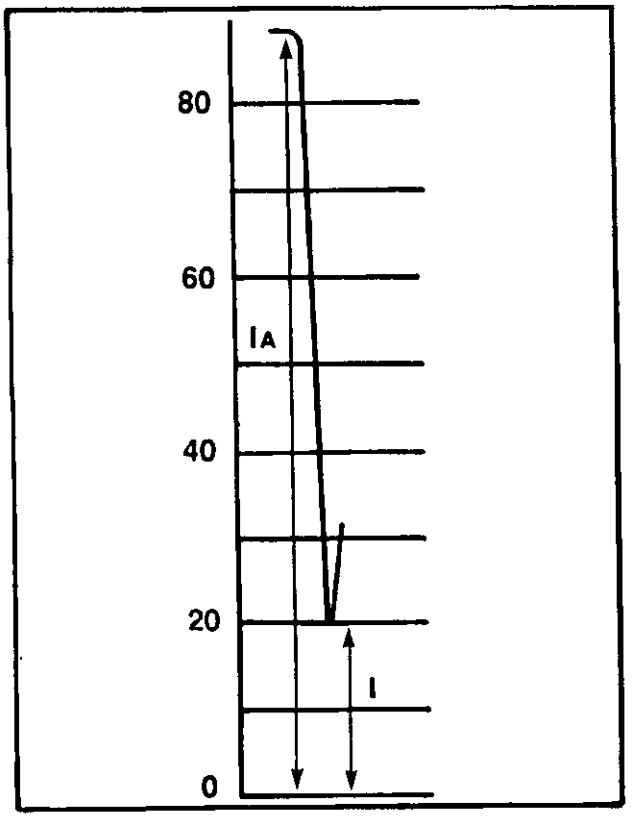


Figure 1.

Spectrum of nitrocellulose in tetrahydrofuran from 5.80 to 6.05 micrometers.

5.2 Analysis of samples.

a. Macro method. Dissolve a 0.3000 g sample (exact weight) in 35 ml of tetrahydrofuran, dilute in a 50 ml volumetric flask, and measure the intensity of the peak at 6.0 micrometers as described in the preparation of the calibration curve (par 5.1). Calculate the percent nitrogen by referring to the calibration curve.

b. Semimicro method. Proceed as in the macro method para. 5.2 (a) but weigh a 30.0 mg sample (exact weight) in a tared 5 ml beaker, preferably on a semimicro balance, dissolve in 3 ml of tetrahydrofuran, and dilute to 5 ml in a volumetric flask. Calculate the percent nitrogen by referring to the calibration curve.

METHOD 209.9.1

NITROGEN CONTENT OF NITROCELLULOSE IN SPHERICAL POWDER (ANALYZER METHOD)

1. SCOPE

1.1 This method is used to determine nitrogen content of nitrocellulose in spherical powder.

2. SPECIMEN

2.1 The specimen shall consist of 2 to 3 grams of propellant.

3. APPARATUS

3.1 Mettler-Heraeus Nitrogen Analyzer or equivalent.

3.2 Mettler Electronic Micro balance, Model 22/BE22 with a BA 25 Digital Display or equivalent.

3.3 Mettler Infrared Model LPII Drying Unit or equivalent.

3.4 Magnetic stirrer and bar.

3.5 U.S. No 70 Sieve - 3 in. diameter.

3.6 500 ml filtering flask with Buchner funnel.

3.7 50-ml beaker.

3.8 60 ml stoppered serum bottle.

3.9 Drying pan (Mettler) or equivalent.

3.10 Constant temperature bath.

4. MATERIALS

4.1 Carbon dioxide, instrument grade

4.2 Oxygen, ultra-high purity grade

4.3 Mercury, triple distilled.

4.4 Acetanilide, reagent, reference standard grade.

4.5 Methyl Alcohol, ACS reagent, acetone-free grade.

4.6 Copper oxide powder - Mettler #5834 or equivalent.

4.7 Copper oxide wire - Mettler #5832 or equivalent.

4.8 Copper wire, reduced, Mettler #5833 or equivalent.

4.9 Silver wool, Mettler #5923 or equivalent.

4.10 Potassium hydroxide, reagent grade, 50% solution.

4.11 Stopcock grease.

4.12 Instrument oil (Silicone).

4.13 Tin boats, Mettler #5677 or equivalent.

5. PROCEDURE

5.1 Instrument start-up.

a. The power switches on the combustion unit and the nitrometer should be "on". Both switch indicator lights will be lit when the power is "on".

b. Check all zone temperatures on the combustion unit. Zone 3 should be 975°C.

c. Check gas pressures. The secondary valves on the regulators should read about 8-9 psig for both gases. The oxygen flow reading on the instrument flow meter should be 8. The carbon dioxide flow meter should read 10.

d. The stopcock on top of the combustion unit should be clean and show no signs of gas leakage. If necessary, remove the stopcock and clean it with a paper towel and cotton swab. Relubricate the stopcock with grease before replacing, and check for gas leakage and ease of turning the stopcock after replacement.

e. Check the combustion and reduction tubes. If the combustion tube is full or the reduction tube is more than two-thirds expended, change the tube.

f. Check the water bath temperature. It should be at 25°C. Change tthe water if necessary and allow time for temperature equilibration.

g. Check the potassium hydroxide solution for excessive insoluble matter or foaming. If necessary, change the potassium hydroxide solution.

5.2 Operation.

a. Determination of Blank Value

(1) Before the blank value is determined, a volume of about 0.200 ml of air must be produced by depressing the push buttons Lower - Ventilation (with the auxilary switch down) - Lift - Measurement - Return - Measurement. Switch the auxilary switch up.

(2) Now make an analysis without a sample, measure the volume and subtract the initial volume.

(3) The resulting difference volume (blank value) must not be more than 0.030 ml (otherwise check for tightness or change the KOH).

(4) When three successive values are equal (± 5 µl), their mean value must be deducted in calculating the analysis.

(5) After an interruption of work (15 minutes or longer), the blank value should be checked.

(6) The blank can be determined by using an empty tin boat, although blank values determined using tin boats have not been different from values determined without the boats.

5.3 Sample Preparation.

a. Transfer 2 to 3 grams of ball powder to a 60 ml serum bottle. Add 40 ml of methyl alcohol, stirring bar and stopper bottle. Place on magnetic stirrer and agitate for 30 minutes.

b. Place a 3 in. US No. 70 sieve into a filtering apparatus.

c. Pour solvent and powder onto the sieve and aspirate for 3-5 minutes.

d. Remove powder from the sieve and place in a infrared drying unit and dry to a constant weight.

e. Cool in a desiccator to ambient temperature before weighing.

f. The sample (15-20 mg) is weighed to the nearest 1 µ in a tin boat. Never touch the sample boats with fingers. Tweezers have been provided for handling the sample boats.

g. The sample boats are sealed and folded as follows. Care must be exerted at all times to make certain no sample leakage occurs.

(1) The ends of the boat are folded inward slightly, using the tweezers.

(2) Holding the tweezers at the very top of the boat, squeeze the top edges together tightly and then push downward with the tweezers still holding the top closed.

(3) Carefully fold the sealed top edge over so that it is flat on the surface of the partially folded boats.

(4) Place one pair of tweezers in the center of the boat, lengthwise, and use the other pair of tweezers to fold the outer edges upward around the first pair.

(5) The final result should be a small compact, neatly folded sample.

h. The samples should be stored in the numbered sample trays until ready for use.

i. Keep the unused sample boats in their covered containers.

5.4 Sample determination.

a. Before the instrument cycle can be initiated, the measuring buret must be at zero and the "Ventilation" switch must be out.

b. Prepare the sample as directed in section 5.3.

c. Check the initial gas volume and record.

d. Insert the prepared sample into the stopcock and move to the middle of the stopcock thru the sample entry tube using plunger. Close the sample entry.

e. Press "Start" to initiate the cycle.

f. After waiting 30 seconds, turn the stopcock counter clockwise one-quarter turn and allow the sample to fall into the combustion tube. Return the stopcock to its initial position by turning it one-quarter turn clockwise.

g. During the course of the cycle, the final gas volume will be automatically checked two times. Upon completion of the cycle, recheck the final volume at least once by pressing "Return" and holding it for about 0.200 ml and subsequently pressing "Measurement" to again measure the volume. Record volume.

5.5 Calibrations.

a. Analyze triplicate samples of the acetanilide (15-20 mg) to the nearest 1 µg. Record volume.

b. Calculate % nitrogen by

$$\% \text{ Nitrogen} = \frac{(\text{Volume in milliliters} - \text{blank}) \times K \times 100}{\text{Weight in milligrams} \times 100}$$

c. Determine factor Fa by

$$Fa = \frac{\text{Theoretical nitrogen value of acetanilide (10.362)}}{\% \text{ nitrogen analyzed}}$$

d. Analyze triplicate samples of spherical powder. Record volume.

e. Calculate % nitrogen by

$$\% \text{ nitrogen} = \frac{(\text{Volume in milliliters of nitrogen} - \text{blank}) \times K \times 100}{\text{Weight in milligrams} \times 10}$$

NOTE: K values are based on temperature and pressure gas laws calculations.

METHOD 209.10.1

NITROCELLULOSE (INFRARED METHOD)

1. SCOPE

1.1 This method may be used for the determination of nitrocellulose (NC) in double base propellant and base grain.

1.2 The nitro group absorbance at 1659 cm^{-1} is used to quantitatively measure the NC. However, nitroglycerin (NG) interfers at this frequency and a diethyl ether (DEE) extraction is necessary. After extraction, the residue containing the NC is dissolved in dimethyl sulfoxide (DMSO) and scanned with a double-beam infrared (IR) spectrophotometer.

1.3 Any materials absorbing at 1659 cm^{-1} and not removed in the extract will interfere. Water absorbs around 1620 cm^{-1} so it must be excluded.

1.4 The precision for this method at the 95% confidence level (CL) is +/- 0.7 at 10 to 20% level of nitrocellulose.

2. SPECIMEN

2.1 The specimen shall consist of approximately 2.5 grams of dried nitrocellulose.

3. APPARATUS

3.1 Spectrophotometer, IR. Any double-beam IR spectrophotometer capable of making quantitative measurements is suitable.

3.2 Cells (2), IR, matched barium fluoride or calcium fluoride. A 0.2 mm path length is recommended for the NC analysis.

4. REAGENTS AND STANDARDS

4.1 Diethyl ether , anhydrous, reagent grade.

4.2 Dimethyl sulfoxide, dry, reagent grade for spectrophotometry.

NOTE: To dry DMSO, shake with dried type 5A molecular sieve. Let solids settle out of the dried DMSO before using.

4.3 Nitrocellulose (NC), MIL-N-244.

4.4 Nitrocellulose (NC) stock solution, 10 mg/ml. Weigh approximately 2.5 g of dried NC to the nearest 1 mg and quantitatively transfer to a 250 ml volumetric flask. Dissolve in dry DMSO and dilute to volume.

NOTE: Dry NC is hazardous material and must be handled with care.

5. CALIBRATION AND STANDARDIZATION

5.1 Pipet 5.00, 10.00, 15.00, and 20.00 ml, aliquots for the NC stock solution into 25-ml volumetric flasks, and dilute to volume with DMSO. In turn, place each of these standards into the 0.2mm IR cell and record the IR spectrum between 1600 cm^{-1} and 1950 cm^{-1} against a solvent reference in the matched cell. Use a double-beam spectrophotometer with settings established for quantitative measurements.

5.2 Measure the maximum absorbance due to NC at 1659 cm^{-1} using the absorbance at 1900 cm^{-1} as a reference point. Determine the absorptivity, a, of NC by plotting absorbance as the ordinate against the concentration of NC in mg/ml and determining the slope of the resulting calibration curve.

6. PROCEDURE

6.1 Extract the sample with DEE according to Method 104.1.3. Take sufficient sample for extraction so that when the residue is diluted to 25 ml, the NC concentration is between 2 and 10 mg/ml. After extraction, quantitatively transfer the dried residue containing the NC into a 25 ml volumetric flask. Dissolve the residue in DMSO and dilute to volume. Allow solids to settle out.

6.2 Fill a 0.2 mm IR cell with the sample solution and scan between 1600 cm^{-1} and 1950 cm^{-1} against a solvent reference in a matched cell. Use the same double beam spectrophotometer and the same instrument settings used for the calibration. Measure the absorbance maximum of the NC peak at 1659 cm^{-1} using the absorbance at 1900 cm^{-1} as a reference point.

NOTE: The same cells used for calibration should be used for the actual samples.

7. CALCULATION

$$\% \text{ NC} = \frac{(A)\,(D)}{(a)\,(W)\,(10)}$$

Where:

A = absorbance of NC at 1659 cm^{-1} in the analyzed solution.

a = absorptivity of NC, absorbance/mg/ml.

W = weight of sample, g.

D = dilution factor, ml.

METHOD 209.11.1

NITROGEN CONTENT OF NITROCELLULOSE
(Ferrous Sulfate Titration Method)

1. SCOPE

1.1 This method is used to determine the nitrogen content of nitrocellulose. The nitrate in the sample is released by strong sulfuric acid, forming nitric acid, which is then titrated with ferrous sulfate ($FeSO_4$). The titration is monitored by glass and platinum electrodes which read the change in millivolt (mv) output from a range of 500-600 mv to a preselected mv endpoint. The change is measured in volume of $FeSO_4$ necessary to produce this change.

2. SPECIMEN

2.1 The specimen shall consist of a 0.5000 ± 0.0500 gm of sample.

3. APPARATUS

3.1 Any pH meter of titrating equipment (manual or automatic) capable of measuring ±1000 mv. If an automatic titrator is used, follow instruction manual.

3.2 Platinum Electrode - Fisher Cat. No. 13-639-115 or equivalent.

3.3 Glass Electrode - Fisher Cat. No. 13-639-4 or equivalent.

3.4 Magnetic Stirrer base with stirring bar.

3.5 Waring blender, explosion-proof with a "Polytron, Rotor-Stator" grinding attachment or equivalent.

3.6 Cooling bath - ice bath or other mechanical cooling system.

3.7 Carboy (painted black for $FeSO_4$).

3.8 Timer (seconds).

3.9 Recorder for automatic titration (optional).

3.10 Desiccator with drying agent (with color indicator).

3.11 Weighing bottles - 1 oz.

3.12 135°C drying oven.

3.13 100°C drying oven.

3.14 45°C drying oven.

3.15 250 ml beaker(s).

4. MATERIALS

4.1 Sulfuric Acid (H_2SO_4) CP 94-97%.

4.2 Potassium Nitrate.

4.3 Ferrous Sulfate ($FeSO_4 \cdot 7H_2O$) Crystals.
350 gm of $FeSO_4$ dissolved in 800 ml H_2O.
Add 1000 ml of 1:1 H_2SO_4:H_2O.
Make up to 2 liters.

4.4 Distilled Water.

4.5 Tissue Paper.

5. SAFETY

5.1 If acid is spilled on the hands or clothing, flush immediately with plenty of water.

5.2 Keep sulfuric acid contaminated tissues under water.

5.3 To prevent acid burn, always wipe the electrodes free of excess acid before retrieving the spent sample beaker on the rinse acid beaker. Wipe with a dabbing motion to prevent static buildup on the electrodes.

6. OPERATIONS

6.1 Weigh 0.5 mg of KNO_3, that has been pulverized to about the grain consistency of salt, in a 1 oz weighing bottle. Dry in a 135° C oven for 4 hours. Place in a desiccator to cool. (Nitrocellulose will be predried in a 45° C oven for 4 hours and then dried in a 100° C oven for 2 hours, or equivalent method.) If the KNO3 or nitrocellulose is out of the oven for more than 3 hours, redry in a 100° C oven for 1 hour.

6.2 Place the stirring bar in a dry 250 ml beaker and add 150 ml of H_2SO_4. Use only clean beakers or beakers that have been used in a previous titration. Beakers that have been used in other analyses have contaminates in the scratches of the beaker(s).

6.3 Place the beaker in the cooling bath and on the stirring base. Start the stirrer.

6.4 Weigh the weighing bottle containing the KNO_3 on an analytical balance.

6.5 Pour the KNO3 into the swirl of the acid and set the timer for 8 minutes. If KNO3 is not dissolved in 8 minutes, dissolving a longer time and/or raising the temperature will aid in complete dissolving.

NOTE: The swirl should be as fast as possible without causing a vortex. A vortex will introduce air into the solution and cause oxidation of the $FeSO_4$.

6.6 Reweigh the bottle to obtain the weight of the sample by difference.

6.7 Lower the electrodes into the acid.

NOTE: The electrodes should have a mininum of 4 hours conditioning time in clean H_2SO_4 before using.

6.8 After 8 minutes, start titrating. Do not titrate so fast that heat builds up in the sample and causes localized oxidation of the sample. Overall titration time (excluding dissolving time) should be approximately 6-8 minutes (nitrocellulose will dissolve in 5 minutes).

6.9 As the end point is neared, slow the titration to the lowest volume increment possible and allow time for each increment to completely disperse before adding the next one.

6.10 When the mv reading has reached the preselected end point, stop the titration and record the volume of $FeSO_4$.

6.11 Raise the electrodes.

6.12 Rinse the electrodes with a beaker of clean H_2SO_4 and allow excessive H_2SO_4 to drain into the beaker while preparing for the next sample.

6.13 Calculate the nitrogen equivalent factor (F) for the titrant.

$$\text{Actual \% N in } KNO^3 = \frac{\text{at wt of N}}{\text{Mol wt of } KNO_3} \times 100 = \frac{14.008}{39.096 + 14.008 + 3(16.000)} \times 100 = 13.8550$$

$$F = \frac{\text{gm N}}{} = \frac{\text{Wt of } KNO_3 \times .13855}{\text{ml of } FeSO_4 \text{ solution}} = \frac{\text{Wt of } KNO_3 \times 0.13855}{\text{ml of } FeSO_4 \text{ solution}}$$

6.14 Repeat paragraph 6.1 through 6.11 using nitrocellulose sample. If the nitrocellulose is grainy or has excessive staple length, it should be pulverized in a Waring blender as a water slurry.

6.15 Calculate percent nitrogen.

$$\% N = \frac{\text{ml } FeSO_4 \text{ solution} \times F}{\text{Wt of sample in gm}} \times 100$$

7. When the electrodes are not in use, they will be kept submerged in a beaker of clean H_2SO_4 but not the pipet. The end of the pipet will be capped to prevent evaporation of the solution. This evaporation will cause recrystallization of the $FeSO_4$ and clog the pipet tip.

METHOD 209.12

NITROGEN CONTENT OF NITROGLYCERIN AND DIETHYLENEGLYCOL DINITRATE (FERROUS SULFATE TITRATION METHOD)

1. SCOPE

1.1 This method is used to determine the nitrogen content of nitroglycerin (NG) and Diethyleneglycol Dinitrate (DEGDN). The nitrate in the sample is released by strong sulfuric acid, forming nitric acid, which is then titrated with ferrous sulfate ($FeSO_4$). The titration is monitored by glass and platinum electrodes which read the change in millivolt (mv) output from a range of 500-600 mv to a preselected mv endpoint. The change is measured in volume of $FeSO_4$ necessary to produce this change.

2. SPECIMEN

2.1 For KNO_3 standard, .5000 ± .050 g sample

2.2 For NG sample, .3750 ± .025 g sample

2.3 For DEGDN sample, .4000 ± .050 g sample

3.0 APPARATUS

3.1 An automatic titration system such as the METROHM 636 titroprocessor by Brinkman, the Fisher Computer-Aided Titrimeter or an equivalent automatic titration unit which can titrate to a fixed end point (or locate the end point) in a potentiometric titration.

3.2 Platinum Electrode. Fisher Cat. No. 13-639-115 or equivalent.

3.3 Glass Electrode. Fisher Cat. No. 13-639-4 or equivalent.

3.4 Magnetic stirrer base with stirring bar.

3.5 Cooling bath. Ice bath or other mechanical cooling system.

3.6 Car boy (painted black for $FeSO_4$).

3.7 Timer (seconds).

3.8 Recorder for automatic titration (optional).

3.9 Desiccator with drying agent (with color indicator).

3.10 Weighing bottles 1 oz.

3.11 135°C drying oven.

3.12 100°C drying oven.

3.13 45°C drying oven.

3.14 250 ml beaker(s).

4.0 **MATERIALS**

4.1 Sulfuric Acid (H_2SO_4) CP 94-97%.

4.2 Potassium Nitrate

4.3 Ferrous Sulfate ($FeSO_4 \cdot 7H_2O$) Crystals
350 g $FeSO_4$ dissolved in 800 ml H_2O
add 1000 ml of 1:1 H_2SO_4:H_2O

4.4 Distilled Water

4.5 Tissue Paper

5.0 **SAFETY**

5.1 If acid is spilled on the hands or clothing, flush immediately with plenty of water.

5.2 Keep sulfuric acid contaminated tissues under water.

5.3 To prevent acid burn, always wipe the electrodes free of excess acid before retrieving the spent sample beaker or the rinse acid beaker. Wipe with a dabbing motion to prevent static buildup on the electrodes.

6. **OPERATIONS**

Standardization of $FeSO_4$ Titrant Using KNO_3

6.1 Weigh 0.5 g of KNO_3, that has been pulverized to about the grain consistency of salt, in a 1 oz. weighing bottle. Dry in a 135°C oven for 4 hours, place in a desiccator to cool. If the KNO_3 is out of the oven for more than 3 hours, redry in a 100°C oven for a minimum 2 hour.

6.2 Place the stirring bar in a dry 250 ml beaker and add 150 ml of $H2SO_4$. Use only clean beakers or beakers that have not been used in a previous titration. Beakers that have been used in other analyses have contaminants in the scratches of the beaker(s).

6.3 Place the beaker in the cooling bath and on the stirring base. Start the stirrer.

6.4 Weigh the weighing bottle containing the KNO_3 on an analytical balance.

6.5 Pour the KNO_3 into the swirl of the acid and set the timer for 8 minutes. If KNO_3 is not dissolved in 8 minutes, dissolving a longer time and/or raising the temperature will aid in complete dissolving.

NOTE: The swirl should be as fast as possible without causing a vortex. A vortex will introduce air into the solution and cause oxidation of the $FeSO_4$.

6.6 Reweigh bottle to obtain weight of sample by difference.

6.7 Lower the electrodes into the acid.

NOTE: The electrodes should have a minimum of 4 hours conditioning time to clean $H2S0_4$ before using.

6.8 After 8 minutes, start titrating. Do not titrate so fast that heat builds up in the sample and causes localized oxidation of the sample. Overall titration time should be approximately 6 - 8 minutes.

6.9 As the end point is neared, slow the titration to the lowest volume increment possible and allow time for each increment to completely disperse before adding the next one.

6.10 When the mv reading has reached the preselected end point, stop the titration and record the volume of $FeSO_4$.

6.11 Raise the electrodes. Wipe excessive acid from the electrodes with a tissue.

6.12 Rinse the electrodes with a beaker of clean H_2SO_4 and allow excessive H_2SO_4 to drain into the beaker while preparing for the next sample. Wipe the electrodes with a tissue before retrieving beaker.

6.13 Calculate the nitrogen equivalent factor (F) for the titrant by the following formula:

$$F = \frac{\text{g N}}{\text{ml } FeSO_4 \text{ solution}} = \frac{(\text{wt of } KNO_3 \text{ in gms}) \times (.13855)}{\text{ml } FeSO_4 \text{ solution}}$$

6.14 Weigh a .35 to .40 g (within 0.1 mg) sample for nitroglycerin (for DEGDN the sample size should be from .35 to .45 g) into a dry 250 ml titration beaker; add 3 ml of glacial acetic acid to desensitize the NG or DEGDN.

6.15 Before adding the stirring bar, pour 150 ml of H_2SO_4 into the beaker. Then, carefully slide the stirring bar down the side of the beaker.

6.16 Place the beaker in the cooling bath and on the stirring unit and start the stirrer.

6.17 Reweigh the weighing bottle to find the weight of the NG sample by difference.

6.18 Lower the electrodes into the beaker containing the NG sample.

6.19 Since the sample is a liquid, there is no dissolving time and the titration may begin immediately. The rate of addition at $FeSO_4$ titrant should be controlled to give an overall titration time of 6 to 8 minutes.

6.20 As the end point is neared, slow the titration to the lowest volume increment possible and allow time for each increment to completely disperse before adding the next one.

6.21 When the mv reading has reached the preselected end point. Record the volume of $FeSO_4$ (in ml) required for the titration.

6.22 Raise the electrodes; wipe excessive acid from the electrodes with a tissue.

6.23 Rinse the electrodes with a beaker of clean H_2SO_4 and allow excessive H_2SO_4 to drain into the beaker while preparing for the next sample. Wipe the electrodes with a tissue before retrieving the beaker.

6.24 Calculate the percent N in the sample.

6.25 **Calculation:**

$$\%N = \frac{(\text{ml } FeSO_4) \times (F) \times (100.0)}{\text{wt of sample in gms}}$$

6.26 When the electrodes are not in use, they will be kept submerged in a beaker of clean H_2SO_4 but not the pipet. The end of the pipet will be capped to prevent evaporation of the solution. This evaporation will cause recrystallization of the $FeSO_4$ and clog the pipet tip.

METHOD 210.1.2

STARCH

1. **SCOPE**

1.1 This method is used for determining the starch content of propellants.

2. **SPECIMEN**

2.1 The specimen shall consist of approximately 5 g of the propellant, weighed to within 0.2 mg.

3. **APPARATUS**

3.1 Glass filtering crucible (tall form).

3.2 Steam bath.

3.3 Filtering crucible

3.4 Watchglass.

3.5 Hotplate.

3.6 Stirring rod, flat-ended.

4. **MATERIALS**

4.1 Nitric acid, 70 percent solution.

4.2 Potassium dichromate, ACS Reagent.

4.3 Sulfuric acid, 40-percent solution.

4.4 Potassium iodide, 10 percent solution.

4.5 Sodium thiosulfate, 0.6N standard solution.

5. **PROCEDURE**

5.1 Prepare the specimen as described in Method 509.3.

5.2 Extract the specimen as specified in Method 104.1. Use a tall form glass filtering crucible for the extraction, and retain the residue in the crucible for the determination.

5.3 Quantitatively transfer the residue in the filtering crucible to a 500 ml flask, and add 200 ml of distilled water and 5 ml of 70-percent nitric acid to the flask. Heat on a steam bath for 3 hours.

NOTE: Break up the granules with a flat-ended stirring rod to assure complete hydrolysis of the starch.

5.4 Filter the mixture through a filtering crucible and wash the residue with 200 ml of hot distilled water by filling the crucible, allowing the water to run through, and repeating the process. Transfer the combined filtrate and washings to a 600 ml beaker.

5.5 Evaporate the filtrate and washings to not less than 10 ml; conduct the first part of the evaporation on a hotplate, but transfer the beaker to a steam bath for the last part ot the evaporation to avoid overheating the residue. Cool to room temperature.

5.6 Add ml to 40 percent sulfuric acid and 1.250 g of potassium dichromate. Cover the beaker with a watchglass, and boil the contents for 30 minutes on a hotplate. Cool to room temperature.

5.7 Transfer the solution to a flask and dilute to 200 ml with distilled water. Add 50 ml of the 10 percent solution of potassium iodide.

5.8 Titrate the liberated iodine with the 0.6N sodium thiosulfate solution, adding starch indicator solution near the end point.

5.9 Calculate the percentage of starch in the propellant.

5.10 **Calculation:**

$$\text{Percent starch} = \frac{13.7\,(1.250 - VFN)}{W}$$

Where:

V = Volume of sodium thiosulfate used, ml.

N = Normality of sodium thiosulfate solution.

F = Milliequivalent weight of potassium dichromate = 0.04904.

W = Weight of specimen corrected for total volatiles.

METHOD 212.1

AURINE

1. SCOPE

1.1 This method is used for determining the aurine content of (E.C.) propellant.

NOTE: (E.C.) propellant (Explosives Company) consists of nitro-cotton mixed with nitrates of potassium and barium with the addition of coloring matter and small quantities of other organic compounds.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5 g of the propellant, weighed to within 0.2 mg.

3. APPARATUS

3.1 Drying tube, 200 ml.

3.2 Volumetric flask.

3.3 Colorimeter with blue filter.

4. MATERIALS

4.1 Solution of equal parts (by volume) of acetone and distilled water, freshly prepared for each determination.

4.2 Aurine.

5. PROCEDURE

5.1 Prepare a colorimeter calibration curve as follows:

a. Using fresh acetone and water solution (par. 4.1), prepare five 250 ml solutions in volumetric flasks containing 5, 10, 15, 20, and 25 mg of aurine, respectively.

b. Within 2 hours after the preparation of these solutions, fill the colorimeter tube with portions of each of solutions, and measure the scale deflections on the meter, using a blue filter in the colorimeter.

NOTE: Aurine solutions are stable for at least 24 hours, if kept out of sunlight. Standardize the colorimeter weekly to avoid instrumental error.

c. On linear graph paper, plot percent aurine against scale readings, and draw a calibration curve.

5.2 Prepare the specimen as described in Method 509.3.

5.3 Pack the bulb of a 200 mm drying tube with glass wool, and transfer the specimen to the tube.

NOTE: The glass wool should be packed tightly enough to prevent propellant grains from passing through, but not tightly enough to cause the filtration to proceed too slowly.

5.4 Extract the aurine in the propellant using ten 15 ml portions of the acetone and water solution, and catch the filtrate in a 250 ml flask. Allow each portion to filter through before adding the next. Stir the specimen in the tube to prevent channeling of the solution and insure complete extraction.

5.5 Fill the flask to the mark with the acetone and water solution, stopper the flask, and shake well.

5.6 Pour a portion of the solution into the colorimeter tube, and measure the scale deflection.

5.7 Using the scale deflection thus obtained, read the percent aurine in the specimen directly from the calibration curve (para. 5.1).

METHOD 213.1.4

NITROGUANIDINE (WATER-EXTRACTION METHOD)

1. SCOPE

1.1 This method is used for determining the nitroguanidine content of triple base propellants.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5 g of the propellant, weighed to within 0.2 mg.

3. APPARATUS

3.1 Glass filtering crucible (tall form).

3.2 Oven.

3.3 Suction filtration apparatus.

4. PROCEDURE

4.1 Prepare the specimen as specified in Method 509.3.

4.2 Extract as directed in Method 104.1, using a mixture of 2 parts of n-pentane and 1 part of methylene chloride (both parts by volume) as the extracting solvent.

4.3 When extraction is complete, place the filtering crucible on a suction filtration apparatus and aspirate until the odor of the solvent is no longer discernible.

4.4 Dry the crucible in an oven at $100 \pm 2^{\circ}C$, and weigh at 2 hour intervals. Consider the weight of the crucible to be constant when loss of weight between weighings does not exceed 3 mg.

4.5 Return the crucible to the suction filtration apparatus. With the aid of very light suction draw eight 200 ml portions of boiling distilled water through the crucible.

NOTE: It is imperative that boiling water be used to ensure efficient extraction.

4.6 When the last 200 ml portion of boiling water has gone through, aspirate the crucible for approximately 5 minutes.

4.7 Then place the crucible in the oven, and dry until loss of weight between weighings at 2 hour intervals does not exceed 3 mg.

4.8 **Calculation:**

$$\text{Percent nitroguanidine} = \frac{100\,(A - B)}{W} - C$$

Where:

A = Weight of crucible prior to water extraction, g.

B = Weight of crucible after water extraction, g.

C = Water soluble constituents in propellant (other than nitroguanidine), percent.

W = Weight of specimen, corrected for total volatiles.

METHOD 213.2

NITROGUANIDINE (SALICYLIC ACID TRANSNITRATION METHOD)

1. SCOPE

1.1 This method is used for determining the nitroguanidine content of propellants.

2. SPECIMEN

2.1 The specimen shall consist of a sample containing 0.120 g max of nitroguanidine.

3. APPARATUS

3.1 Beaker, 250 ml.

3.2 Beaker, 400 ml.

3.3 Watchglass.

3.4 Filter paper, Whatman No. 41, or equal.

3.5 Steam bath.

3.6 Titration flask (figure 1)

3.7 Hot plate.

3.8 Reflux condenser.

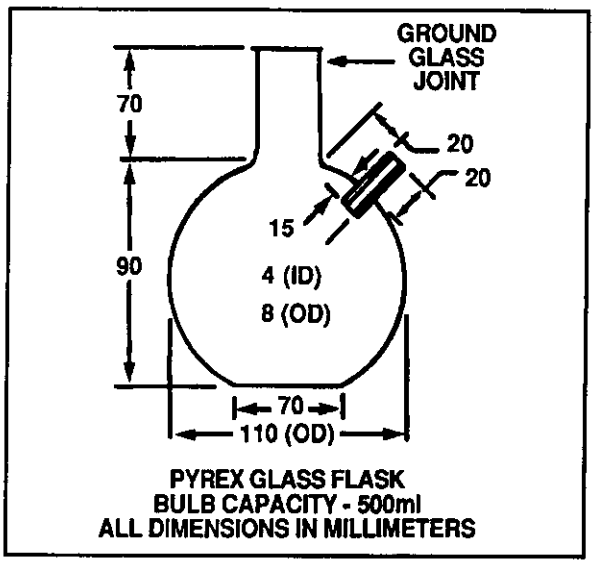


Figure 1. *Titration Flask.*

4. MATERIALS

4.1 Acetone.

4.2 Two parts of n-pentane and 1 part of methylene chloride by volume.

4.3 Salicylic acid solution, containing 0.5 mg of salicylic acid per 5 ml of concentrated sulfuric acid.

4.4 Sulfuric acid, 50 percent solution.

4.5 Inert gas (carbon dioxide or nitrogen).

4.6 Titanous chloride, 0.2N standard solution as specified in Method 601.1.

4.7 Ammonium thiocyanate, 20 percent solution as specified in Method 706.1.

4.8 Ferric ammonium sulfate, 0.15N standard solution as specified in Method 603.1.

5. PROCEDURE

5.1 Prepare the specimen as specified in Method 509.3.

5.2 Place thte specimen in a 250 ml beaker, and add 25 ml of acetone. Cover the beaker with a watchglass, and allow the soluble matter to dissolve.

5.3 When the specimen has dissolved, slowly add 25 ml of distilled water, while stirring constantly.

5.4 Place the beaker on the steam bath, and evaporate the contents until the odor of acetone is not longer discernible.

5.5 Add 100 ml of 2 parts of n-pentane and 1 part of methylene chloride to the residue in the beaker, cover with the watchglass, and place the beaker on the steam bath. Heat the contents of the flask for 30 minutes, then cool to room temperature.

5.6 Decant the supernatant liquid through the filter paper.

5.7 Add an additional 50 ml of 2 parts of n-pentane and 1 part of methylene chloride, and heat the flask for 15 minutes more on the steam bath. Cool to room temperature, and decant through the previously used filter paper.

5.8 Wash the residue paper in the beaker twice, each time with a 25 ml portion of 2 parts of n-pentane and 1 part of methylene chloride, and pour the washings through the filter paper. Discard the filtrate.

5.9 Place the filter paper in the beaker, and add 50 ml of distilled water. Cover the beaker with the watch glass, and place it on a hot plate. Boil the contents vigorously for 15 minutes.

5.10 Decant the hot liquid through a fresh piece of filter paper, catching the filtrate in a 400 ml beaker.

5.11 Add 25 ml of the hot distilled water to the residue, and boil for 10 minutes more.

5.12 Again decant the supernatant liquid through the same filter paper, cath the filtrate in the 400 ml beaker.

5.13 Repeat the process (para 5.11 and 5.12) two more times with 20 ml portions of hot water.

5.14 Place the beaker containing the filtrate on a steam bath, and heat until only a thoroughly dried residue remains.

5.15 Dissolve the residue in 5 ml of the salicylic acid solution (para. 4.3), and allow the reaction to proceed for 30 minutes. Then add 10 ml of 50-percent sulfuric acid, stirring continually.

5.16 Attach a source of inert gas to the titration flask (figure 1), and allow the gas to flow gently for five minutes to displace the air in the flask. Continue the flow of gas through the flask throughout the remainder of the determination.

5.17 Quantitatively transfer the contents of the beaker to the titration flask. Wash out the beaker with three 5 ml portions of 50 percent sulfuric acid, and add the washings to the beaker.

5.18 Add 40 ml of 0.2N titanous chloride solution to the flask.

5.19 Add a few glass beads to the flask (to prevent bumping), and connect the flask to a reflux condenser. Place the flask and condenser on a hot plate and boil for ten minutes.

5.20 Without disconnecting the condenser, remove the flask from the hot plate. Increase the current of inert gas (to keep air from entering the flask during cooling), and cool the solution to room temperature by immersing the flask in cold water. Then disconnect the condenser.

5.21 Add 5 ml of 20-percent ammonium thiocyanate solution, and titrate with 0.15N ferric ammonium sulfate solution to the end point, indicated by the first permanent red coloration.

5.22 Conduct a blank determination using the same reagents in the same quantities as in steps 5.15 through 5.21.

5.23 Calculate the percentage of nitroguanidine.

5.24 **Calculation:**

$$\text{Percent nitroguanidine} = \frac{1.735\,(A - B)\,N}{W}$$

Where:

A = Volume of ferric ammonium sulfate solution used for blank, ml.

B = Volume of ferric ammonium sulfate solution used for specimen, ml.

N = Normality of ferric ammonium sulfate solution.

W = Weight of specimen, corrected for total volatiles, g.

METHOD 213.3.1

NITROGUANIDINE (SPECTROPHOTOMETRIC METHOD)

1. SCOPE

1.1 This method is used for determining spectrophotometrically the nitroguanidine content of propellants. This method is not recommended when nitroguanidine is a major constituent.

2. SPECIMEN

2.1 The specimen shall consist of approximately 1.0 g of the propellant, weighed to within 0.2 mg.

3. APPARATUS

3.1 Spectrophotometer, ultraviolet (Beckman Instruments, Inc., Model DU, or equivalent).

3.2 Silica cells, 10 mm light path length.

3.3 Buret.

3.4 Beaker, 250 ml.

3 5 Watchglass.

3.6 Steam bath.

3.7 Hotplate.

3.8 Filter paper, Whatman No. 41, or equivalent.

3.9 Volumetric flask, 1000 ml.

3.10 Pipet, accurately calibrated.

3.11 Volumetric flasks, 250 ml.

4. MATERIALS

4.1 Acetone.

4.2 Nitroguanidine, pure.

5. PROCEDURE

5.1 Prepare the specimen as specified in Method 509.3.

5.2 Place the specimen in a 250 ml beaker, and add 25 ml of acetone. Cover the beaker with a watchglass, and allow the soluble materials to dissolve.

5.3 When the specimen has dissolved, slowly add 15 ml of distilled water, stirring constantly.

5.4 Place the beaker on the steam bath, and evaporate the contents until the odor of acetone is no longer discernible.

5.5 Add 100 ml of distilled water to the residue in the beaker, cover with a watchglass, and place the beaker on the hotplate. Boil the contents vigorously for 15 minutes. Cool to room temperature.

5.6 Decant the supernatant liquid through the filter paper, catching the filtrate in a 1000 ml volumetric flask.

5.7 Add 200 ml of hot distilled water to the residue in the beaker, and boil for 15 minutes more. Cool to room temperature.

5.8 Again decant the supernatant liquid through the same filter paper, catching the filtrate in the volumetric flask.

5.9 Repeat the process (para 5.7 and 5.8) two more times.

5.10 Fill the flask to the mark with distilled water.

5.11 Using the pipet, transfer a 25 ml aliquot of the solution to a 250 ml volumetric flask, and dilute to the mark with distilled water.

5.12 Transfer a 15 ml aliquot of this solution to a second 250 ml flask, and dilute to the mark with distilled water.

5.13 Transfer a portion of this solution to a silica cell. Fill a matched cell with distilled water for the reference.

NOTE: If matched silica cells are not available, unmatched cells may be used. However, correct for any difference between them by filling both cells with distilled water, measuring the absorbance of both at 264 nanometers and determining the difference in absorbance. Correct the reading for the absorbance of the propellant solution accordingly.

5.14 Place the cells in the spectrophotometer and obtain the absorbance of the solution at 264 nanometers.

5.15 Determine the spectrophotometric factor for nitroguanidine as follows:

a. Weigh 0.1000 g of pure nitroguanidine that has been dried for 2 hours at 100°C.

b. Dissolve this nitroguanidine with approximately 150 ml of distilled water, and transfer quantitatively to a 1000 ml volumetric flask. Dilute to the mark with distilled water.

c. Using aliquots of this solution, prepare six solutions of nitroguanidine ranging in concentration from 0.6 to 1.25 mg per 250 ml.

d. Determine the absorbance of each solution at 264 nanometers.

e. Divide the concentration in mg of nitroguanidine for each of these solutions by its corresponding absorbance value.

5.16 Calculate the percentage of nitroguanidine.

5.17 **Calculation:**

$$\text{Percent nitroguanidine} = \frac{100\,AB}{W}$$

Where:

A = Absorbance of solution obtained from specimen.

B = Spectrophotometric factor for nitroguanidine.

W = Weight of specimen represented by aliquot taken, corrected for total volatiles, mg.

METHOD 213.4

NITROGUANIDINE (TITANOUS CHLORIDE-BUFFER METHOD)

1. SCOPE

1.1 This method is used for determining the nitroguanidine content of propellants provided that other reducible materials has been separated.

2. SPECIMEN

2.1 The specimen shall consist of propellant, containing approximately 1 g of nitroguanidine, weighed to within 0.2 mg.

3. APPARATUS

3.1 Filter paper, Whatman No. 41 or equivalent, 12.5 cm diameter.

3.2 Paper extraction thimbles, 22 by 80 mm.

3.3 Beaker, 600 ml.

3.4 Stirring rod, glass, 200 mm.

3.5 Watchglass, l00 mm diameter.

3.6 Funnel, 75 mm diameter.

3.7 Volumetric flask, 500 ml.

3.8 pH meter, equipped with glass and calomel electrodes.

3.9 Pipet, 50 ml.

3.10 Buret, 50 ml.

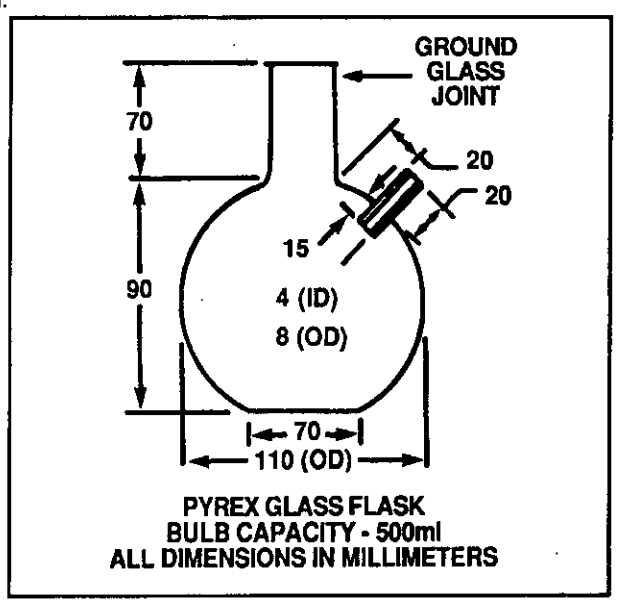


Figure 1. *Titration Flask.*

3.11 Titration flask (figure 1).

3.12 Magnetic stirrer with 1 inch to 1 1/2 inch bar covered with glass, polyethylene or other suitable material.

4. MATERIALS

4.1 n-Pentane.

4.2 Methylene chloride, anhydrous.

4.3 Sodium acetate buffer solution, prepared as follows:

a. Dissolve a quantity of sodium acetate trihydrate in an equal weight of water.

b. Using the pH meter, adjust the pH of the buffer solution to 9.5 ± 0.5 by the addition of 30 to 50 percent sodium hydroxide solution or glacial acetic acid, as needed.

4.4 Inert gas (carbon dioxide or nitrogen).

4.5 Titanous chloride, 0.2N standard solution as specified in Method 601.1.

4.6 Hydrochloric acid, 1:1 solution (by volume).

4.7 Ammonium thiocyanate, 20 percent solution as specified in Method 706.1.

4.8 Ferric ammonium sulfate, 0.15N standard solution as specified in Method 603.1.

5. **PROCEDURE**

5.1 Prepare the specimen as specified in Method 509.3.

5.2 Wrap the weighed specimen in a circle of filter paper and insert the wrapped specimen into a paper thimble.

5.3 Extract as directed in Method 104.1, using a mixture of 2 parts of pentane and 1 part of methylene chloride (both parts by volume) as the extracting solvent.

5.4 When extraction is complete, remove the thimble and let it air-dry at least 15 minutes. Remove the paper and sample from the thimble.

CAUTION: Use care to avoid tearing the paper.

5.5 Immerse the paper in l50 ml of hot water contained in a 600 ml beaker and macerate the paper with a stirring rod.

5.6 Cover the beaker with a watchglass and boil 10 minutes. Decant the liquor through a filter paper into a 500 ml volumetric flask.

5.7 Repeat the water extraction with two more 150 ml portions of water, collecting these in the volumetric flask also.

5.8 Add sufficient water to the flask to nearly fill the chamber. Let the contents cool to room temperature, fill with water to the mark and mix.

5.9 Using the buret, determine the volume of buffer solution which must be added to a mixture of 50 ml of propellant water- extract solution and 50 ml of 0.2N titanous chloride solution to adjust the pH to 2.30 ± 0.05.

NOTE: The volume of buffer solution required need not be separately determined for each specimen but should be determined for each batch of 0.2N titanous chloride solution and buffer solution and redetermined weekly. It should, however, be specially determined in the case of propellants

containing water extractible constituents which are likely to have a major effect on the pH of the solution. In the following paragraphs, it is essential to add the solutions in the order given.

5.10 Attach a source of inert gas to the titration flask and allow the gas to flow gently for 5 minutes to displace the air in the flask. Continue the flow of gas through the flask throughout the remainder of the determination.

5.11 Accurately measure into the titration flask 50 ml of 0.2N titanous chloride solution and the required volume of buffer solution (para. 5.9). Insert a magnetic stirrer bar into the flask, turn on the magnetic drive unit, and commence stirring. Continue stirring throughout the determination.

5.12 After at gleast 30 seconds of mixing, transfer 50 ml of the water-extract (para. 5.8) and stir for 5 ± 0.5 minutes more.

5.13 Add 25 ml of 1:1 hydrochloric acid solution and 5 ml of 20 percent ammonium thiocyanate solution, and titrate with 0.15 N ferric ammonium sulfate solution until a permanent red color appears.

5.14 Run a blank determination in accordance with paragraphs 5.10 to 5.13 but replace the aliquot of propellant water extract with 50 ml of water.

5.15 Calculate the nitroguanidine content of the propellant.

5.16 **Calculation:**

$$\text{Percent nitroguanidine} = \frac{1.7345\,(A - B)\,N}{W}$$

Where:

A = Wolume of ferric ammonium sulfate solution required for the blank, ml.

B = Volume of ferric ammonium sulfate solution required for the propellant extract, ml.

N = Normality of the ferric ammonium sulfate solution.

W = Weight of the specimen represented by the aliquot taken, corrected for total volatiles, g.

METHOD 213.5.1

NITROGUANIDINE, NITROGLYCERIN, AND ETHYL CENTRALITE (LIQUID CHROMATOGRAPHY METHOD)

1. SCOPE

1.1 This method is used for determination of nitroguanidine (NGu), nitroglycerin (NG), and ethyl centralite in multi-base propellants. The extraction method specified within this procedure provides a propellant extract for quantitative chromatographic analysis. With two ultraviolet (UV) detectors in series, NGu can be determined simultaneously with NG and ethyl centralite. NG_u is determined by external standardization. NG and ethyl centralite are determined by internal standardization.

1.2 The detector wavelength specified for NG_u provides an analysis when NG_u is a major constituent in the propellant and aids in prevention of interference from most other common propellant formulated ingredients, impurities, and degradation products as well as process solvents such as diethyl ether, alcohols, and acetone.

1.3 Of course, any ingredient having the same retention time as the desired components and responds to the specified ultraviolet wavelengths will interfere.

2. SPECIMEN

2.1 The specimen shall normally consists of approximately 3 to 4 g of propellant weighed to within 0.5 mg. The sample weight may be adjusted based on concentrations of components in the propellants.

3. APPARATUS

3.1 Liquid chromatograph equipped with constant mobile phase flow system, constant temperature column heating capability, a 340 nm ultraviolet detector for NG_u, a 254 nm ultraviolet detector for the other components, a fixed volume sample injection system, and recorders.

3.2 Sample injection system (Rheodyne Model 7120 injection valve or equivalent), 10 microliters (or as required).

3.3 Integrator, electronic digital (Hewlett-Packard Model 3370 or equivalent), - Optional, See Note 6.1.

3.4 Recorders, analytical (compatible with detectors).

3.5 Column, 0.46 x 25 cm, reverse phase ODS-Sil-X-1 (Perkin Elmer No. 089-0707) or equivalent.

3.6 Flask, 250 ml flat bottom, extraction.

3.7 Stopper, appropriate size solid rubber.

3.8 Flasks, 100 ml, volumetric.

3.9 Pipet, 5 ml.

3.10 Pipet, 100 ml.

3.11 Shaker, horizontal.

4. **MATERIALS**

4.1 N, N-Dimethylformamide (DMF), reagent grade.

4.2 Methanol, reagent grade.

4.3 Water, distilled.

4.4 NG, MIL-N-246.

NOTE: NG is highly explosive material and must be handled with extreme care.

4.5 NG_u, MIL-N-494.

4.6 Diethylphthalate (DEP), MIL-D-218.

4.7 Ethyl centralite, MIL-E-255.

4.8 Internal standard solution (for NG and ethyl centralite analysis): 20 g DEP per liter of DMF.

4.9 Extraction solvent: 75% by volume DMF and 25% by volume distilled water.

5. **PROCEDURE**

5.1 Calibration

a. Prepare three or more standards, containing known weights of the components to be analyzed, in 100 ml volumetric flasks. (The concentration of the standards should cover the ranges expected for the samples). Weigh to an accuracy of ± 0.2 mg.

b. For NG and ethyl centralite analyses, pipet 5 ml of internal standard solution (0.1000 g DEP) into each flask.

c. Dilute each standard to volume with extraction solvent.

d. Test each standard per paragraphs 5.3 and 5.4. The order of elution is shown in the two superimposed chromatograms in Figure 1.

e. Prepare a calibration curve for each component. For NGu plot peak heights vs concentration of standards. For NG and ethyl centralite plot the ratios of peak areas (or peak heights) of component/internal standard vs concentrations of standards.

f. Plots should be linear to assure sample weights, sample dilution, and size of injected sample are suitable for concentration of components in sample and for the liquid chromatograph employed. Once standardization linearity is established only two standards, representing concentration range of samples, are needed for future calibration.

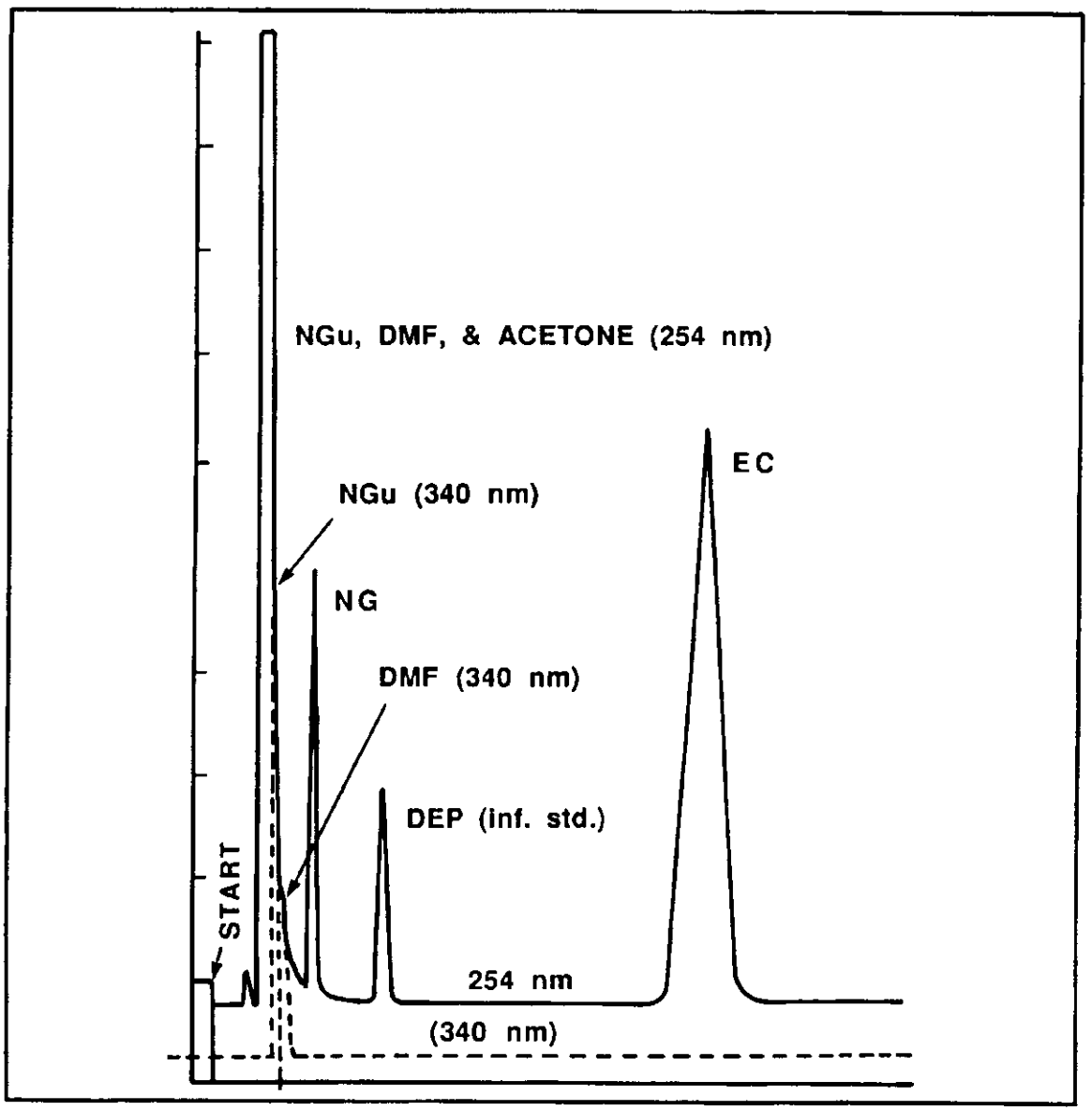


Figure 1. *Liquid Chromatographic Separation Propellant Extract.*

g. Obtain the slope (K_i) and Y-axis intercept (b_i) for each calibration curve as follows:

$$\text{Slope } (K_i) = \frac{Y_2 - Y_1}{X_2 - X_1}$$

$$\text{Intercept } (b_i) = Y_2 - K_i X_2$$

Where:

Y = peak height of NG_u or ratio of component to internal standard peak areas (or peak heights) for NG or ethyl centralite.

X = Corresponding concentration of standards.

h. Use the slopes and Y axis intercept to obtain a simplified equation for each ingredient to be calculated.

$$\% C_i = \frac{(A - b_i)\,(100)\,(N)}{(K_i)\,Wg}$$

Where:

$\% C_i$ = percent ot ingredient in propellant

A = test sample peak height for NGu or test sample ratio of component to internal standard peak areas (or peak heights) for NG or ethyl centralite.

K_i = slope of calibration curve.

b_i = Y-axis intercept value

Wg = grams of sample extracted

N = ratio of volume of extraction solvent in sample to that of standard (105/100 for NG_u calcuation). For NG and EC by internal standard technique, N = 1.

5.2 Sample extraction.

a. Prepare the specimen as described in Method 509.3.

b. Add approximately 3 to 4 grams of prepared specimen, weighed to within ± 0.5 mg, to a 250 ml flat bottom extraction flask.

c. Pipet 100 ml of extraction solvent and 5 ml of internal standard solution (0.1000 g DEP) into the extraction flask. Immediately stopper flask.

NOTE: If only NG_u is to be determined, omit the 5 ml of internal standard.

d. Place the prepared flask on a horizontal shaker at a low speed for gentle agitation at ambient conditions to extract the sample. The DMF will swell the propellant to facilitate removal of desired propellant ingredients without dissolving the nitrocellulose.

e. Extraction times may vary with propellant type and particular ingredients involved. A minimum of eight hours is usually sufficient for removal ot NGu, NG, and ethyl centralite from a triple base propellant such as M30.

f. Remove the flask from the shaker and allow solids to settle (15 minutes is usually sufficient).

g. The extract is ready to be tested once the instrument has stabilized.

5.3 Instrument conditions.

a. Wavelength of detectors: 254 nm for NG and ethyl centralite and 340 nm for NG_u.

b. Column temperature: 50°C

c. Mobile phase: degassed methanol/water (50/50 by volume).

NOTE: Solvent ratio may be varied to aid in separation of components.

d. Mobile phase flow rate: 1.3 ml/min (approximately 700 psig).

NOTE 1 psi = 6.9 kPa

e. Sample size: 10.0 microliters (or as required).

f. Recorder speed: 0.2 in/min (or as required).

5.4 Sample testing.

a. Once the liquid chromatograph has stabilize, inject a 10.0 microliter aliquot of the extract into the liquid chromatograph and monitor peak areas with the electronic digital integrator or peak heights with the recorder.

b. Components will elute from the column through the detectors as shown in the two superimposed chromatograms in Figure 1.

c. Using peak heights or the integrated peak areas, calculate the percentage of ingredients by the simplified equations obtained during calibration.

6. NOTES

6.1 Liquid chromatograph ultraviolet detectors are concentration detectors and a constant mobile phase flow rate is a necessity to obtain reproducible peak areas.

METHOD 213.6.1

NITROGUANIDINE
(NON-AQUEOUS TITRIMETRIC METHOD)

1. SCOPE

1.1 This method can be used for the assay of nitroguanidine, and for its determination in the presence of non-interfering substances such as HMX and RDX.

1.2 Nitroguanidine (NG_u) is dissolved in acetic anhydride and titrated potentiometrically with a standard solution of perchloric acid in glacial acetic acid. Emf's are monitored by any convenient method such as the first or second derivative method.

2. SPECIMEN

2.1 The specimen shall consist of 5 mg of (NG_u) per 10 ml of solution.

3. APPARATUS

3.1 Automatic titrator or pH meter.

3 2 Glass or platinum indicating electrode.

3.3 Modified calomel electrode consisting of a ceramic fiberjunction calomel electrode (Beckman No. 39402 or equivalent) in which the salt bridge is a saturated solution of tetramethylammonium chloride in methanol.

3.4 Automatic or standard 10 ml microburet.

3.5 Ultrasonic generator and tank for solution of samples.

3.6 Standard volumetric glassware.

4. MATERIALS

4.1 Acetic anhydride, reagent grade.

4.2 Glacial acetic acid, reagent grade.

4.3 Tetramethylammonium chloride in methanol, saturated solution.

4.4 Potassium acid phthalate or sodium acetate trihydrate, reagent grade.

4.5 0.05 n-Perchloric acid in glacial acetic acid. Add 4.25 ml of 70% perchloric acid and 20 ml of acetic anhydride to 500 ml of glacial acetic acid. Dilute to 1 liter with glacial acetic acid.

5. STANDARDIZATION OF TITRANT

5.1 Weigh to the nearest 0.1 mg approximately 100 mg of sodium acetate trihyrate, or approximately 150 mg of potassium acid phthalate, into a 50 ml volumetric flask.

5.2 Dissolve in and dilute to volume with acetic acid. (Several minutes suspension in the tank of an ultrasonic generator promotes solution of samples).

5.3 Pipet at least three 10 ml aliquots of the standard solution into a 150 ml beaker containing a stirring bar.

5.4 Dilute to about 50 ml with acetic acid.

5.5 Titrate at least 3 samples manually or automatically with the titrant to be standardized.

5.6 Calculate the normality of the titrant from:

$$N = \frac{\text{(mg standard per aliquot) / (molecular weight of standard)}}{\text{(ml of titrant to endpoint)}}$$

5.7 If the endpoint is determined manually it can easily be calculated if equal increments of titrant are added near the endpoint, according to the method of Lingane.

5.8 The range of triplicates should not be greater than 1 part per 100.

6. PROCEDURE

6.1 Prepare samples containing no more than 5 mg of NG_u per 10 ml of solution. This can be done by weighing separate samples and dissolving in 50 ml of acetic anhydride, or by preparing a solution in a volumetric flask from which aliquots can be pipetted.

6.2 Because NG_u does not dissolve easily in acetic anhydride an ultrasonic generator should be used to speed up dissolution of samples.

6.3 Titrate samples containing about 15 mg of NG_u per 50 ml of solution with standard titrant.

6.4 Determine the endpoint as described under 5.6 and 5.7

7. CALCULATION:

$$\%\ NG_u = \frac{\text{(ml titrant) (Normality titrant) (104.065) (100)}}{\text{mg sample}}$$

Where 104.065 is the molecular weight of NG_u

8. TITRATION CURVE

A typical titration curve for the titration of NG_u in acetic anhydride with 0.05 N-perchloric acid in glacial acetic acid is shown in figure 1.

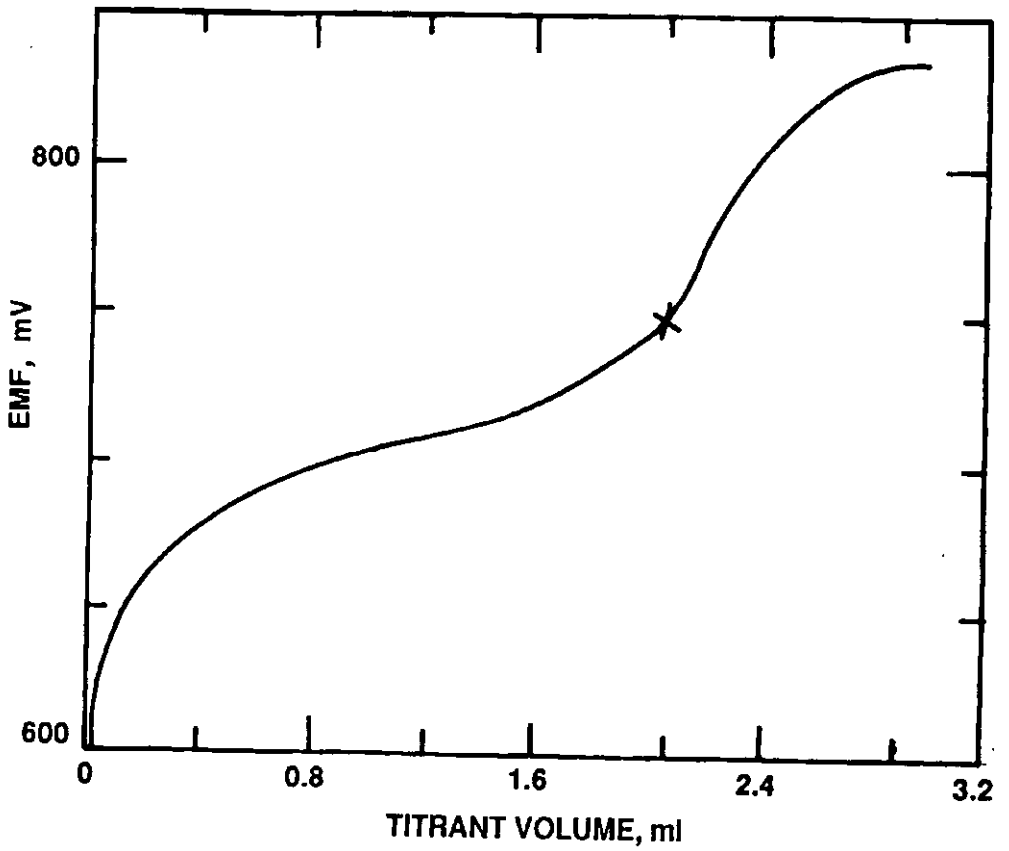


Figure 1. *Titration of 9.79 mg of NO in acetic anhydride.*

9. LIMITATIONS OF METHOD

The method is limited to the micro and semimicro scale because of the limited solubility of NG_u in acetic anhydride, approximately 0.05 nm (5mg) per ml. Titrations are also feasible if NG_u is dissolved in glacial acetic acid and sufficient acetic anhydride is added for an anhydride: acetic acid ratio of 4:1. This increases the amount of NG_u that can be dissolved. However, as the amount of acetic acid increases, the steepness and magnitude of the endpoint break decreases. Other basic compounds will interfere. Because compounds such as RDX and HMX are weakly acidic, NG_u can be determined in their presence. Binders such as Estane and Viton do not interfere.

METHOD 216.1

AMMONIUM PERCHLORATE (NON-AQUEOUS TITRIMETRY)

1. SCOPE

1.1 This procedure is for the non-acqueous titrimetric measurement of ammonium perchlorate (AP) in cast propellant and casting powder. The sample is weighed out, dissolved in acetone and the ammonium ion is titrated as an acid directly with methanolic potassium (KOH). Potentiometric detection of the end point is employed using a glass-calomel electrode system. The use of the inert solvent, acetone, prevents interference from other propellant components (Note 2).

1.2 The presence of any other materials that titrate as stronger acids than the ammonium ion will interfere with the determination. Excessive absorption of carbon dioxide will slightly affect the end point.

1.3 The standard deviation of this method is $\pm$ 0.47.

2. SPECIMEN

2.1 The propellant specimen shall be sufficient to contain 0.2-0.4 grams of AP.

3. APPARATUS

3.1 Potential measuring system, an automatic recording titrimeter, a manual pH meter or the equivalent is suitable in conjuction with a glass-calomel electrode couple.

4. MATERIALS

4.1 Acetone.

4.2 Methyl Alcohol.

4.3 Benzoic Acid, primary standard.

4.4 Methanolic KOH, 0.1N. Dissolve about 5.6 g of KOH in methyl alcohol and make up to one liter.

5. STANDARDIZATION.

5.1 Accurately weigh out to the nearest 0.1 mg about 0.30 to 0.40 g of benzoic acid.

5.2 Quantitatively transfer to a beaker.

5.3 Add 100 ml of acetone and stir into solution.

5.4 Using a glass-calomel electrode system and a suitable potential measuring device, potentiometrically titrate the benzoic acid with the 0.1N methanolic KOH.

5.5 Select the end point where the mV/ml ratio is the greatest.

Calculate the AP titer (g AP/ml titrant) of the KOH as follows:

$$T = \frac{W}{V} \times 0.9621$$ Where:

T = AP titer (g AP/ml titrant).

W = Weight of benzoic acid titrated, g.

V = Volume of titrant required, ml.

0.9621 = Conversion factor.

6. **PROCEDURE**

6.1 Accurately weigh out to the nearest 0.1 mg, sufficient sample to contain about 2-3 meq of AP (note 3).

6.2 Quantitatively transfer to a beaker and add about 100 ml of acetone.

6.3 Stir until all solubles are in solution.

6.4 Using the glass - calomel electrode system and a suitable potential measuring device, titrate the sample with the methanolic 0.1N KOH.

6.5 Select the end point where the mV/ml ratio is the greatest.

6.6 A solvent blank should be run and corrections made, if necessary (Note 1).

6.7 **Calculation:**

$$\text{Percent AP} = \frac{VT}{W} 100$$ Where:

V = Volume of titrant required, ml.

T = AP titer of KOH titrant, g AP/ml titrant.

W = Sample weight, g.

NOTE 1: Excessive absorption of carbon dioxide will effect the end point break. A nitrogen purge before titration may be necessary. Usual precaution to protect the methanolic KOH from CO_2 is necessary.

NOTE 2: This procedure can also be used on the residue from a methylene chloride or ether extraction (Method 104.1).

NOTE 3: If sample weight is too small, a larger sample weight may be used, the solution made up to volume and an aliquot taken for analysis.

METHOD 217.2.1

AVAILABLE STABILIZER
(DIPHENYLAMINE OR ETHYL CENTRALITE)

1. SCOPE

1.1 This method is used for determining the percentages of diphenylamine and ethyl centralite (when present together) in propellants that contain no other brominatable material. This method is also used for determining the persentage of "available stabilizer" calculated as diphenylamine or ethyl centralite but does not distinguish between them and their primary degradation products.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5 gm of propellant, weighed to within 0.2 mg.

3. APPARATUS

3.1 Balloon flask, one-liter, fitted with a two- hole rubber stopper containing a steam inlet tube and a gooseneck tube about 20 cm high and 11 mm o.d.

3.2 Steam generator, consisting of a two-liter balloon flask with a two-hole rubber stopper, an exit tube for the steam, and a 3-foot length of glass tubing extending vertically through the stopper (to serve as a pressure equalizer) (Fig. 1)

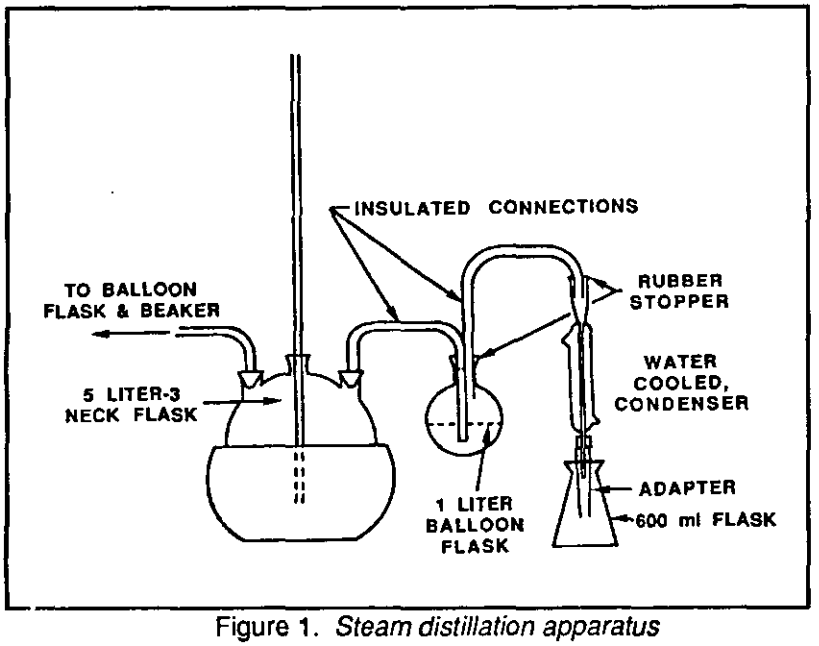


Figure 1. *Steam distillation apparatus*

3.3 Condensate trap, consisting of a "T" tube with a short piece of rubber tubing attached, and a pinch clamp to close the tubing. This trap may be in the steam line between the steam generator and the one-liter balloon flask.

3.4 Liebig condenser, 18-inch, with an adapter capable of reaching to the bottom of a 750-ml Erlenmeyer flask.

3.5 Erlenmeyer flask, 500 ml.

3.6 Separatory funnel, one-liter.

3.7 Crucibles, pyrex fritted glass, medium porosity, low form, 30 ml capacity.

3.8 Beaker, 400 ml.

3.9 Steam bath in a well ventilated hood (maintained at approximately 75 C on the surface).

3.10 Dessicator containing an indicating dessicant.

4. **MATERIALS**

4.1 Sodium hydroxide, 30 percent solution, prepared by dissolving 300 gm of sodium hydroxide in 700 ml of water.

4.2 Methylene chloride.

4.3 Sodium chloride, technical.

4.4 Bromine, reagent grade.

4.5 Ethyl alcohol, 10 percent aqueous solution.

5. **PROCEDURE**

5.1 Extract the specimen as follows:

NOTE: Freshly manufactured propellant may be extracted as specified in Method 104.1.

a. Place the specimen in the one-liter balloon flask and add 100 ml of distilled water and 100 ml of 30 percent sodium hydroxide solution.

b. Place the two-hole stopper on the flask and connect the gooseneck tube to the condenser.

c. Insert the adapter on the end of the condenser into the Erlenmeyer flask containing 25 ml of distilled water. The end of this adapter should be made to dip below the surface of the water.

NOTE: For propellants containing 4 to 5 percent ethyl centralite, or 1 to 3 percent diphenylamine, use a 750 ml Erlenmeyer flask.

d. Connect the flask to the steam generator and distill a total of 350 to 400 ml. An auxiliary heater may be used under the flask containing the propellant.

NOTE: For propellants containing 4 to 5 percent ethyl centralite or 1 to 3 percent diphenylamine, collect from 450 to 500 ml of distillate.

e. Disconnect the stem generator. Remove the Erlenmeyer flask and add approximately 5 gm of sodium chloride to the distillate.

f. Transfer the distillate to a separatory funnel and return the flask to its position under the condenser.

g. Disconnect the condenser from the balloon flask and clamp it in a vertical position. Wash down the inside of the condenser and the inside and outside of the adapter with approximately 75 ml of methylene chloride, collecting the washings in the Erlenmeyer flask. Also remove the gooseneck tube from the balloon flask and wash its insides with methylene chloride, collecting the washings in the Erlenmeyer flask.

h. Transfer all the washings to the separatory funnel, stopper the funnel, and shake vigorously for several minutes.

i. Drain the solvent layer into a 400 ml beaker and retain the aqueous layer in the separatory funnel.

j. Add 75 ml of methylene chloride to the aqueous portion, shake, then transfer the solvent layer to the 400 ml beaker.

k. Repeat step (j).

5.2 Determine the percentage of diphenylamine and ethyl centralite as follows:

NOTE: If only diphenylamine or only ethyl centralite is present, evaporate the solvent with a current of dry air and proceed with a standard volumetric bromination as described in Method 201.1 or 202.2, as applicable.

a. Adjust the volume of methylene chloride in the 400 ml beaker to approximately 150 ml.

b. Brominate the solution and determine (gravimetrically) the percentage of diphenylamine as described in Method 201.2. However, when filtering the tetrabromdiphenylamine, catch the filtrate and washings in a thoroughly clean 400 ml beaker, and retain them for the determination of ethyl centralite.

c. To the filtrate, add 100 ml of hot distilled water and place the beaker on the steam bath maintained at 75° C on the surface.

d. With a stream of air directed on the surface of the liquid to assist in the removal of alcohol from the solution, heat the beaker for 4 hours to permit the precipitate to coagulate. Stir the contents occasionally. Also, during the last 3 hours, wash down the sides of the beaker occasionally with small portions of ethyl alcohol.

e. After the dibrom-ethyl centralite has become thoroughly coagulated, filter the hot solution through a tared pyrex filtration crucible. Use a rubber policeman to be sure that all the dibrom-ethyl centralite is removed from the beaker.

f. Wash the beaker thoroughly, first with water, then with two 5 ml portions of the 10 percent ethyl alcohol, and finally with water. Transfer all the washings to the crucible.

g. Dry the crucible for 1 hour at 105 ± 2°C, then cool it to room temperature in a dessicator.

h. Determine the increase in weight of the crucible to within 0.2 mg.

i. Calculate the percentage of ethyl centralite in the propellant.

j. **Calculation:**

$$\text{Percent ethyl centralite} = \frac{62.97\ A}{B}$$

Where:

A = Weight of dibrom-ethyl centralite (increase in weight of the crucible).

B = Weight of sample, corrected for total volatiles.

METHOD 217.3.1

DIPHENYLAMINE OR ETHYL CENTRALITE (STEAM DISTILLATION VOLUMETRIC BROMINATION METHOD)

1. SCOPE

1.1 This method is suitable for determining the diphenylamine (DPA) or ethyl centralite (EC) content in either aged or newly manufactured propellants. Other propellant ingredients that steam distill and are brominatable will interfere. This method may be used for determining the percentage of "available stabilizer" calculated as diphenylamine or ethyl centralite but does not distinguish between them and their primary degradation products.

2. SPECIMEN

2.1 The nominal content of the stabilizer in the propellant controls the weight of specimen required. The specimen shall consist of approximately the weight of propellant given in table below, weighed within 0.2 mg.

Nom Content, Pct	wt of Specimen, g
DPA	EC
< 0.5	< 4.0 .....5.0
0.5 to 1.0	4 to 6 .....2.5
> 1.0	> 6 .....1.25

3. APPARATUS

3.1 Steam distillation apparatus. A stopper should be placed in a steam outlet of the 3 necked flask if only one distillation is being conducted. (figure 1).

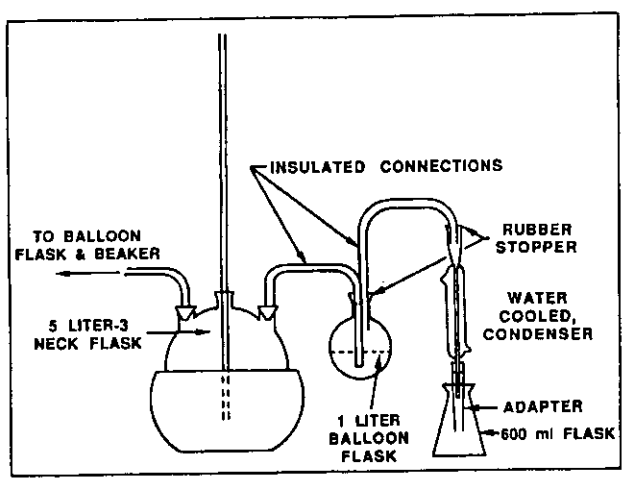


Figure 1. *Steam distillation apparatus.*

3.2 Iodine titration flask (with stopper), 1 liter.

3.3 Pipet, 25 ml.

4. **MATERIALS**

4.1 Sodium hydroxide, 15 percent solution, prepared by dissolving 3O g of sodium hydroxide in distilled water to give 200 ml of solution.

4.2 Glacial acetic acid.

4.3 Potassium iodide, 15 percent solution.

4.4 Hydrochloric acid, 38 percent solution.

4.5 Sodium thiosulfate, 0.2N standard solution as specified in Method 602.1.

4.6 Potassium bromate-bromide solution, 0.2N standard solution as specified in Method 605.1.

4.7 Starch indicator solution as specified in Method 701.1.

5. **PROCEDURE**

5.1 Distillation of specimen. Distill the specimen as follows:

a. Place the specimen in the short necked flask of the steam distillation apparatus shown in Figure 1 and add 200 ml of the sodium hydroxide solution. (figure 1.)

NOTE: Use a ground sample. (Use method 509.3 for sample preparation and use a 20 mesh screen.)

b. Place the two hole stopper in the flask, and connect the gooseneck tube to the condenser.

c. Insert the adapter on the end of the condenser into a 600 ml beaker containing l00ml glacial acetic acid. The end of this adapter should be made to dip below the surface of the acid.

d. Pass steam through the short necked flask at a rate of 7 to 9 ml/min and collect 400 ± 25 ml of the distillate. Transfer the contents of the beaker to the 1:1 iodine titration flask.

e. Wash the condenser with three 10 ml portions of glacial acetic acid and collect the washing in the iodine flask. Remove the iodine flask.

5.2 Analysis of specimen.

a. To the solution in the iodine flask, add 25 ml of the potassium bromate-bromide solution accurately measured to within 0.03 ml.

b. Moisten the stopper of the flask with a drop of 15 percent potassium iodide solution and add 7 ml of 38 percent hydrochloric acid to the flask, noting the time. Stopper the flask immediately, swirl the contents for a few seconds, and allow the bromination to proceed for 1.0 ± 0.25 minutes from the time of addition of the hydrochloric acid.

c. At the end of the brominating time, add 10 ml of 15 percent potassium iodide solution to the gutter of the iodine flask, cautiously loosen the stopper to allow the solution to enter slowly and then mix the contents of the flask by swirling.

d. Wash down the gutter of the flask with distilled water, and titrate the resulting solution immediately with 0.2N sodium thiosulfate until the solution assumes a light yellow color.

e. Add 5 ml of the starch indicator solution, and continue the titration carefully until the blue color of the solution disappears.

f. Make a blank determination, using 400 ml of water, 130 ml of glacial acetic acid and 25.0 ml of the potassium bromate-bromide solution. Use procedural steps described in 5.2b through 5.2e.

g. Calculate the percentge of diphenylamine or ethyl centralite in the specimen on the volatiles free basis.

h. **Calculations:**

$$\text{Percent Diphenylamine} = \frac{2.115\ (A - B)\ N}{W}$$

$$\text{Percent Ethyl Centralite} = \frac{6.71\ (A - B)\ N}{W}$$

Where:

A = Sodium thiosulfate required for the blank, ml.

B = Sodium thiosulfate required to titrate the liberated iodine in the solution containing the brominated specimen, ml.

N = Normality of the sodium thiosulfate solution.

W = Weight of the specimen, corrected for total volatiles, g.

METHOD 217.4.1

DIPHENYLAMINE AND ETHYL CENTRALITE IN ADMIXTURE OR SEPARATELY (DISTILLATION GRAVIMETRIC AND VOLUMETRIC BROMINATION)

1. SCOPE

1.1 This method is suitable for determining the diphenylamine and ethyl centralite contents of either aged or newly manufactured propellants. Ingredients that steam distill and are brominatable will interfere and propellants containing such ingredients should be analyzed by method 201.4.1.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5 g of propellant weighed to within 0.2 mg.

3. APPARATUS

3.1 Steam distillation apparatus (figure 1). A stopper should be placed in a steam outlet of the 3 necked flask if only one distillation is being conducted.

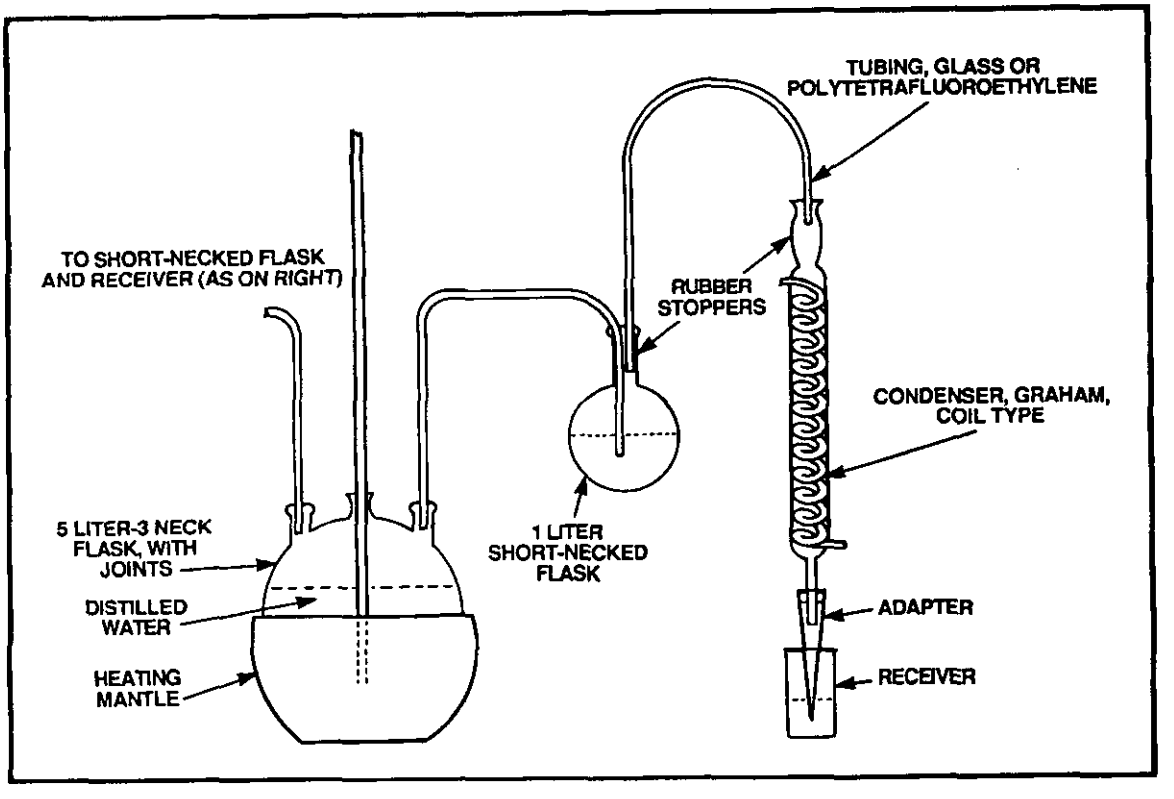


Figure 1. *Steam distillation apparatus.*

3.2 Steam bath.

3.3 Desiccator.

3.4 Erlenmeyer flask, 750 ml.

3.5 Separatory funnel, 1 liter.

3.6 Crucible, fritted-glass, medium porosity, 30 ml capacity. medium.

3.7 Iodine titration, 250 ml.

3.8 Volumetric flask, 250 ml.

3.9 Pipet, 100 ml.

4. **MATERIALS**

4.1 Sodium hydroxide, 15 percent solution. Dissolve 15 g of sodium hydroxide in distilled water and dilute to 100 ml with distilled water.

4.2 Methylene chloride.

4.3 Sodium chloride.

4.4 Bromine.

4.5 Ethyl alcohol, 95 percent.

4.6 Glacial acetic acid.

4.7 Potassium iodide, 15 percent solution.

4.8 Hydrochloric acid, 38 percent solution.

4.9 Potassium bromate-bromide, 0.2N standard solution as specified in method 605.1.

4.10 Sodium thiosulfate, 0.1N standard solution as specified in Method 602.1.

4.11 Starch indicator solution as specified in Method 701.1.

5. **PROCEDURE**

5.1 Carry out a steam distillation on a solution of specimen as follows:

a. Place the specimen in the short necked flask of the steam distillation apparatus shown in figure 1 and add 200 mL of the sodium hydroxide solution.

NOTE: Use a ground sample in case of large grains.

b. Place the 2 hole stopper in the flask, and connect the gooseneck tube to the condenser.

c. Insert the adapter on the end of the condenser into the 750 ml Erlenmeyer flask containing 25 ml of distilled water.

d. Connect the flask to the steam generator and pass steam through the short necked flask at a rate of 7 to 9 ml/min. For propellants containing up to 1 percent diphenylamine or 4 percent ethyl centralite, collect 350 to 400 ml of distillate. For propellants containing 1 to 3 percent diphenylamine or 4 to 6 percent ethyl centralite, collect from 450 to 500 ml of distillate.

e. Wash the condenser with three 20 ml portions of methylene chloride and collect the washings in the 750 ml Erlenmeyer flask. Add approximately 5 g of sodium chloride to the distillate.

5.2 Extract the diphenylamine and (or) ethyl centralite as follows:

Wash the distillate into the 1 liter separatory funnel with water, stopper, and shake vigorously for several minutes. Allow the layers to separate and drain of lower methylene chloride portion into a 250 ml volumetric flask. Extract twice more with 60 ml of methylene chloride and add the methylene chloride layers to the 250 ml volumetric flask. Dilute to the 250 ml mark with methylene chloride.

5.3 Determine the diphenylamine as follows:

a. Pipet a 100 ml aliquot of the methylene chloride solution from the 250 ml volumetric flask into a 250 ml beaker. Place the beaker on the steam bath and add enough bromine (0.6 ml for each percent of diphenylamine and ethyl centralite) drop by drop to assure a slight excess. Allow the contents to come to a boil. Remove the beaker from the steam bath and evaporate the methylene chloride and excess bromine by means of a current of dry air until the odor of solvent is gone.

b. To the residue in the beaker add 40.0 ml of 95 percent ethyl alcohol and heat to boiling. Add 40.0 ml of distilled water and note the time. Allow the beaker to remain on the steam bath for exactly 10 minutes.

NOTE: If no precipitate appears at this stage, diphenylamine is absent. In that case, proceed with the determination of ethyl centralite as described in para. 5.4.

c. Filter the hot solution through a tared filtering crucible and wash with about 50 ml of boiling 47.5 percent ethyl alcohol and then with 50 ml of hot distilled water (temperature around 80°C).

d. Heat the crucible for 2 hours at 105 ± 2°C cool in a desiccator, and weigh.

e. Calculate the percentage of diphenylamine.

f. **Calculation:**

$$\text{Percent DPA} = \frac{34.90 \times A \times 2.5}{W}$$

Where:
A = weight of tetrabromdiphenylamine (increase in weight of crucible), g.

W = weight of specimen, corrected for total volatiles, g.

5.4 Determine the ethyl centralite as follows:

a. Pipet a 100 ml aliquot from the methylene chloride solution in the 250 ml volumetric flask into a 250 ml beaker. Evaporate off the methylene chloride by means of a current of dry air. Dissolve the residue in glacial acetic acid, transfer to a 100 ml volumetric flask with glacial acetic acid, and dilute to the mark with glacial acetic acid.

b. Pipet a 50.0 ml aliquot of the acetic acid solution into a 250 ml iodine titration flask, add 25 ml of the potassium bromate-bromide solution from a buret and then add 5 ml of 38 percent hydrochloric acid. Stopper the flask immediately, swirl the contents for a few seconds, and allow the bromination to proceed for 1.0 $\pm$ 0.25 minutes from the time of addition to the hydrochloric acid.

c. At the end of the brominating time, add 10 ml of 15 percent potassium iodide solution, and swirl the flask. Wash down the gutter and walls of the flask with distilled water and titrate immediately with 0.1N sodium thiosulfate solution until the solution assumes a light yellow color. Add 5 ml of the starch indicator solution and continue the titration carefully until the blue color disappears. Make a blank determination, using 50 ml of glacial acetic acid and exactly the same volume of the potassium bromate-bromide solution as for the sample.

d. Calculate the percentage of ethyl centralite.

e. **Calculation:**

$$\text{Percent ethyl centralite} = 6.71\left[(A-B)Nx5 - \frac{\%DPA \times W}{2.115}\right]$$

Where:

A = Sodium thiosulfate required for the blank, ml.

B = Sodium thiosulfate required for the sample, ml.

N = Normality of sodium thiosulfate solution.

W = Weight of specimen, corrected for total volatiles, g.

METHOD 218.1.2

2-NITRODIPHENYLAMINE (VOLUMETRIC BROMINATION METHOD)

1. SCOPE

1.1 This method is used for determining the 2-nitrodiphenylamine content of propellants containing nitrate esters or nitro compounds. Other brominatable compounds must be absent.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5 g of the propellant, weighed to within 0.2 mg.

3. APPARATUS

3.1 Iodine titration flask (with stopper), 250 ml.

3.2 Volumetric flask, 100 ml.

4. MATERIALS

4.1 Glacial acetic acid.

4.2 Methylene chloride.

4.3 Potassium bromate-bromide, 0.5N standard solution as specified in Method 605.1.

4.4 Hydrochloric acid, 38 percent solution.

4.5 Potassium iodide, 10 percent solution.

4.6 Sodium thiosulfate, 0.2N standard solution as specified in Method 602.1

4.7 Starch indicator solution as specified in Method 701.1.

5. PROCEDURE

5.1 Prepare the specimen as specified in Method 509.3.

5.2 Extract the specimen and dry the extract as specified in Method 104.1.

5.3 Dissolve the dried residue of the extraction in 10 ml of glacial acetic acid.

5.4 Transfer the solution quantitatively to a 250 ml iodine titration flask; rinse the extraction flask with several 10 ml portions of glacial acetic acid; and transfer the rinsings to the titration flask, using a total of 50 ml of acetic acid.

5.5 To the 50 ml solution in the iodine titration flask, add 25 ml of methylene chloride, and an accurately measured portion of 10 ml ot the 0.5N solution of potassium bromate-bromide.

5.6 Moisten the stopper of the flask with a drop of 10 percent potassium iodide solution, and add 5 ml of 38 percent hydrochloric acid to the flask, noting the time. Stopper the flask immediately, swirl the contents for a few seconds, and allow the bromination to proceed for 1.0 $\pm$ 0.25 minutes from the time of the addition of the hydrochloric acid.

5.7 At the end of the brominating time, add 25 ml of 10 percent potassium iodide solution, and swirl the contents of the flask.

5.8 Wash down the gutter and walls of the flask with distilled water, and titrate the resulting solution immediately with 0.2N sodium thiosulfate solution until near the end point, as indicated by the disappearance of the strong iodine color.

5.9 Add 5 ml of the starch indicator solution, and continue the titration carefully until the blue color disappears.

CAUTION: The solution must be vigorously shaken as the end point is approached so that all the iodine dissolved in the methylene chloride will be titrated.

5.10 Make a blank determination, using exactly the same volumes of the potassium bromate-bromide solution, glacial acetic acid and methylene chloride (para. 5.4 and 5.5).

5.11 Calculate the percentage of 2 nitrodiphenylamine in the propellant as follows:

5.12 **Calculation:**

$$\text{Percent 2-nitrodiphenylamine} = \frac{3.570\,(A - B)\,N}{W}$$

Where:

A = *Sodium thiosulfate required for the blank, ml.*

B = Sodium thiosulfate required to titrate the liberated iodine in the solution containing the brominated specimen.

N = Normality of sodium thiosulfate solution.

W = Weight of the specimen corrected for total volatiles, g.

METHOD 218.2.1

2-NITRODIPHENYLAMINE (TITANOUS CHLORIDE-BUFFER METHOD)

1. SCOPE

1.1 This method is used for determining the 2-nitrodiphenylamine content of freshly manufactured single-base propellants containing no other nitro compounds.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5 g of the propellant, weighed to within 0.2 mg.

3. APPARATUS

3.1 Titration flask (figure 1).

3.2 Rubber stopper for inlet tube of titration flask.

3.3 Steam bath.

4. MATERIALS

4.1 Ethyl alcohol, 95 percent (MIL-E-463, Grade 1).

4.2 Potassium hydroxide, 0.5N alcoholic solution.

4.3 Glacial acetic acid (JAN-A-465).

4.4 Sodium acetate buffer solution prepared as directed in method 213.4, para 4.3.

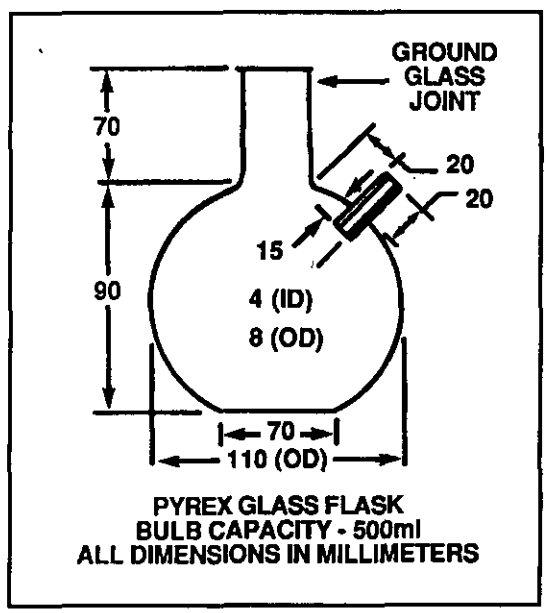


Figure 1. *Titration Flask*

4.5 Inert gas (carbon dioxide or nitrogen).

4.6 Titanous chloride, 0.2N standard solution as specified in Method 601.1.

4.7 Hydrochloric acid, 15 percent solution.

4.8 Ammonium thiocyanate, 20 percent solution as specified in Method 706.1.

4.9 Ferric ammonium sulfate, 0.15N standard solution as specified in Method 603.1.

5. PROCEDURE

5.1 Prepare the specimen as specified in Method 509.3.

5.2 Extract the specimen as described in Method 104.1. For the extraction, use the titration flask (para 3.1) with its inlet tube plugged by the rubber stopper.

5.3 Dissolve the residue trom the extraction in 10 ml of 95 percent ethyl alcohol, and add 10 ml of the 0.5N alcohol potassium hydroxide solution.

5.4 Heat the flask on a steam bath for two hours.

5.5 Dry the contents of the flask under a slow stream of dry air until the odor of alcohol is no longer discernible.

5.6 Dissolve the residue in 40 ml of glacial acetic acid. Add 25 ml of 20 percent sodium acetate buffer solution.

NOTE: If the phthalate ester has not been completely saponified by the potassium hydroxide, it will appear as an oily, immiscible liquid, upon the addition of the sodium acetate solution. Discard any determination in which the phthalate ester has not been completely saponified.

5.7 Remove the rubber stopper from the inlet tube of the flask. Attach a source of inert gas to the inlet tube, and allow the gas to flow gently for five minutes to displace all the air in the flask. Continue the flow of gas throughout the remainder of the determination.

5.8 After the gas has flowed for five minutes, add in 2-ml increments a total of 40 ml of the 0.2N titanous chloride solution, swirling the flask after each addition to insure complete reduction of the 2 nitrodiphenylamine. Then swirl the flask for another 15 minutes.

5.9 Add 25 ml of the 15 percent hydrochloric acid solution and 5 ml of the 20 percent ammonium thiocyanate solution.

5.10 Titrate with the standard 0.15N ferric ammonium sulfate solution to the end point (indicated by the first permanent red coloration).

5.11 Conduct a blank determination using the same reagents in the same quantities as in steps 5.6 through 5.10 above.

5.12 Calculate the percentage of 2-nitrodiphenylamine.

5.13 **Calculation:**

$$\text{Percent of 2-nitrodiphenylamine} = \frac{3.570\,(A - B)N}{W}$$

Where:

A = volume of ferric ammonium sulfate solution used for blank, ml.

B = Volume of ferric ammonium sulfate solution used for specimen, ml

N = Normality of ferric ammonium sulfate solution.

W = Weight of specimen, corrected for total volatiles, g.

METHOD 218.4.3

2-NITRODIPHENYLAMINE (SPECTROPHOTOMETRIC METHOD)

1. SCOPE

1.1 This method is suitable for determining the 2-nitrodiphenylamine (2-NDPA) content of newly manufactured propellants. Aged propellants containing compounds that absorb in the spectral region at which measurement is made (420-430 nanometers) should not be determined by this method. The standard deviation of this method for determination in triplicate is ± 0.02 percent 2-NDPA.

2. SPECIMEN

2.1 The sample shall consist of an accurately weighed specimen of the propellant. Sample weight shall be calculated from the nominal percentage of 2-NDPA in the sample to give a concentration of 0.005 to 0.015 mg/ml in the reading cell specimen (para. 5.5).

3. APPARATUS

3.1 Extraction apparatus as specified in Method 104.1.

3.2 Spectrophotometer.

3.3 Absorption cells, approximately l0 mm light path length.

3.4 Volumetric flasks, 100, 250, and 500 ml capacities.

3.5 Pipets, 1, 2 and 5 ml capacities, or buret.

4. MATERIALS

4.1 2-Nitrodiphenylamine.

4.2 Ethyl alcohol, 95 percent.

4.3 Acetic acid, glacial.

5. PROCEDURE

5.1 Prepare a standard curve as follows:

a. Weigh 0.2 g of 2-NDPA to ± 0.1 mg. Transfer to a 500 ml volumetric flask, dissolve and dilute to volume with ethyl alcohol. The final concentration of this solution should be between 0.4 to 0.5 mg/ml.

b. Transfer 1.0, 2.0, 3.0, and 4.0 ml aliquots to 100 ml volumetric flasks, dilute to volume with ethanol and mix thoroughly.

c. Transfer a portion of each of these solutions to absorption cells. Fill a similar cell with ethyl alcohol for references.

d. Scan the most concentrated solution between 420 and 430 nanometers (nm) and determine the wavelength giving maximum absorbance. Measure the absorbance of each solution at the wavelength corresponding to the maximum absorbance.

e. Using linear graph paper, plot absorbance (ordinate) vs concentration, mg 2-NDPA/l00 ml (abscissa).

5.2 Prepare the specimen as specified in Method 509.3.

5.3 Place the specimen (para. 2.1) in a Soxhlet or Roweg extractor (or equivalent) and extract as specified in Method 104.1.

5.4 Dissolve the solvent free extract in approximately 50 ml of acetic acid. Quantitatively transfer the solution, with the aid of additional acetic acid, to a 250 ml volumetric flask. Dilute to volume with acetic acid and mix thoroughly.

5.5 Transfer a 5.0 ml aliquot of the acetic acid solution to a 100 ml volumetric flask, dilute to volume with ethanol and mix thoroughly.

5.6 Fill an absorption cell with the ethanol solution obtained in para. 5.5 and fill a matched absorption cell with ethanol.

5.7 Set the instrument at the wavelength corresponding to the previously determined absorption maximum and determine the absorbance of the sample in relation to that of the ethanol.

5.8 From the absorbance obtained, refer to the calibration curve to determine the concentration of 2-NDPA and then calculate the weight percent in the sample.

5.9 **Calculation:**

$$\text{Wt \% 2-NDPA} = \frac{C \times F}{W \times 10}$$

Where:

C = Mg 2-NDPA per 100 ml of solution obtained from calibration curve.

F = Aliquot factor (50 for 5.0 ml aliquot).

W = Weight of sample, g.

METHOD 218.5.1

2-NITRODIPHENYLAMINE (2-NDPA) RESORCINOL (LIQUID CHROMATOGRAPHY METHOD)

1. SCOPE

1.1 This (liquid chromatography (LC) method may be used for the determination of 2-nitrodiphenylamine (2-NDPA) and Resorcinol in Composite Modified Double Base (CMDB) Propellant.

1.2 Resorcinol and 2-NDPA (as well as nitroglycerin and triacetin) are extracted from CMDB propellant by an ascending elution with diethyl ether on a small silica gel column. The extracted materials are subsequently removed from the column by a descending elution with 1,2 dimethoxyethane and analyzed by high speed LC.

1.3 The concentration of the substances to be measured should approximate the concentration of the standard. Any other species will interfere that elute along with the species of interest and have absorbance at the same wavelength.

1.4 Proper handling procedures should be used for all explosive, flammable, or hazardous samples and reagents.

1.5 The precision for this method at the 95% confidence level (CL) is ± 0.027 at the 1.0% level of 2-NDPA.

1.6 The precision for this method at the 95% CL is ± 0.037 at the 0.7% lead of resorcinol.

2. SPECIMEN

2.1 The specimen shall consist of 1 to 2 grams of propellant.

3. REAGENTS

3.1 Diethyl ether, reagent grade.

3.2 1, 2-Dimethoxyethane (glyme), "distilled in glass", UV cutoff 220 nm, Burdick and Jackson Laboratories, Inc., Muskegon, Michigan.

3.3 n-Heptane, free from UV contaminants.

3.4 Silica gel, type # 60, particle size 63-200 μE. Merck, MCB, reagents or equal.

3.5 2-Nitrodiphenylamine, Kodak Laboratory Chemicals, or equal. Recrystallized from n-heptane.

3.6 Resorcinol, analytical reagent grade, Mallinckrodt Chemicals, or equal.

4. APPARATUS

4.1 Pasteur capillary, glass, disposable pipets, length 9 in body od 7mm, capillary od, 1 mm, WVWR Catalog No. 14672-380 or equal.

4.2 Liquid Chromatograph, Modular, consisting of:

a. Dupont Zorbax Sil column, 7.9mm ID x 25 cm, Dupont Co., Analytical Instruments Division, or equal.

b. Detector, UV-Visible, Varian Techtron, Series 6357 with LC flow cell accessories, Varian Instruments Division, or equal.

c. Pump, gradient elution, two M-6000 pumps (6000 psi rated) interfaced with a M-660 solvent programmer, Waters Associates, or equal.

NOTE: 1 psi = 6.9 kPa.

d. Sample injection valve, Model 706-L, modified with 1 mm stainless steel tubing (loop) to produce constant injection volume of approximately 65 µL, Disc Instruments Inc., or equal.

e. Pipet extraction columns - prepare the pipet extraction columns by packing Pasteurcapillary disposable pipets with silica gel, type # 60 (about 3 in) and sealing at both ends with a small wad of glass wool. Leave sufficient room at the top of the pipets for the propellant sample and an additional wad of glass wool.

5. PROCEDURES

5.1 Sample Preparation. Grind the propellant sample by rubbing on a clean, flat, medium coarse tile. Add about l00 mg of powdered propellant to the top of a tared pipet extraction column, reweigh the column and obtain the sample weight by difference. Add a wad of glass wool to hold the propellant sample on the column and to provide a wick for the elution step.

5.2 Place the pipet column (sample end down) into a 25 ml volumetric flask containing about 5 ml of diethyl ether and allow the ether to ascend the column to the glass wool plug at the tip of the column.

5.3 Remove the pipet column from the volumetric flask and remove the plug of propellant residue from the top of the column. Wash the propellant extract from the column with 5-7 ml of diethyl ether into a 25 ml volumetric flask. Remove the diethyl ether by evaporation with a stream of dry nitrogen, add 20 ml of n-heptane and bring the 25 ml volumetric flask to volume with glyme. The sample is now ready for analysis by LC.

5.4 Standards. Weigh l00 mg of 2-NDPA and 70 mg of resorcinol into a 100 ml volumetric flask. Dissolve and dilute to volume with glyme, by means of a pipet or flask containing 20 ml of n-heptane. Dilute to volume with glyme.

5.5 LC Analysis

Instrument Conditions. The LC should be equilibrated at the following conditions.

a. Mobile phase - 35 percent glyme in n-heptane.

b. Flow rate - 2.0 ml/min

c. Detector setting - 280 nm.

5.6 Analysis. With the sample injection valve lever in the "fill" position, flush the injection valve with 2-5 ml of standard solution and move the lever to the "inject" position. When the standard has eluted from the LC, measure the peak heights obtained for 2-NDPA and resorcinol (2-NDPA) will elute first.).

Inject sample solution in the same manner as above and calculate the percentage of each component.

6. **Calculation:**

$$\% \text{ Component} = \frac{A \times B \times 25}{C \times D \times 10}$$

Where:

A = peak height of component in sample.

B = concentration of component in standard, mg/ml.

C = peak height of component in standard.

D = sample weight in grams.

METHOD 219.1

OXAMIDE (PERMANGANATE TITRATION METHOD)

1. SCOPE

1.1 This method is used for determining the oxamide content of propellants. The presence of other compounds which react with potassium permanganate will cause interference.

2. SPECIMEN

2.1 The specimen shall consist of a portion of the propellant containing approximately 200 mg of oxamide (as determined from the detailed specification for the propellant). Weigh the specimen to within 0.2 mg.

3. APPARATUS

3.1 Glass extraction thimble with fritted disk, 30 ml.

3.2 Beakers, 400 ml.

3.3 Funnel.

3.4 Suction flask, 500 ml.

3.5 Hotplate.

4. MATERIALS

4.1 Sodium hydroxide, 5 percent solution.

4.2 Sulfuric acid solution, consisting of one part 95 percent sulfuric acid and one part distilled water.

4.3 Potassium permanganate, 0.1N standard solution as specified in Method 606.1.

5. PROCEDURE

5.1 Prepare the specimen as specified in Method 509.3.

5.2 Extract the specimen as specified in Method 104.1 Use the 30 ml glass extraction thimble. Retain the residue in the thimble.

5.3 Dry the residue in the extraction thimble, and quantitatively transfer it to a 400 ml beaker, using a stream of distilled water.

5.4 Add 50 ml of distilled water to the beaker, and boil the residue for 1 hour.

5.5 Place the thimble (used in the extraction) in a funnel on a 500 ml suction flask and apply suction to the flask. Carefully decant the boiling supernatant liquid in the beaker through the thimble into the suction flask.

5.6 Boil the residue in three more 50 ml portions of distilled water each for 1 hour in the 400 ml flask; decant each through the thimble into the suction flask.

5.7 Transfer the residue in the beaker to the thimble and wash it with four 10 ml portions of boiling water. Also wash the bottom of the thimble and the funnel, with a stream of hot distilled water, and catch the washings in the suction flask.

5.8 Quantitatively transfer the filtrate in the suction flask to a clean 400 ml beaker, and add 20 ml of 5 percent sodium hydroxide solution. Heat the beaker on a hotplate for 30 minutes, then cool to room temperature.

5.9 Neutralize the solution in the beaker with the sulfuric acid solution; then add an excess of 40 ml of the sulfuric acid solution.

5.10 While slowly stirring the solution, titrate with the 0.1N standard potassium permanganate solution at a rate of approximately 25 to 35 ml per minute, until the appearance of the first pink color.

5.11 Allow the solution to stand until the pink color disappears, then heat it to approximately 80 to 90°C.

5.12 Continue the titration drop by drop, allowing each drop to become decolorized before adding the next. The titration may be considered complete when the pink coloration persists for 30 seconds.

5.13 Calculate the percentage of oxaide in the propellants.

5.14 **Calculation:**

$$\text{Percent oxamide} = \frac{4.40\ VN}{W}$$

Where:

V = Volume of potassium permanganate solution used in titration, ml.

N = Normality of the potasium permanganate solution.

W = Weight of sample corrected for total volatiles, mg.

METHOD 219.2.1

OXAMIDE (SPECTROPHOTOMETRIC METHOD)

1. SCOPE

1.1 This method is used for determining the oxamide content of nitrocellulose-base propellants.

2. SPECIMEN

2.1 The specimen shall consist of a portion of the propellant containing approximately 50 mg of oxamide (as determined from the detailed specification for the propellant). Weigh the specimen to within 0.2 mg.

3. APPARATUS

3.1 Steam distillation apparatus. The apparatus is the same as figure 1, Method 201.4, except that a 750 ml Erlenmeyer flask is used to collect the distillate. The adapter should be long enough to reach to the bottom of the 750 ml Erlenmeyer flask.

3.2 Volumetric flask, 1000 ml, 500 ml, and 50 ml.

3.3 Buret, 25 ml.

3.4 Pipets, 50 ml, 5 ml, and 1 ml.

3.5 Spectrophotometer.

4. MATERIALS

4.1 Sodium hydroxide, 10 percent solution.

4.2 Nessler reagent. Dissolve 70 g of potassium iodide in 60 ml of water, add 100 g of mercuric iodide, swirl to dissolve, dilute to approximately 150 ml, and add slowly, with stirring, to a cool solution of 160 g of sodium hydroxide in 500 ml of water. Dilute to 1 liter with water and allow to stand overnight or longer.

4.3 Standard nitrogen solution (1 ml = 0.060 mg of oxamide). Dry ammonium chloride in an oven at 110°C, dissolve 0.7280 g in water, dilute to 1 liter in a volumetric flask, pipet a 50 ml aliquot into a 500 ml volumetric flask, and dilute to the mark with water.

5. PROCEDURE

5.1 Preparation of calibration curve:

a. Transfer 4.0, 6.0, 8.0, 10.0 and 12.0 ml of standard nitrogen solution to 50 ml volumetric flasks. Carry along a reagent blank.

b. Dilute to about 45 ml with water, add 1.00 ml of Nessler reagent and swirl. Dilute to the mark and shake.

c. Measure the absorbance in 15 to 30 minutes at 415 nanometers in a spectrophotometer that has been set to l00 percent transmittance with the reagent blank.

d. Plot milligrams of oxamide against absorbance.

5.2 Prepare the specimen as specified in Method 509.3.

5.3 Extract the specimen as specified in Method 104.1.3 using methylene chloride as the solvent. Retain the residue in the thimble.

5.4 Dry the residue in the thimble by means of stream of air.

5.5 Quantitatively transfer the residue to the 1-liter boiling flask, and add 150 ml of the 10 percent sodium hydroxide solution. Add l00 ml of water to the 750 ml Erlenmeyer flask. Place the Erlenmeyer so that the adapter dips below the surface of the water. Assemble the apparatus and steam distill at a rate of 5 to 7 ml condensate per minute.

NOTE: Do not apply heat to the 1-liter boiling flask containing the propellant.

5.6 Collect about 225 to 250 ml of the distillate, open the release valve, shut off the heat, and disconnect the gooseneck tube from the condenser by loosening the rubber stopper from the 1 liter flask.

5.7 Raise the condenser so that the tip is above the liquid and wash down the condenser and adapter with distilled water.

5.8 Dilute the distillate to 500 ml in a volumetric flask with distilled water.

5.9 Pipet a 5 ml aliquot into a 50 ml volumetric flask, dilute to about 45 ml with water, add 1.00 ml of Nessler reagent, and swirl.

5.10 Dilute to the mark with water, shake, and measure the absorbance in 15 to 30 minutes at 415 nanometers in a spectrophotometer set at 100 percent transmittance with the reagent blank.

5.11 Correct the nitrocellulose by carrying through the entire procedure including the methylene chloride extraction and amount of nitrocellulose equal to that in the sample.

5.12 Convert the reading to milligrams of oxamide by referring to the calibration curve and calculate the percent oxamide.

METHOD 219.3.1

OXAMIDE (VOLUMETRIC METHOD)

1. SCOPE

1.1 This method is used for determining the oxamide content of nitrocellulose-base propellants.

2. SPECIMEN

2.1 The specimen shall consist of a portion of the propellant containing approximately 200 mg of oxamide (as determined from the detailed specification for the propellant). Weigh the specimen to within 0.2 mg.

3. APPARATUS

3.1 Steam distillation apparatus. This apparatus is the same as figure 1, Method 201.4, except that a 750 ml Erlenmeyer flask is used to collect the distillate. The adapter should be long enough to reach to the bottom of the 750 ml Erlenmeyer flask.

3.2 Buret, 50 ml.

3.3 Pipet, 100 ml.

4. MATERIALS

4.1 Sodium hydroxide, 10% solution.

4.2 Hydrochloric acid, 0.1N solution.

4.3 Sodium hydroxide, 0.1N standard solution.

4.4 Methyl red indicator, as specified in Method 702.1.

5. PROCEDURE

5.1 Prepare the specimen as specified in Method 509.3.

5.2 Extract the specimen as specified in Method 104.1 using methylene chloride as the solvent. Retain the thimble and residue.

5.3 Dry the thimble and residue. Quantitatively transfer the residue to the 1-liter boiling flask, and add 200 ml of 10% sodium hydroxide. Pipet 100 ml of 0.1 N hydrochloric acid into the 750 ml Erlenmeyer flask, add 5 drops of methyl red indicator, and place the flask so that the adapter dips below the surface of the liquid. Assemble the apparatus and steam distill at a rate of 5 to 7 ml of condensate per minute.

NOTE: Do not apply heat to the 1-liter boiling flask containing the propellant.

5.4 Collect about 250 to 300 ml of distillate, open the release valve, shut off the heat, and disconnect the gooseneck tube from the condenser by loosening the rubber stopper from the 1-liter flask.

5.5 Raise the condenser so that the tip is above the liquid and wash down the condenser and adapter with distilled water.

5.6 Titrate the excess acid in the Erlenmeyer flask with standard 0.1N sodium hydroxide solution to a faint orange end point.

5.7 Carry a blank determination through all the steps of the procedure after the extraction step.

5.8 Consult graph to obtain "C" value (correction for nitrocellulose) corresponding to the weight of nitrocellulose in the sample.

5.9 Calculate the percent oxamide in propellant.

5.10 **Calculation:**

$$\text{Percent oxamide} = \frac{4.40\,[(B-A)N - C/10]}{W}$$

Where:

B = Volume of standard 0.1N sodium hydroxide solution required for blank, ml.

A = Volume of standard 0.1N sodium hydroxide solution required to neutralize excess acid in distillate, ml.

C = Volume of standard 0.1N sodium hydroxide solution, ml, required to correct for ammonia generated by the hydrolysis of nitrocellulose

N = Normality of sodium hydroxide solution.

W = Weight of sample corrected for total volatiles.

6. **PREPARATION OF GRAPH TO OBTAIN "C"**

6.1 Weigh accurately 1.0, 2.0, 3.0, 3.5, 4.0 and 4.5 g samples of pure nitrocellulose (preferably 12.0 - 13.2%N) and carry each sample through the entire procedure including the methylene chloride extraction. Run a blank determination.

6.2 Plot ml of standard 0.1N sodium hydroxide solution consumed against g of nitrocellulose.

NOTE: The above correction graph need to prepared only once. An alternative method for obtaining "C" is to carry through the procedure on an amount of nitrocellulose equal to the amount in the sample.

METHOD 219.4.1

OXAMIDE (INFRARED METHOD)

1. SCOPE

1.1 This method is applicable to the determination of oxamide over a wide range of concentrations in casting powders or propellants containing nitroglycerin (NG), 2-nitrodiphenylamine (2-NDPA), nitrocellulose (NC), and cyclotetramethylene- tetranitramine (HMX). However, the sample weights called out here apply to compositions containing about five percent oxamide. The precisions at the 95% confidence level (CL) is $\pm$ 0.15 at the 5.0% level of oxamide.

1.2 The NG and 2-NDPA are separated by Soxhlet extraction and measured by established spectrophotometric procedures. The HMX and NC in the residue are separated from the oxamide by an extraction - centrifugation procedure. Acetone is used to dissolve the HMX and NC in this step while the insoluble oxamide is recovered by centrifugation. All three components are subsequently determined by infrared (IR) spectrophotometry.

2. SPECIMEN

2.1 The specimen shall consist of 2 to 3 grams of propellant.

3. APPARATUS

3.1 Cells, 2 each, CaF_2, matched, 0.2 mm path length.

3.2 Centrifuge tubes, 50 ml.

3.3 Centrifuge.

3.4 Extraction apparatus, Soxhlet.

3.5 Oven, vacuum drying.

3.6 Spectrophotometer, IR, Beckman IR-12 or equivalent.

3.7 Steam bath.

4. REAGENTS

4.1 Acetone, reagent grade.

4.2 Diethyl ether (DEE), anhydrous, reagent grade.

4.3 Dimethyl sulfoxide (DMSO), reagent grade.

4.4 Oxamide reagent grade, Kodak Laboratory Chemicals, or equal. Dry in vacuum oven at 105°C for several hours.

5. STANDARDIZATION

5.1 Weigh approximately 0.200 g of dried oxamide to the nearest 0.1 mg and transfer to a 100 ml volumetric flask. Dissolve in DMSO and dilute to volume. Pipet, 5, 10, 15 and 20 ml aliquots of the oxamide stock solution into 25 ml volumetric flasks and dilute to volume with DMSO. In turn place each of these standards into a 0.2 mm CaF_2 cell and record the IR spectrum between 1600 and 1900 cm^{-1} against a solvent reference. Measure the oxamide maximum absorbance at 1680 cm^{-1} and subtract the baseline absorbance at 1900 cm^{-1}. Determine the absorptivity, a, of oxamide by plotting absorbance against concentration and measuring the slope of the calibration curve.

6. PROCEDURE

6.1 Extract a 1.0 g sample (weighed to the nearest 0.1 mg) with for 72 hours in Soxhlet apparatus.

6.2 After extraction transfer the dried insoluble residue to a 50 ml centrifuge tube. Add 40 ml of acetone and disperse the sample thoroughly. Centrifuge for five minutes. Carefully decant the supernatant liquid into a 50 ml beaker. Evaporate the acetone carefully on a steam bath. Repeat the extraction with three more 40 ml portions of acetone. Evaporate the acetone as above and dry the beaker and centrifuge tube in a vacuum oven at 105°C for several hours.

6.3 Dissolve the oxamide residue in the centrifuge tube in DMSO. Transfer the solution to a 50 ml volumetric flask and dilute to volume. Fill a 0.2 mm CaF_2 IR cell with the sample solution and scan from 1600 to 1900 cm^{-1} against a solvent blank in the reference cell. Measure the absorbance of oxamide at 1680 cm^{-1} and subtract the baseline absorbance at 1900 cm^{-1}.

7. Calculation:

$$\% \text{ Oxamide} = \frac{AD}{10aW}$$

Where:

A = absorbance of oxamide at 1680 cm^{-1}.

D = dilution, ml.

a = absorptivity of oxamide at 1680 cm^{-1}, ml/mg.

W = weight of sample, g.

METHOD 221.1.1

PHTHALATE ESTERS (SAPONIFICATION-SPECTROPHOTOMETRIC METHOD)

1. SCOPE

1.1 This method is used for determining spectrophotometrically the percentage of phthalate esters in single-base propellants.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5 g of the propellant, weighed to within 0.2 mg.

3. APPARATUS

3.1 Volumetric flask, 500 ml.

3.2 Volumetric flasks, 100 ml.

3.3 Ultraviolet spectrophotometer (Beckman Instruments, Inc., Model DU, or equivalent).

3.4 Silica cells, 10 mm light path length.

3.5 Steam bath.

3.6 Filter paper, Whatman No. 42 or equivalent.

3.7 Separatory funnel, 500 ml.

3.8 Beaker, 600 ml.

3.9 Watchglass (ribbed).

3.10 Hotplate.

4. MATERIALS

4.1 Ethyl alcohol, 95 percent.

4.2 Potassium hydroxide, 0.5N alcoholic solution, consisting of approximately 16 g of potassium hydroxide (85 percent in 550 ml of 95 percent ethyl alcohol).

4.3 Sodium chloride.

4.4 Potassium hydroxide, (solid).

4.5 Isopropyl ether.

4.6 Hydrochloric acid, 38 percent solution.

4.7 Blank solution, consisting of 10 ml of 38 percent hydrochloric acid and 10 g of sodium chloride, dissolved in 1 liter of distilled water.

4.8 Potassium acid phthalate, reference standard, National Bureau of Standards Sample No. 185 (dried for 2 hours at 110°C).

5. **PROCEDURE**

5.1 Prepare the specimen as specified in Method 509.3.

5.2 Extract the specimen and dry the extract as specified in Method 104.1.

5.3 Dissolve the residue in 10 ml of 95 percent ethyl alcohol, and add 10 ml of the 0.5N alcoholic potassium hydroxide solution.

5.4 Cover the flask with a small watchglass, and heat it on a steam bath for 2 hours. Then cool to room temperature.

5.5 Add 5 ml of distilled water and 5 ml of 38 percent hydrochloric acid to the flask, and dilute the solution to approximately 100 ml with distilled water.

5.6 Add 5 g of sodium chloride, and agitate the solution until the sodium chloride is completely dissolved.

NOTE: The addition of the sodium chloride will aid in the separation of the liquid layers, and will prevent excessive foaming.

5.7 Filter the solution through Whatman No. 42 filter paper into a 600 ml beaker, and wash the residue on the filter paper with 100 ml of distilled water. Discard the filter and residue.

5.8 Make the filtrate alkaline to litmus paper (pH approximately 9) using solid potassium hydroxide.

5.9 Quantitatively transfer the filtrate to a 500 ml separatory funnel, using distilled water. Add 100 ml of isopropyl ether, and agitate the mixture thoroughly for 5 minutes.

5.10 Allow the mixture to separate into 2 layers; draw off the lower (aqueous) layer into the 600 ml beaker. Wash the remaining (ether) layer with three 10 ml portions of distilled water, and draw the washings off into the beaker.

5.11 Cover the beaker with a ribbed watchglass. Place on a hotplate set at medium heat and allow the solution to evaporate to approximately 50 ml. Remove the beaker from the hotplate and allow it to cool to room temperature.

5.12 Add 5 ml of 38 percent hydrochloric acid, and filter the solution through No. 42 Whatman filter paper into a 500 ml volumetric flask. Wash the beaker with 100 ml of warm distilled water and pour the washings through the filter paper into the volumetric flask. Allow the solution to cool to room temperature and fill the flask to the mark with distilled water.

5.13 Calculate the weight of the phthalic acid present in the solution as follows:

a. Obtain the nominal weight in mg of phthalate ester by multiplying the sample weight in mg by the percentage of phthalate ester as given in the detail specification and dividing by 100. Multiply this weight by 166.13.

b. Divide the result by the molecular weight of the phthalate ester in the propellant.

5.14 Transfer an aliquot of the solution, containing 5 to 9 mg of phthalic acid, to a 100 ml volumetric flask, and dilute to the mark with blank solution (para 4.7).

5.15 Transfer a portion of this solution to a silica cell. Fill a matched cell with blank solution for the reference.

NOTE: If matched silica cells are not available, unmatched cells may be used. However, correct for any difference between them by filling both cells with blank solution measuring the absorbance of both at 275 nanometers and determining the difference in absorbance. Correct the reading for the absorbance of the propellant solution accordingly.

5.16 Place the cells in the spectrophometer and obtain the absorbance of the solution at 275 millimicrons.

5.17 Determine the spectrophotometric factor for phthalic as follows:

a. Weigh 0.1200 g of pure potassium acid phthalate (para 4.8) that has been dried for 2 hours at 110°C.

b. Dissolve the potassium acid phthalate in 50 to 100 ml of distilled water, and quantitatively transfer the solution to a 500 ml volumetric flask.

c. Add 5 ml of 38 percent hydrochloric acid, and dilute to the mark with distilled water.

d. Using aliquots of this solution, prepare five solutions of phthalic acid ranging in concentration from 5 to 9 mg per 100 ml.

NOTE: The phthalic acid content of potassium acid phthalate is 81.35 percent.

e. Determine the absorbance of each solution at 275 nanometers.

f. Divide the concentration of phthalic acid for each of these solutions by its corresponding absorbance value. The average of the six quotients thus obtained should be used as the spectrophotometric factor for phthalic acid.

5.18 Calculate the percentage of phthalate ester in the propellant.

5.19 **Calculation:**

$$\text{Percent phthalate ester} = \frac{ABC}{1.6613W}$$

Where:

A = Corrected absorbance for the cell containing the propellant solution (para 5.16).

B = Spectrophotometric factor for phthalic acid (para 5.17).

C = Molecular weight of the phthalate ester in the propellant.

W = Weight of specimen represented by the aliquot taken, corrected for total volatiles, mg.

METHOD 222.1.1

PLASTICIZERS, ESTER (INFRARED METHOD)

1. SCOPE

1.1 This method may be used for determining phthalates, acetates, and other ester plasticizers in casting liquid and propellants containing only one such ester.

2. SPECIMEN

2.1 The specimen shall consist of sufficient liquid or propellant to give an extract having absorbance of approximately 0.2 to 0.8 in the chosen cell under the conditions described in paragraph 5.1 Ester concentrations of about 0.4 g per 100 ml are satisfactory for most esters when 0.2 mm cells are used. The specimen shall be weighed to within 0.2 mg.

3. APPARATUS

3.1 Extraction apparatus, Soxhlet or equivalent.

3.2 Volumetric flask, 100 ml or as required.

3.3 Double-beam infrared spectrophotometer.

3.4 Infrared spectrophotometer cells, two, matched, preferably with calcium fluoride or barium fluoride windows, suggested path length of 0.2 mm.

4. MATERIALS

4.1 Extraction solvent; methylene chloride, reagent grade.

4.2 Infrared solvent. One of the following:

Methylene chloride (MCl)
1, 2 Dichloroethane (DCE)

4.3 Nitroglycerin, MIL-N-246.

4.4 Esters conforming to appropriate specifications.

5. PROCEDURE

5.1 Prepare a calibration curve as follows:

5.1.1 Choose either MCl or DCE as solvent and prepare five solutions of known concentrations of the ester in that solvent at the applicable concentration range. For 0.2 mm cells a suitable range for most esters is from 0.2 to 0.8 g per 100 ml.

5.1.2 Set the zero and 100 percent lines of the infrared spectrophotometer at 1745 cm^{-1} (5.75 micrometers).

5.1.3 Fill the reference cell with the solvent and place it in the reference beam.

5.1.4 Fill the sample cell with each of the ester solutions in turn and scan from 1950 to 1650 cm^{-1} (5.1 to 6.1 micrometers). Record absorbance at the peak of the band that occurs at about 1745 cm^{-1} (5.75 micrometers). Subtract absorbance at 1900 cm^{-1} (5.26 micrometers). The difference is net absorbance.

5.1.5 Prepare a graph of net absorbance vs ester concentration in g per 100 ml.

5.2 Determine nitroglycerin correction as follows:

5.2.1 Prepare two or more solutions of the ester in the concentration range to be used in the analysis. Before diluting the solutions to volume, add an accurately weighed portion of nitroglycerin to each. For 0.2 mm cells, appropriate nitroglycerin concentrations are 1.25 to 2.50 g per 100 ml.

5.2.2 Scan and determine net absorbance as in paragraph 5.1.5.

5.2.3 For each solution calculate.

$$A = \frac{B - C}{D}$$

Where:

A = correction per gram of nitroglycerin per 100 ml.

B = net absorbance of the solution.

C = absorbance due to ester alone, from graph.

D = concentration of nitroglycerin, g per 100 ml.

5.2.4 Calculate the average value of A for the ester.

5.2.5 For each casting liquid or propellant, calculate the nitroglycerin correction (in absorbance units) as follows:

$$\text{Correction} = A \times E \times F \times 0.01$$

Where:

E = g of casting liquid or propellant per 100 ml of solution.

F = nominal percent of nitroglycerin in the casting liquid or propellant.

5.3 Determine the ester content of the specimen as follows:

5.3.1 If the specimen is a casting liquid, weigh it into a volumetric flask and dilute with MCl or DCE.

5.3.2 If the specimen is a propellant, extract with MCI. If the DCE is the preferred infrared solvent, evaporate the MCI. Dilute to 100ml (or as required) with the preferred solvent.

NOTE: The wave number of the carbonyl absorbance band differs slightly from one ester to another, and the nitroglycerin correction (the quantity designated "A") must be determined for each ester.

5.3.3 Scan and calculate net absorbance as in paragraph 5.1.2 through 5.1.5.

5.3.4 Subtract the nitroglycerin correction calculated as in paragraph 5.2.5.

5.3.5 *Determine the ester concentration from the graph.*

5.3.6 **Calculation:**

$$\% \text{ Ester in specimen} = \frac{G \times H}{J}$$

Where:

G = concentration of ester in g per 100 ml from graph.

H = volume of solution, ml.

J = weight of specimen, g.

METHOD 223.1

RESORCINOL (VOLUMETRIC BROMINATION METHOD)

1. SCOPE

1.1 The resorcinol content in nitrocellulose base propellants is determined by a volumetric bromination method. The calculated results for resorcinal must be corrected for the 2 nitrodiphenylamine or ethyl centralite content, where present, as determined by an independent method. Unsaturated hydrocarbons or other compounds which will react with bromine solution will cause interference.

1.2 The standard deviation of this method is 0.03 percent in the range of 1-2 percent resorcinol. This precision includes random and operator error.

2. SPECIMEN

2.1 The specimen consist of 5 grams weighed to an accuracy of ± 0.1 mg.

3. APPARATUS

3.1 Soxhlet apparatus.

3.2 Iodine flask, 250 ml.

3.3 Volumetric flask, 250 ml.

3.4 Steam bath.

4. MATERIALS

4.1 Acetic acid (glacial).

4.2 Diethyl ether.

4.3 Methylene chloride

4.4 Hydrochloric acid solution (50 percent by volume), prepared by adding 500 ml of 12N hydrochloric acid to 500 ml of distilled water.

4.5 *Potassium iodide solution (15 percent by weight)*, prepared as follows:

a. Weigh approximately 150 g of potassium iodide into a two liter beaker, and add 850 ml of water.

b. Store in a tinted glass bottle and add two pellets of potassium hydroxide to stabilize the solution.

4.6 Potassium bromate - bromide solution (0.2N). Prepare the solution in accordance with Method 605.1 with the exception that standardization of the solution is not required.

4.7 *Sodium thiosulfate* (0.2N), as specified in Method 602.1.

4.8 Starch-Indicator solution.

4.9 Potassium hydroxide, pellets.

4.10 Water, distilled or deionized.

5. PROCEDURE

5.1 Weigh accurately approximately 5 g of the sample to within 0.1 mg in a Soxhlet extraction thimble.

NOTE: Sample weights and aliquot size should be modified as necessary, based on nominal composition to insure accurate results.

5.2 Add 100 ml of diethyl ether or methylene chloride to the Soxhlet flask, connect the apparatus, and extract for a minimum of 16 hours on a steam bath.

5.3 Evaporate the solvent left in the extraction flask with a stream of air.

5.4 Take up the extract with glacial acetic acid and transfer the solution quantitatively to a 250 ml volumetric flask and dilute to the mark with glacial acetic acid.

5.5 Add a 50 ml aliquot of the solution into a 250 ml iodine flask.

5.6 Pipette 25.0 ml of potassium bromate-bromide solution and 10 ml of 1:1 hydrochloric acid solution to the flask and immediately stopper.

5.7 Allow the bromination to proceed for 3 minutes plus or minus 15 seconds from the time of the hydrochloric acid addition.

5.8 At the end of bromination, cool the flask slightly and add 15 ml of potassium iodide solution to the lip of the flask and remove the stopper sufficiently to allow the potassium iodide solution to enter the flask without allowing any bromine vapors to escape.

5.9 Shake the flask thoroughly with stopper in place.

5.10 Wash down the stopper well and walls of the flask with approximately 20 ml of distilled water.

5.11 Tritrate the solution immediately with 0.2N sodium thiosulfate solution until the strong color of iodine has disappeared.

5.12 Add 5 ml of the starch indicator solution and continue to titrate carefully and slowly with vigorous agitation until the blue color disappears.

5.13 Make a blank determination using exactly the same procedure except use 50 ml of the glacial acetic acid in place of the sample.

5.14 Calculate the percentage of resorcinol.

5.15 **Calculations:**

$$\text{Percent of resorcinol} = \frac{(B - A)\,(N)\,(0.01835)\,(100)\,(5)}{W}$$

Where:

W = Sample weight, g.

A = Sample titration, ml.

B = Blank titration, ml.

N = Normality of sodium thiosulfate.

0.01835 = Equivalence factor for resorcinol.

5 = Aliquot factor.

When it is known that other material present undergo bromination, corrections shall be made; for example, the 2-nitrodiphenylamine correction is as follows:

$$\text{Correction formula (C)} = \frac{(D)\,(W)}{(5)\,(N)\,(3.57)}$$

Where:

C = ml consumed by 2-nitrodiphenylamine.

D = Percent 2-nitrodiphenylamine as determined by an independent method.

W = Sample weight, g.

N = Normality of the sodium thiosulfate.

3.57 = Equivalence factor to convert 2-nitrodiphenylamine to resorcinol.

5 = Aliquot factor.

Application of the correction formula for calculating the weight percent of resorcinol:

$$\text{Percent of resorcinol} = \frac{(B\text{-}A\text{-}C)\,(N)\,(0.01835)\,(100)\,(5)}{\text{sample weight}}$$

METHOD 224.1.1

ETHYLENE DIMETHACRYLATE (INFRARED METHOD)

1. SCOPE

1.1 This method is used for determining the ethylene dimethacrylate (also known as ethylene glycol dimethacrylate) content of propellants that contain no other esters.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5 g of the propellant weighed to within 0.2 mg.

3. APPARATUS

3.1 Volumetric flasks, 100 mL.

3.2 Medicine dropper.

3.3 Extraction flask, 125 mL.

3.4 Funnel.

3.5 Perkin-Elmer Model 21 Infrared spectrophotometer or equivalent.

3.6 Sodium chloride cell, thickness about 0.4 mm.

4. MATERIALS

4.1 Methylene Chloride.

5. PROCEDURE

5.1 Prepare a calibration curve as follows:

a. Add 0.05 to 0.35 g portions of ethylene dimethacrylate to six tared dry 100 mL volumetric flasks (preferably of the short neck type) by means of a medicine dropper and calculate the exact weight (to 0.1 mg) by difference.

b. Dilute to 100 mL with methylene chloride.

c. Run the infrared spectrum from 5.5 to 6.0 micrometers using a 0.4 mm cell.

NOTE: Satisfactory instrument settings for the Perkin-Elmer Model 21 spectrophotometer are: Program 927, gain 5 response 1, and suppression 0.

d. Measure the absorbance of the band by the base-line technique.

e. Plot grams of ethylene dimethacrylate against absorbance.

5.2 Prepare the specimen as described in Method 509.3.

5.3 Extract the specimen overnight (16 hours) as described in Method 104.1 with 85 mL of methylene chloride, using a Soxhlet extractor and a 125 mL extraction flask. About 75 mL of solution will remain after the extraction.

5.4 Transfer to a dry 100 mL volumetric flask with a dry funnel and dilute to the mark with methylene chloride.

5.5 Run the spectrum as in 5.1 (c).

5.6 Measure the absorbance as in 5.1 (d).

5.7 Convert the absorbance to grams of ethylene dimethacrylate by referring to the calibration curve.

5.8 Calculate the percentage of ethylene dimethacrylate in the propellant.

5.9 **Calculation:**

$$\text{Percent ethylene dimethacrylate} = \frac{100A}{W}$$

Where:

A = Weight of ethylene dimethacrylate, as obtained from calibration curve, g.

W = Weight of specimen, corrected for total volatiles, g.

METHOD 224.2.1

ETHYLENE DIMETHACRYLATE (BROMINATION METHOD)

1. SCOPE

1.1 This method is used for determining the ethylene dimethacrylate (also known as ethylene glycol dimethacrylate) content of propellants that contain no other brominatable material. Diphenylamine, usually present in propellants containing this ester, is determined independently and accounted for in the bromination procedure.

2. SPECIMEN

2.1 The specimen shall consist of approximately 4 g of the propellant weighed to within 0.2 mg.

3. APPARATUS

3.1 Graduate cylinder, 25 ml.

3.2 Volumetric flasks, 100 ml and 25 ml.

3.3 Pipets, 2 ml, 10 ml and 20 ml.

3.4 Iodine flask, 500 ml.

3.5 Burets, 25 ml, and 50 ml.

3.6 Funnel, long-stemmed.

4. MATERIALS

4.1 Glacial acetic acid.

4.2 Potassium bromate-bromide solution, 0.2N as specified in Method 605.1.

4.3 Sodium thiosulfate solution, 0.2N standard solution as specified in Method 602.1.

4.4 Starch indicator solution as specified in Method 701.1.

4.5 Potassium iodide, 10 percent solution.

4.6 Hydrochloric acid, 38 percent.

5. PROCEDURE

5.1 In order to determine the proper factor, the ethylene dimethacrylate (not necessarily the same lot) used in the manufacture of the propellant should be assayed by the following procedure:

a. Add approximately 15 ml of glacial acetic acid to a dry 100 ml volumetric flask by means of a long stemmed funnel.

b. Weigh the volumetric flask to 0.1 mg and add approximately 2 ml of ethylene dimethacrylate by means of a pipet.

c. Weigh again to 0.1 mg and calculate the weight of the sample by difference. Dilute to the 100 ml mark with glacial acetic acid.

d. Into a 500 ml iodine flask measure 25.00 ml of 0.2N potassium bromate-bromide solution with a buret, a 10 ml aliquot of the sample, and 10 ml of hydrochloric acid.

e. Immediately stopper the flask and allow to stand for 20 minutes in the dark.

f. Add 10 ml of 10 percent potassium iodide solution to the gutter of the flask and allow this solution to trickle through the loosened stopper.

g. Swirl, wash down the gutter and sides of the flask with water from a wash bottle, and titrate immediately with standard 0.2 N sodium thiosulfate solution until the color is light yellow.

h. Add 5 ml of starch indicator solution and titrate carefully until the blue color of the solution disappears.

i. Run a blank determination using the same volume of potassium bromate-bromide solution and 10 ml of glacial acetic acid (instead of sample).

j. Calculate the percent monomer.

k. **Calculation:**

$$\text{Percent ethylene dimethacrylate monomer} = \frac{4.953\ (B - A)\ N}{S}$$

Where:

B = Thiosulfate solution required for blank, ml.

A = Thiosulfate solution required for sample, ml.

N = Normality of thiosulfate solution.

S = Weight of sample in aliquot, g.

5.2 Prepare specimen as described in Method 509.3.

5.3 Extract the specimen as described in Method 104.1.3 with 100 ml of methylene chloride overnight using a Soxhlet extractor and a 125 ml extraction flask.

5.4 Evaporate off the methylene chloride with a stream of dry air (approximately 2 liters per minute) by means of a glass tube that extends initialy to about 1 inch from the surface of the liquid. The evaporation should be carried out to the point at which the odor of methylene chloride is only faintly discernible. Place in a vacuum desiccator (25 mm of mercury) for 3 hours. Weigh the solvent extractive matter if desired.

5.5 Add a few ml of glacial acetic acid, transfer to a 25 ml volumetric flask with glacial acetic acid, and dilute to the mark with glacial acetic acid.

5.6 Into a 500 ml iodine flask measure 25.00 ml of potassium bromate-bromide solution (0.2N) with a buret, 20 ml aliquot of the sample (equivalent to 3.2 g) and 10 ml of hydrochloric acid. Continue as described in steps 5.1(e) to 5.1(i).

5.7 Determine the diphenylamine content of the propellant volumetrically after a steam distillation as described in Method 217.3.

5.8 Calculate the percentage of ethylene dimethacrylate in the propellant.

5.9 **Calculation:**

$$\text{Percent ethylene dimethacrylate} = \frac{495.3\ (B - A)\ N - D \times W}{(W)\ (M^{2.115})}$$

Where:

B = Thiosulfate solution required for blank, ml.

A = Thiosulfate solution required for sample, ml.

D = Percent diphenylamine in sample.

W = Weight of the specimen, corrected for total volatiles, gm.

N = Normality of thiosulfate solution.

M = Percent ethylene dimethacrylate monomer in the ethylene dimethacrylate used in the manufacture of the propellant as determined in 5.1.

METHOD 224.3.1

ETHYLENE DIMETHACRYLATE (SAPONIFICATION METHOD)

1. SCOPE

1.1 This method is used for determining the ethylene dimethacrylate (also known as ethylene glycol dimethacrylate) content of propellants that contain no other esters or compounds that react significantly with alkali.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5 g of the propellant weighed to within 0.2 mg.

3. APPARATUS

3.1 Pipet, 10 ml.

3.2 Medicine dropper.

3.3 Reflux condenser, water cooled.

3.4 Graduate cylinder, 50 ml.

3.5 Erlenmeyer flask, 250 ml.

3.6 Buret, 50 ml.

3.7 Hotplate.

4. MATERIALS

4.1 Ethyl alcohol, 95 percent.

4.2 Potassium hydroxide, approximately 0.45 N alcoholic solution. Dissolve 30 g of ACS grade potassium hydroxide (85 percent) pellets in a mixture of 600 ml of 95 percent ethyl alcohol and 50 ml of water, filter through a Whatman No. 41 filter paper, dilute to 1 liter with 95 percent ethyl alcohol in a glass bottle and cover with a tight fitting rubber stopper.

4.3 Hydrochloric acid, 0.1N standard solution.

4.4 Phenolphthalein indicator solution as specified in Method 703.1.

5. PROCEDURE

5.1 Prepare specimen as described in Method 509.3.

5.2 Extract the specimen, as described in Method 104.1.3 with 100 ml of methylene chloride overnight with a Soxhlet extractor and a 250 ml Erlenmeyer flask as the receiving flask.

5.3 Evaporate the methylene chloride with a stream of dry air (approximately 2 liters per minute) by means of a glass tube that extends initially to about 1 inch from the surface of the liquid. The evaporation should be carried out to the point at which the odor of methylene chloride is only faintly discernible. Place in a vacuum desiccator (25 mm of mercury) for 3 hours. Weigh the solvent extractive matter if desired.

5.4 Add 10 ml of 95 percent ethyl alcohol around the sides of the flask and swirl.

5.5 Add 3 drops of phenolphthalein solution.

5.6 Add alcoholic potassium hydroxide (approximately 0.45N) with a medicine dropper until the solution is just pink and then add 0.1N hydrochloric acid dropwise with a medicine dropper until the pink color just disappears.

5.7 Add 10.00 ml of alcoholic potassium hydroxide solution (approximately 0.45N) with a pipet and reflux under a water condenser for 30 minutes.

5.8 Add 50 ml of water through the top of the condenser and remove the flask.

5.9 Cover with a watch glass and cool to room temperature.

5.10 Add 3 more drops of phenolphthalein indicator solution and titrate with 0.1N hydrochloric acid to the disappearance of the pink color.

5.11 Carry a blank titration through the determination (steps 5.4 to 5.10 inclusive).

5.12 Calculate the percentage of ethylene dimethacrylate in the propellant.

5.13 **Calculation:**

$$\text{Percent ethylene dimethacrylate} = \frac{9.906\,[B - (A - 0.4)]\,N}{W}$$

Where:

B = Hydrochloric acid required for blank, ml.

A = Hydrochloric acid required for sample, ml.

N = Normality of hydrochloric acid.

W = Weight of the specimen, corrected for total volatiles, g.

0.4 = Correction for N-nitrosodiphenylamine and 2-nitrodiphenylamine.

METHOD 225.1.1

SALICYLATE SALTS (COLORIMETRIC METHOD)

1. SCOPE

1.1 This method is used for determining the salicylate content of heavy metal salts in propellants on the basis of the colorimetric reaction with ferric ion. This method describes a procedure for lead salicylate, but appropriate calculations can be used to convert the results to other metal salts.

2. SPECIMEN

2.1 The specimen shall consist of exactly 1.0000 g of propellant previously ground to a particle diameter that will pass through a 20 mesh screen.

3. APPARATUS

3.1 Spectrophotometer, Beckman Model DU or a Bausch and Lomb Photoelectric Colorimeter using a filter in the 500-550 nm range, or an equivalent photometer.

3.2 Volumetric flasks 1-liter, 200 ml and 25-ml.

3.3 Pipets, 5 ml, 10 ml, and 20 ml.

3.4 A pH meter.

4. MATERIALS

4.1 Acetic acid, glacial.

4.2 Acetic acid, 6 percent solution prepared by diluting 60 ml of glacial acetic acid with 940 ml of distilled water.

4.3 Acetic acid solution, one percent prepared by diluting 13 ml of glacial acetic acid to 1 liter with distilled water. The pH of this solution should be approximately 2.7. If it is outside the range of 2.6 - 2.8, adjustment of the pH should be made by adding acetic acid or potassium hydroxide solution to arrive at pH 2.7.

4.4 Ferric alum solution prepared as follows:

a. Dissolve 6 g of ferric ammonium sulfate dihydrate in 50 ml of water. Add 0.1 ml of 30 percent hydrogen peroxide, and boil until the peroxide is destroyed (2 minutes). Add 5 ml of 1:1 sulfuric acid solution and heat until the solution is clear.

b. Cool, dilute to 90 ml with water, and adjust to a pH of 1.4 with 10 percent potassium hydroxide solution using a pH meter. Finally, dilute to 100 ml. This solution will last indefinitely when stored in a glass stoppered flask.

4.5 Sodium salicylate, (alternatively, salicylic acid may be used.)

5. **PROCEDURE**

5.1 Prepare a standard curve as follows:

a. Prepare a standard solution of salicylate by adding exactly 0.2000 g of sodium salicylate to about 900 ml of water in a beaker, then regulate the pH to 2.7 by the addition of 6 percent acetic acid solution. Transfer to a 1 liter volumetric flask and dilute to the mark with distilled water.

b. Establish points for the calibration curve by withdrawing aliquots of 1 ml, 2 ml, 4 ml, 5 ml, and 6 ml. Place each of the aliquots in a 25 ml volumetric flask, add 0.25 ml of the ferric alum solution and dilute to the mark with one percent acetic acid (pH 2.7) solution. Allow 5 minutes for full color development. Obtain readings of these solutions against a ferric alum blank. The blank is made up exactly the same as the solutions above but without adding salicylate. Wavelength 520 nm is used for all absorbance readings.

c. The concentration scale is more conveniently plotted in terms of lead salicylate, using the data of column 3 in Table I.

TABLE I.

Salicylate standard solution ml	Mg of Sodium salicylate, present in 25ml	Theoretical lead salicylate equivalence, mg per 25 ml	Absorbance values
1	0.2	0.30	to be determined
2	0.4	0.60	to be determined
4	0.8	1.20	to be determined
5	1.0	1.50	to be determined
6	1.2	1.80	to be determined

From the standard graph a table can be prepared for routine work giving percent lead salicylate readings corresponding to small increments of absorbance when the prescribed weight of sample and size of aliquots have been employed.

d. For the curve expressing lead salicylate (or the table based on such a curve) the salicylic acid assay of the lead salicylate used in manufacturing should be known. Thus the proper correction can be made in constructing the curve or table. Alternatively the commercial lead salicylate itself could be used in the preparation of the standard curve using essentially the same procedure as for propellants in preparing the samples. Many samples of commercial lead salicylate will be 98-99 percent pure, in which case the error introduced by basing all the results on a theoretically pure basis is negligible.

5.2 Transfer the accurately weighed specimen to a 500 ml Erlenmyer flask, add 40 ml of six percent acetic acid and several boiling chips to prevent bumping.

5.3 Connect to a condenser and allow the mixture to reflux gently on a hot pate for 30 minutes.

5.4 Allow the flask to cool for five minutes then remove the condenser. Cool the flask by immersing it in ice water for 10 minutes, then decant the liquid through a Whatman No. 1 (or equivalent) filter paper, into a 200 ml volumetric flask, retaining as much of the solid sample in the 500 ml flask as possible.

NOTE: By this cooling procedure 2-nitrodiphenylamine is removed from solution; it is necessary that the filtrate be clear before volumetric dilution.

5.5 Connect the 500 ml flask with residue to the condenser and add 40 ml of 6 percent acetic acid through the condenser. Reflux the mixture gently on a hot plate for 15 minutes. Cool exactly as was done previously and filter. Wash the flask, residue, and filter paper several times with small portions of water from a wash bottle and dilute exactly to the mark of the 200 ml volumetric flask with distilled water.

5.6 Withdraw aliquots of either 10 ml or 20 ml from the 200 ml volumetric flask, transferring to a 25 ml volumetric flask. The size of the aliquot chosen is to be based on the anticipated formulated content of lead salicylate in the powder. If the percentage of lead salicylate is 2 percent or less, use a 20 ml aliquot. If the percentage is greater than 2 percent, use a 10 ml aliquot.

5.7 Add 0.25 ml of the ferric alum solution and make up to the mark with weak acetic acid (pH 2.7) solution.

5.8 Transfer the colored solution to a 1-cm cell of the spectrophotometer.

5.9 Prepare a blank for spectrophotometric comparison by transferring 0.25 ml of the ferric alum solution to a 25 ml volumetric flask and diluting to the mark with the weak acetic acid (pH 2.7) solution. Transfer this solution to the reference 1 cm cell of the spectrophotometer.

5.10 Make all absorbance readings at 520 nm on the spectrophotometer. When a filter instrument is used, the filter transmitting in the 500-550 nm range is selected.

5.11 From the absorbance value, the percentage of lead salicylate is read directly from the standard graph when 1 g samples and 20 ml aliquots are used. The value of the percentage can be doubled if 10 ml aliquots are used.

METHOD 226.2.1

DINITROTOLUENE, STABILIZERS, AND PLASTICIZERS (GAS CHROMATOGRAPHIC METHOD)

1. SCOPE

1.1 This method may be used for determining dinitrotoluene (DNT), diphenylamine (DPA), dibutylphthalate (DBP), dimethylphthalate (DMP), dioctylphthalate (DOP), 2-nitro-diphenylamine (2-NDPA), ethylene dimethacrylate (EDM) and other stabilizers and plasticizers in single-base propellants. Materials having the same retention times as the desired components will interfere.

2. SPECIMEN

2.1 *Accurately, weigh to within* ± 0.2 *mg a* 5 *gram sample of the propellant to be tested.* This size sample will produce an extract of concentrations per Table I for the listed percentage ranges. Some variation in sample weight may be necessary for samples of different compositions.

3. APPARATUS

3.1 Extraction *apparatus: Soxhlet or equivalent.*

3.2 Volumetric flask: 100 ml or as required.

3.3 Gas chromatograph: F & M series 5750 with dual flame ionization detector or equivalent.

3.4 Columns: *Pair of FM 19001A standard columns for Series 5750, ANAL., 6 ft- SS - 1/8" OD,* 10% silicone rubber UC-W98 (F & M Cat. No. 8501 - 3840) on 80 - 100 mesh Diatoport S (F & M Cat No. 8501 - 6302) or equivalent.

3.5 Syringe: 10 microliter, maximum capacity.

4. MATERIALS

4.1 Methylene chloride: reagent grade.

4.2 Dinitrotoluene.

4.3 Diphenylamine, technical.

4.4 Dibutylphthalate, technical.

4.5 Dimethylphthalate.

4.6 Dioctylphthalate.

4.7 2-nitrodiphenylamine.

4.8 Ethylene dimethacrylate.

4.9 Ethyl centralite.

4.10 Air: prepurified (breathing quality).

TABLE I

Extracted Ingredients

Ingredients	Analytical solution Concentration, mg/100 ml	Range Percentage
DNT	250 - 750	5.0 - 15.0
DPA	25 - 85	0.5 - 1.7
DBP	100 - 300	2.0 - 6.0
DMP	150 - 250	3.0 - 5.0
2-NDPA	90 - 110	1.8 - 2.2
DOP	200 - 300	4.0 - 6.0
EDM	100 - 400	2.0 - 8.0

4.11 Hydrogen: Ultra high purity grade (UHP).

4.12 Helium.

4.13 Internal standard solution. 20.0 grams ± 0.2 milligram of ethyl centralite dissolved and diluted to 500 ml with methylene chloride.

NOTE: Another component may be substituted for ethyl centralite in the internal standard solution, if it does not interfere with other components in the sample extract.

5. PROCEDURE

5.1 Instrument conditions.

a. Column temperature. 200° C, except for propellants that contain DOP use 230° C.

b. Injection port. 240° C. For propellants containing DOP use 270° C.

c. Flame detector. 270° C.

d. Recorder speed. 1.0 inch/minute (or as required).

e. Sample size. 1.0 microliter (or as required).

f. Gas flows (NOTE: 1 psi = 6.9 kPa).

	Carrier	Hydrogen	Air
Rotameter Reading	2.0	2.5	3.5
Tank Pressure, psig	100	15	33
Flow, cm^3/min	60	30	500

NOTE: The above flow conditions are suitable for F & M Scientific Gas Chromatograph series 5750. These conditions may vary with other instruments and columns. Refer to the operating manual for instrument being used. The same operating conditions must be maintained for standards as for test samples.

5.2 Determination of components.

a. Either of the following methods (A or B) may be used for determination of dinitrotoluene (DNT), stabilizers, and plasticizers of single-base propellants. Method A is more applicable for large groups of samples or continuous analysis. Method B may be preferred for only a single sample.

b. Method A (use of internal standard)

(1) Prepare the specimen as described in Method 509.3 Extract the specimen with methylene chloride as described in Method 104.1.

(2) Allow extract to cool and transfer to 100 ml volumetric flask.

(3) Add by pipet 5.0 ml of internal standard solution (para 4.13 ---- 0.1000 g).

(4) Dilute to 100 ml with methylene chloride.

(5) Prepare (in 100 ml volumetric flasks) three or more standards of the compounds to be analyzed. Standard range should cover that expected in the samples.

(6) To each standard add by pipet 5 ml of internal standard solution (para 4.13).

(7) Dilute to 100 ml with methylene chloride.

(8) After instrument conditions have stabilized, inject 1.0 microliter (or as required) of each standard in gas chromatograph and obtain its chromatogram.

(9) Obtain peak heights (minus backgrounds) for each desired ingredient. See 5.3.

(10) Prepare standard graphs by plotting the ratio of peak heights of ingredients to ethyl centralite versus grams of ingredient per 100 ml of solution. Check calibration weekly or as needed.

(11) Repeat paragraphs 8 and 9 using test sample.

(12) From the ratios of peak heights of desired ingredients to that of ethyl centralite, obtain from standard graphs (para 10) grams of ingredients per 100 ml of solution.

(13) Determine percent of ingredient from the following equation:

$$\text{Percent} = \frac{(\text{grams of component per 100 ml})\ (100)}{\text{Sample Weight}}$$

c. Method B (use of single external standard)

(1) Extract the specimen with methylene chloride.

(2) Allow solvent to cool, transfer to 100 ml volumetric flask, and dilute to 100 ml with methylene chloride.

(3) Using methylene chloride as the solvent, prepare 100 ml of standard solution of known concentration of ingredients to be tested. The concentration of the ingredients should be approximately the nominal value of the expected for the test sample.

(4) After instrument has stabilized, inject 1.0 microliter (or as required) of standard solution (para 3) in gas chromatograph and obtain its gas chromatogram.

(5) Measure heights of peaks (minus backgrounds) that is attributed to desired ingredients. See 5.3.

(6) Repeat paragraph 4 and 5 using test sample.

(7) Retention times of ingredients in extracted samples should equal those of standard.

(8) Determine percentage of desired ingredients.

(9) **Calculation:**

$$\text{Percent} = \frac{(A_2)\,(H_2)\,(W_1)\,(100)}{(A_1)\,(H_1)\,(W_s)}$$

Where:

A_1 = Attenuator setting for standard

A_2 = Attenuator setting for unknown.

H_1 = Peak height attributed to standard.

H_2 = Peak height attributed to unknown.

W_1 = Gram(s) of component per 100 ml of standard solution.

W_s = Original sample weight before extraction.

5.3 Notes

a. A small amount of 2,6 DNT is usually present in the 2,4 DNT as an impurity. The sum of the peak heights of 2,6 DNT and 2,4 DNT shall be used for obtaining that attributed to total DNT, assuming equal response.

b. For instruments that have disc integrators or electronic digital integrators, area of the peaks may be used, where applicable, instead of peak heights.

METHOD 227.1

SULFATE (SPECTROPHOTOMETRIC METHOD)

1. SCOPE

1.1 *This method is used for determining* spectrophotometrically the percentage of sulfate in nitrocellulose-base propellants and nitrocellulose. Sulfur in a form other than sulfate interferes.

2. SPECIMEN

2.1 The specimen shall consist of a sample of propellant or nitrocellulose containing sulfate equivalent to 0.1 to 0.2 mg of sulfur but do not use a sample greater than 0.4 gram. The proper sample size can be ascertained from the specification requirements.

3. APPARATUS

3.1 Distillation apparatus (shown in Figure 1) shall be borosilicate glass. The internal diameter *of the tubing is 0.6 mm.* The 50 ml round bottom flask is held with a clamp about 1 foot above the table. The inlet tube of the adapter is connected to a tank of nitrogen with flexible plastic tubing conforming to Type II of federal specification L-T-790.

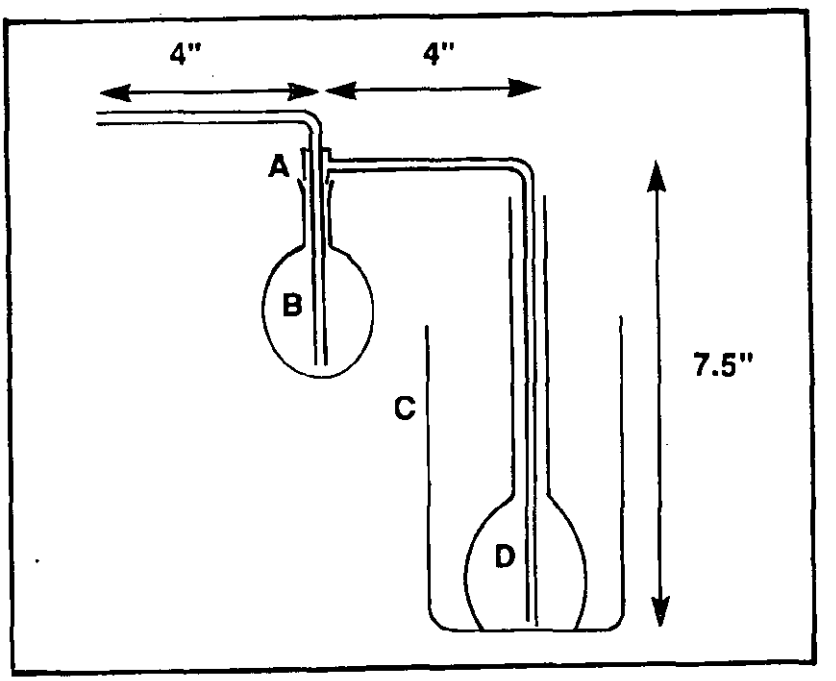


Figure 1. *Distillation apparatus*

A. 19/38 ground glass joint.
B. 50-ml round bottom flask.
C. 1-liter beaker surrounded by asbestos cloth.
D. 100-ml volumetric flask.

3.2 Regulator for nitrogen tank with needle valve.

NOTE: If the regulator does not have a satisfactory needle valve, insert a needle valve into the system (Lab crest Needle Valve, 1 1/4 mm, Fisher and Porter Geig, or equivalent).

3.3 Round bottom flasks 50 ml with 19/38 ground glass joints.

3.4 Volumetric flasks, 100 ml

3.5 Erlenmeyer flask, 500 ml, with ground glass stopper.

3.6 Bunsen burner.

3.7 Electric timer.

3.8 Spectrophotometer, Beckman Model DU or B, or equivalent.

4. MATERIALS

4.1 Standard potassium sulfate solution (1 ml = 0.02 mg of S). Dissolve 0.1088 gram of potassium sulfate (previously dried at 120° C) in water and dilute to 1 liter in a volumetric flask.

4.2 Hydriodic-hypophosphorous-hydrochloric acid reagent. Transfer 200 ml of hydriodic acid (57%), 50 ml of hypophosphorous acid (50%), and 100 ml of hydrochloric acid (38%) to a 500 ml Erlenmeyer flask (ground glass stopper). Add several glass beads, heat to boiling without a cover, boil 5 minutes, and cool to room temperature.

4.3 Lead citrate reagent. Dissolve 10 grams of lead nitrate in 200 ml of water. Add 40 grams of citric acid monohydrate and stir with a stirring rod to dissolve. If salts settle out on standing overnight, use the supernatant liquid.

4.4 Nitric acid-perchloric acid-magnesium nitrate reagent. Mix 300 ml of nitric acid, 100 ml of perchloric acid (70%), and 50 ml of water. Add 20 grams of $Mg(NO_3)_2 \cdot 6H_2O$ and stir to dissolve.

4.5 Sodium hydroxide, approximately 0.1N solution.

4.6 Ammonium hydroxide (28%).

4.7 Ice, cracked.

4.8 Nitrogren.

5. PREPARATION OF CALIBRATION CURVE

5.1 Pipet 0.2, 2, 5, 10, and 12.5 ml aliquots of standard sulfate solution (1 ml = 0.02 mg of S) into 50 ml round bottom flasks (with 19/38 ground joints). Carry along a blank. Add 5 drops of approximately 0.1N sodium hydroxide solution and evaporate just to dryness on a hot plate or over a Bunsen burner. Allow to cool to room temperature.

5.2 Attach the adapter of the apparatus to an empty 50 ml round bottom flask and insert the exit tube into a 100 ml volumetric flask containing approximately 90 ml of water. Connect up the nitrogen and regulate the flow to 55 to 65 bubbles per seconds.

5.3 Add 30 ml of ammonium hydroxide to six 100 ml volumetric flasks and dilute to approximately 90 ml with water. Place the flasks into cracked ice contained in a tray. After a few minutes place one of these flasks into the asbestos-covered beaker and fill the beaker to the top with cracked ice.

5.4 With the nitrogen flowing (as previously adjusted per instructions in Par. 5.2) insert the adapter into the flask containing the sample and insert the exit tube into the volumetric flask contained in the beaker. Take care that the apparatus fits together properly and that the exit tube reaches to the bottom of the volumetric flask. Raise the adapter, add 15 ml of the hydriodic-hypophosphorous-hydrochloric acid reagent, and immediately reconnect the apparatus. Start a timer, heat the round-bottom flask with a Bunsen burner until the solution comes to an incipient boil, and then move the burner back and forth so as to maintain the solution at or just below an incipient boil (this will require about a 2 second interval after each pass). Incipient boiling is indicated by bubbles at the interface of the solution and the sides of the flask. The total heating time is 5 minutes. At the end of this 5 minute period lower the beaker, remove the volumetric flask, and wash down the exit tube of the adapter with water from a wash bottle (use less than 5 ml of water). Immediately add 5 ml of lead citrate solution, swirl, and dilute to the mark. Within 5 minutes measure the transmittance at 400 nanometers with a spectrophotometer that has been set to 100% transmittance with distilled water.

Calculate the actual percent transmittance as follows:

$$\text{Actual \% transmittance} = \frac{\text{\% transmittance of sample vs water}}{\text{\% transmittance of blank vs water}} \times 100$$

Prepare a calibration curve by plotting on semilog paper percent transmittance (log scale) against mg of sulfur.

6. PROCEDURE

6.1 If the material is nitrocellulose, dry it by heating at 40-45°C for two hours and then at 98-102 °C for two hours.

6.2 Weigh the sample of propellant or nitrocellulose into a 50 ml round bottom flask with a 19/38 ground glass joint. Use a sample containing preferably 0.1 to 0.2 mg of sulfur but do not use a sample greater than 0.4 gram. Secure the flask with a clamp attached to a ring stand. Add 7 ml of nitric acid-perchloric acid-magnesium nitrate reagent. Brush the flame of a Bunsen burner back and forth across the bottom of the flask in such a manner that the heat is not sufficient to cause the solution to foam out of the flask. When the excessive foaming has ceased, place the Bunsen burner under the flask, heat until the salts at the bottom of the flask are completely dry, and then heat for approximately 2 more minutes. Allow to cool and proceed with the addition of the hydriodic-hypophosphorous-hydrochloric acid reagent and distillation as in the preparation of the calibration curve. Carry a blank through the entire procedure.

CAUTION: A perchloric acid hood is recommended for the operations involving the fuming with perchloric acid.

6.3 **Calculation:**

$$\% \text{ Sulfur} = \frac{\text{mg of sulfur as read from curve}}{\text{grams of sample x 10}}$$

Where:

% Na_2SO_4 = 4.43 x % sulfur

% K_2SO_4 = 5.43 x % sulfur

% H_2S0_4 = 3.06 x % sulfur

% $S0_4$ = 3.00 x % sulfur

NOTE: Rinse the volumetric flasks with dilute nitric acid (1 to 1) before using them for the next determination in order to remove lead salts that adhere to the sides. Rinse the spectrophotometer cells with concentrated nitric acid daily.

METHOD 228.1.1

CANDELILLA WAX

1. SCOPE

1.1 This method is used for determining the wax content of double base propellants.

2. SPECIMEN

2.1 The specimen shall consist of approximately 10 grams of propellant weighed to within 0.2 gm.

3. APPARATUS

3.1 Extraction apparatus.

3.2 100 or 150 ml beaker.

3.3 Filtering crucible, glass fritted disc, medium porosity or equivalent.

3.4 Fisher Filtrator.

3.5 60 - 70° C oven.

3.6 Sieve, 20 mesh.

3.7 Steam table

4. MATERIALS

4.1 Methylene chloride, reagent grade.

4.2 Acetic acid, 68%.

4.3 Diethyl ether.

5. PROCEDURE

5.1 Weigh duplicate 10 gram samples, ground to pass a 20 mesh sieve, and extract with diethyl ether for 24 hours in a Soxhlet extraction apparatus.

5.2 Evaporate the ether under a stream of dry air on a steam table.

5.3 Add 20 milliliters of glacial acetic acid to dissolve the residue. (If the residue does not dissolve easily, warm on the steam chest to dissolve and cool before continuing).

5.4 Add 10 milliliters of water, mix well and let stand for 30 minutes. (This will precipitate the wax).

5.5 Pour into medium porosity glass crucibles (washed and rinsed with acetone, but not weighed) let stand for 5 minutes.

5.6 Filter with gentle suction and wash the flasks and crucibles with 68 percent acetic acid until no color remains. (Do not let the crucibles go dry until the washing is completed).

5.7 Dry the crucibles in an oven at 60 to 70° C for 3 hours, or overnight, and also dry the extraction flasks in the oven or on the steam chest.

5.8 Put 50 milliliters of methylene chloride in each extraction flask, heat to boiling (if using a hot plate, heat one flask at a time and do not leave it) and slowly pour the methylene chloride through the corresponding crucible in a Fisher Filtrator, catching the methylene chloride in a tared 100 to 150 milliliter beaker.

5.9 Evaporate the methylene chloride under a hood, on a steam bath using an air current.

5.10 Dry the beaker in an oven at 60 to 70° C for 2 hours, cool in a desiccator and weigh.

5.11 Run a blank by evaporating 50 milliliters of methylene chloride in a tared beaker.

5.12 Dry in an oven, cool and reweigh. The gain in weight is the blank.

5.13 **Calculation:**

$$\text{Percent Wax} = \frac{(A - B)\ 100}{W}$$

Where:

A = Gain in weight of the beaker used for sample.

B = Blank for 50 milliliters of methylene chloride.

W = Sample weight

NOTE: The beaker containing the wax for the final weighing should not show any orange color which would indicate 2-NDPA remaining in the wax. The color should be no darker than the same amount of wax melted in a similar beaker.

METHOD 229.1.1

2, 4, 6, 8 CYCLOTETRAMETHYLENE TETRANITRAMINE (HMX) (INFRARED METHOD)

1. SCOPE

1.1 This infrared (IR) method may be used for the determination of HMX in propellant and base grain.

1.2 The nitro group absorbance at 1569 cm^{-1} is used to quantitatively measure the HMX. However, stabilizers such as 2- nitrodiphenylamine and resorcinol interfere at this wave number, and diethyl ether (DEE) extraction is necessary. After extraction, the residue containing the HMX is dissolved in dimethyl sulfoxide (DMSO) and scanned with a double-beam IR spectrophotometer.

1.3 Any materials absorbing at 1569 cm^{-1} and not removed in the extract will interfere.

1.4 The precision for this method at the 95% confidence level (CL) is ± 0.3 at 10 to 35% level of HMX.

2. SPECIMEN (see 6)

3. APPARATUS

3.1 Spectrophotometer, IR. Any double-beam IR spectrophotometer capable of making quantitative measurements is suitable.

3.2 Cells (2), IR, matched barium fluoride or calcium fluoride. A 0.2 mm path length is recommended for the HMX analysis.

3.3 Extraction apparatus, Soxhlet.

4. REAGENTS AND STANDARDS

4.1 Diethyl ether, anhydrous, reagent grade.

4.2 Dimethyl sulfoxide, dry, reagent grade.

NOTE: To dry, DMSO, shake with activated type 5A molecular sieve. Let solids settle out of the dried DMSO before using.

4.3 HMX, 98% minimum purity, Holston Ordance Works, Kingsport, Tennessee.

4.4 Stock solution, HMX, 10 mg/ml. Weigh approximately 2.5 g of dried HMX to the nearest 1 mg and quantitatively transfer to a 250 ml volumetric flask. Dissolve in dry DMSO and dilute to volume. Use the same lot of HMX that was used in propellant to compensate for RDX present.

5. CALIBRATION AND STANDARDIZATION

5.1 Pipet 5.00, 10.00, 15.00 and 20.00 ml aliquots of the HMX stock solution into 25 ml volumetric flasks, and dilute to volume with DMSO.

5.2 In turn, place each of these standards into the 0.2 mm IR cell and record the IR spectrum between 1500 cm^{-1} and 1950 cm^{-1} against a solvent reference in the matched cell. Use a double-beam spectrophotometer with settings established for quantitative measurements.

5.3 Measure the maximum absorbance due to HMX at 1569 cm^{-1} using the absorbance at 1900 cm^{-1} as a reference point. Determine the absorptivity, a, of HMX by plotting absorbance as the ordinate against the concentration of HMX in mg/ml and determine the slope of the resulting calibration curve.

6. **PROCEDURE**

6.1 Extract the DEE according to Method 104.1.3. Take sufficient sample for extraction so that when the residue is diluted to 25 ml, the HMX concentration is between 2 and 10 mg/ml.

6.2 After extraction, quantitatively transfer the dried residue containing the HMX into a 25 ml volumetric flask. Dissolve the residue in DMSO and dilute to volume. Allow solids to settle out.

6.3 Fill a 0.2 mm IR cell with the sample solution and scan between 1500 cm^{-1} and 1950 cm^{-1} against a solvent reference in a matched cell. Use the same double-beam spectrophotometer and the same instrument settings used for the calibration.

6.4 Measure the absorbance maximum of the HMX peak at 1569 cm^{-1} using the absorbance at 1900 cm^{-1} as a reference point.

7. **Calculation:**

$$\% \text{ HMX} = \frac{(A)\ (2.5)}{(a)\ (W)}$$

Where:

A = absorbance of HMX at 1569 cm^{-1} in the sample solution.

a = absorptivity of HMX, ml/mg.

W = weight of sample, g.

2.5 = factor including 25.00 ml dilution volume, conversion from milligram to grams, and presentation of answer in percent.

NOTE: The same cells used for calibration should be used for the actual samples.

METHOD 230.1.1

SOL-GEL EXTRACTION AND FUNCTIONAL GROUP ANALYSIS (ANB-3066 PROPELLANT)

1. SCOPE

1.1 This method may be used for sol-gel extraction of ANB-3066 propellant and the subsequent analysis for carboxyl and imine content.

2. SPECIMEN

2.1 The specimen shall consist of 5 to 10 grams of propellant.

3. APPARATUS

3.1 Erlenmeyer flask, 500-ml.

3.2 Centrifuge tubes, 50-ml.

3.3 Beaker, tared, 250-ml.

3.4 Shaker, wrist action.

3.5 Centrifuge.

3.6 Microburet

3.7 Vacuum desiccator.

3.8 Pipette, 50-ml.

4. MATERIALS

4.1 Toluene, Analytical reagent

4.2 Methanol, Analytical reagent.

4.3 Hydrochloric acid, concentrated, Analytical reagent.

4.4 Chloroform, Analytical reagent (see Note 1).

4.5 Thymol blue indicator, 0.3% in methanol.

4.6 Alcoholic potassium hydroxide (0.1N).

4.7 Chlorobenzene, Analytical reagent (see note 2).

4.8 Crystal violet indicator, 0.3% in glacial acetic acid.

4.9 Hydrobromic acid in glacial acetic acid (0.1N).

5. **PROCEDURE**

EXTRACTION

5.1 Weigh 5 to 10 grams of propellant to the nearest 0.1 mg and transfer to a 500-ml Erlenmeyer flask.

NOTE: When cured propellant is tested, prepare propellant shavings with thickness not to exceed 0.01 inch (0.25 mn).

5.2 Add 50 ml of toluene and shake for 15 minutes.

5.3 Decant the solution into a 50 ml centrifuge tube.

5.4 Centrifuge the sample at 1500 rpm for 15 minutes.

5.5 Decant the solution from the centrifuge tube into a tared 250 ml beaker.

5.6 Repeat 5.2 thru 5.4 three additional times decanting the solution into the same beaker.

5.7 Set the beaker containing the decanted solution in a well ventilated area and allow to evaporate overnight.

5.8 Weigh the beaker plus sol fraction and calculate the percent sol in the sample.

5.9 Transfer the solids from the centrifuge tube back into the extraction flask using a small amount of methanol.

5.10 Add 50 ml of methanol to the extraction flask and shake 5-10 minutes. Decant off and discard solution.

5.11 Add 25 ml methanol and 25 ml concentrated hydrochloric acid and place samples in hood.

NOTE: The hydrochloric acid-methanol mixture dissolves the aluminum and ammonium perchlorate. The reaction generates heat.

5.12 While the samples are still warm, shake on the shaker until all of the aluminum has dissolved (usually 15 minutes is sufficient). Discard solution.

5.13 Add 50 ml of methanol to the gel samples and shake for 5-10 minutes. Discard solution.

5.14 Repeat 5.13 six (6) more times.

5.15 Remove sample from flask and hand squeeze to remove most of the methanol.

5.16 Air dry the samples for two hours with good ventilation, then place in a vacuum desiccator at 50° C overnight at 100 mm Hg pressure.

5.17 Weigh the gel and calculate the percent gel in the sample.

6. CARBOXYL TITRATION

6.1 Cut the gel into small pieces and add 50 ml chloroform. Dissolve the sol in 50 ml chloroform.

6.2 Allow samples to stand for about two hours.

6.3 Add about 10 drops of thymol blue indicator solution and titrate with standardized alcoholic potassium hydroxide (0.05N) to a blue color. Use a microburet. Color must hold 15-20 seconds at the endpoint.

6.4 Run a blank titration on 50 ml of chloroform used in 6.1.

6.5 Calculate the carboxyl concentration in equivalents per 100 g of sol or gel.

7. IMINE TITRATION

7.1 Cut the gel into small pieces and add 25 ml of chlorobenzene. Dissolve the sol in 25 ml chlorobenzene (see 4.7).

7.2 Allow sample to stand about 2 hours.

7.3 Add about 10 drops of crystal violet indicator and titrate with standardized HBr solution, using a microburet. Titrate to green color with sol. Titrate to yellow with gel.

7.4 Calculate the imine concentration in equivalents per 100 g of sol or gel.

8. CALCULATIONS

8.1 Percent Sol

$$\% \text{ Sol} = \frac{\text{Wt of Sol} \times 100}{\text{Sample Wt}}$$

8.2 Percent Gel

$$\% \text{ Gel} = \frac{\text{Wt of Gel} \times 100}{\text{Sample Wt}}$$

8.3 Percent Binder

$$\% \text{ Binder} = \% \text{ Sol} + \% \text{ Gel}$$

8.4 Percent Recovery

$$\% \text{ Recovery} = \frac{\% \text{ Binder} \times 100}{B}$$

Where B is nominal percent binder in propellant (11.81% for ANB-3066).

[redacted]

3.2 Filter paper.

3.3 Beaker.

3.4 Volumetric flask, 250 ml

3.5 Pipet, 25 ml.

3.6 Iodine titration flask, 250 ml

4. MATERIALS

4.1 Nitric acid, 35 percent solution.

4.2 Ferric ammonium sulfate indicator solution as specified in Method 705.1.

4.3 Nitrobenzene.

4.4 Silver nitrate, 0.05N standard solution as specified in Method 607.1.

4.5 Potassium thiocyanate, 0.05N standard solution as specified in Method 608.1.

5. PROCEDURE

5.1 Prepare the specimen by cutting with a powder cutter or a microtome.

WARNING: Do not grind propellants containing perchlorates in a mill unless given a thorough safety review and approval by all concerned safety offices.

5.2 Determine the current that will cause a fuse wire for the calorimetric bomb to glow for several seconds before disintegrating.

5.3 Place the specimen in the cup of the bomb, and add 25 ml of distilled water to the bottom of the bomb.

5.4 Connect a fuse wire to the electrodes and arrange it so that it is in close contact with the specimen. Seal the bomb assembly securely.

5.5 Place the bomb behind a shield and ignite the contents using the current as determined in paragraph 5.2. Allow the bomb to cool to room temperature, then slowly release the gas pressure, and disassemble the bomb.

5.6 Transfer the contents of the bomb to a beaker, using small portions of distilled water. Wash all the fittings of the bomb with distilled water and transfer the washings to the beaker.

5.7 Filter the combined washings into another beaker, and wash the filter with distilled water.

5.8 Evaporate the contents of the beaker to less than 250 ml, cool to room temperature, and transfer to a 250 ml volumetric flask. Dilute to the mark with distilled water.

5.9 Transfer a 25 ml aliquot of the solution to a 250 ml iodine titration flask, using a pipet. Add 10 ml of the 35 percent nitric acid solution, 3 to 5 ml of the ferric ammonium sulfate indicator solution, and 1 to 2 ml of the nitrobenzene.

5.10 Add 50.0 ml of 0.05N silver nitrate solution. Shake the flask vigorously for several seconds to coagulate the silver chloride in the nitrobenzene.

5.11 Titrate the excess silver nitrate to the first permanent coloration with 0.05N potassium thiocyanate.

5.12 Calculate the percentage of perchlorate compound in the propellant.

5.13 **Calculation:**

$$\text{Percent potassium perchlorate} = \frac{F\,(A - BC)\,N}{W}$$

Where:

A = Silver nitrate solution, ml.

B = Potassium thiocyanate solution, ml.

C = Silver nitrate solution equivalent to 1 ml of potassium thiocyanate solution, ml.

N = Normality of silver nitrate solution.

W = Weight of specimen represented by the aliquot taken, corrected for total volatiles, mg.

F = Milliequivalent weight, multiplied by 100, of compound.

F = 13.86 for potassium perchlorate.

F = 11.7 for ammonium perchlorate.

METHOD 304.1.3

BARIUM NITRATE (GRAVIMETRIC METHOD)

1. SCOPE

1.1 This method is used to determine the barium nitrate content of propellants not containing ions which cause barium to precipitate.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5 g of propellant weighed to within 0.2 mg.

3. APPARATUS

3.1 Evaporating dish, porcelain, 90 mm.

3.2 Steam bath in a well ventilated hood.

3.3 Nichrome triangle.

3.4 Filtering crucible.

3.5 Filter paper, Whatman No. 42 or equivalent.

3.6 Oven.

3.7 Muffle furnace.

3.8 Desiccator containing an indicating desiccant.

3.9 Hot Plate

4. MATERIALS

4.1 Nitric acid, 70 percent solution.

4.2 Hydrochloric acid, 38 percent solution.

4.3 Sulfuric acid, 5 percent solution.

5. PROCEDURE

5.1 Place 5 g of the propellant sample in a 90 mm porcelain evaporating dish, add 10 to 15 ml of nitric acid, and heat the dish on a steam bath in a hood until the reaction starts. Remove the dish from the steam bath, and allow it to stand in the hood until the evolution of fumes has nearly ceased. Replace the dish on the steam bath until only a gummy mixture remains.

5.2 Place the dish on a nichrome triangle supported by a tripod, and heat the dish with a low flame directed at the side of the dish until nearly all of the carbonaceous matter is burned off. Then place the dish in the muffle oven at approximately 600° C for about one half hour or until all the carbonaceous matter is burned to ash.

CAUTION: High temperature must be avoided, when heating the dish on a nichrome triangle, they result in fusion of the salts with the porcelain dish.

5.3 Allow the dish to cool to room temperature, and rinse the sides first with 5 ml of distilled water and then with 5 ml of 38 percent hydrochloric acid. Cover the dish with a watchglass, and heat on a steam bath for 5 to 10 minutes.

5.4 After the heating period, dilute the contents with distilled water to approximately 25 ml and filter the solution through Whatman No. 42 filter paper into a 150 ml beaker. Wash the residue thoroughly with approximately 50 ml of distilled water. Dilute to filtrate and washings to approximately 75 ml.

5.5 Heat the solution to boiling on a hotplate, and slowly add 10 ml of 5 percent sulfuric acid while stirring. Allow the solution to digest on the steam bath for at least 1 hour.

5.6 Filter the solution through an ignited tared filtering crucible, and wash the precipitate with distilled water.

NOTE: If a determination of the percentage of potassium salts in the specimen is desired retain the filtrate.

5.7 Dry the crucible in an oven at 100° C for approximately 1 hour.

5.8 Ignite the crucible in a muffle furnace at a dull red heat for 15 to 30 minutes.

5.9 Cool to room temperature in a desiccator, and weigh.

5.10 Determine the weight of the precipitate, and calculate the percentage of barium nitrate as follows:

5.11 **Calculation:**

$$\text{Percent barium nitrate} = \frac{112A}{W}$$

A = Weight of precipitate, g.

W = Weight of specimen corrected for total volatiles, g.

METHOD 305.1.2

CALCIUM CARBONATE-SODIUM SULFATE-GRAPHITE (MORPHOLINE METHOD)

1. SCOPE

1.1 This method is used for determining the calcium carbonate, sodium sulfate and graphite content of propellants. The presence of other materials insoluble in morpholine will affect this test.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5 g of propellant, weighed to within 0.2 mg.

3. APPARATUS

3.1 Beaker, 250 ml.

3.2 Hotplate with variable heat control, in a well-ventilated hood.

3.3 Gooch crucible.

3.4 Stirring rod

3.5 Desiccator containing an indicating desiccant.

3.6 Oven.

3.7 Muffle furnace.

4. MATERIALS

4.1 Morpholine.

4.2 Diethyl ether, anhydrous.

4.3 Hydrochloric acid, 3 N solution.

5. PROCEDURE

5.1 Place the specimen in the 250 ml beaker. Add 50 ml of morpholine, and heat on the hotplate inside the hood until the propellant is dissolved.

WARNING: Morpholine fumes are flammable. Do not allow fumes to go over the top of the beaker. If the fumes are rising too high, remove the beaker from the hotplate and cool the contents, then replace and heat cautiously until the propellant is dissolved.

5.2 Filter the hot solution through the tared Gooch crucible, pouring it down a stirring rod.

5.3 Place 25ml of morpholine in the beaker and heat until white fumes appear. Pour the fuming morpholine down the stirring rod into the Gooch crucible, seeing to it that the hot liquid washes down the sides of the crucible.

5.4 Allow the beaker and crucible to cool to room temperature and wash out the beaker with anhydrous ethyl ether. Transfer the washings to the Gooch crucible with the aid of a rubber policeman.

5.5 When all the ether has passed through the crucible, wipe the outside of the crucible with a clean towel, and place it in an oven at 100° C for 30 minutes. Then cool to room temperature in the desiccator.

5.6 Determine the percentage of sodium sulfate in the propellants as follows:

a. Weigh the crucible.

b. Wash the residue in the crucible with four 25 ml portions of warm distilled water and a small amount of ether. When the odor of ether is no longer discernible, place the crucible in the oven at 100° C for 30 minutes. Cool the crucible in the desiccator for 20 minutes.

c. Weigh the crucible.

d. Calculate the percentage of sodium sulfate.

e. **Calculation:**

$$\text{Percent sodium sulfate} = \frac{100A}{W}$$

Where:

A = Loss in weight between weighings in steps a and c, gm.

W = Weight in specimen, gm, corrected for total volatiles.

5.7 Determine the percentage of calcium carbonate in the propellant as follows:

a. After determining the weight of the crucible for the calculation of sodium sulfate, wash the residue in the crucible, first with 50 ml of 3N hydrochloric acid, and then with 25 ml of anhydrous ethyl ether.

b. Dry the crucible again for 30 minutes at 100°C and cool to room temperature.

c. Weigh the crucible.

d. Calculate the percentage of calcium carbonate.

e. **Calculation:**

$$\text{Percent calcium carbonate} = \frac{100B}{W}$$

Where:

B = Loss of weight between weighings in steps 5.6 c and 5.7 c, g.

W = Weight in specimen, g, corrected for total volatiles.

5.8 Determine the percent of graphite in the propellants as follows:

a. After determining the weight of crucible for the calculation of calcium carbonate, ignite the crucible in a muffle furnace at 600 to 650° C maintaining the heat until all carbonaceous matter has been burned off.

b. Remove the crucible from the furnace, cool in the desiccator for approximately 30 minutes and weigh.

c. Determine the loss in weight as a result of igniting the crucible, and calculate the loss as the percentage of graphite in the propellant.

d. **Calculation:**

$$\text{Percent graphite} = \frac{100C}{W}$$

Where:

C = Loss in weight of crucible between weighings in steps 5.7 c and 5.8 b, g.

W = Weight in specimen, g, corrected for total volatiles.

METHOD 306.1.4

TIN (IODIMETRIC METHOD)

1. SCOPE

1.1 This method is used for determining the tin content of propellants. The presence of other metals that react with iodine will cause interference.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5 g of the propellant, weighed to within 0.2 mg.

3. APPARATUS

3.1 Erlenmeyer flask, 500 ml.

3.2 Buret, 50 ml.

3.3 Rubber stopper, three hole.

3.4 Inlet tube for gas.

3.5 Glass plug (for buret hole).

3.6 Hot plate in well ventilated hood.

4. MATERIALS

4.1 Nitric acid, 70 percent

4.2 Sulfuric acid, concentrated.

4.3 Perchloric acid, 70 percent.

4.4 Hydrochloric acid, 38 percent.

4.5 Antimony trichloride, 2 percent solution. Dissolve 2 g of antimony trichloride in 50 ml of hydrochloric acid and dilute to 100 ml with water.

4.6 Lead, granular (also known as test lead).

4.7 Potassium iodide, 10 percent solution, freshly prepared.

4.8 Starch indicator solution, prepared as specified in Mehod 701.1.

4.9 Standard jpotassium iodate solution, 0.025N. Dry potassium iodate at 180°C for 2 hours. Dissolve 1.7835 g in 100 ml of water containing 2 g of sodium hydroxide and 20 g of potassium iodide. Dilute to 2 liters in a volumetric flask. This is a primary standard.

5. PROCEDURE

5.1 Prepare the sample as described in Method 509.3, if required.

5.2 Place 5 g of the sample into the 500 ml Erlenmeyer flask. Add 80 ml of nitric acid, 25 ml of sulfuric acid, and 5 ml of perchloric acid.

5.3 Place on a hot plate and heat until color of the solution has changed from brown to grey (the grey is due to graphite) and copious white fumes are evolved. Continue heating for 1 to 1 1/4 hours. Disregard any graphite that remains unattacked.

CAUTION: A perchloric acid hood is recommended.

5.4 Allow to cool. Add 225 ml of water, 75 ml of hydrochloric acid, 2 drops of antimony trichloride solution, and 10 g of granular lead.

5.5 Connect the flask so as to maintain an inert atmosphere, place the flask on a hot plate and boil moderately for 45 minutes.

5.6 While maintaining the inert atmosphere, cool to 10°C in an ice bath (disregard the white precipitate of lead chloride that may settle out.

5.7 Add 5 ml of potassium iodide solution and 10 ml of starch solution and titrate with standard potassium iodate solution to a persistent blue color. Carry a blank through the determination. This bank need be determined only once weekly. It will usually be 0.1 to 0.15 ml.

5.8 Calculate the percentage of tin.

5.9 **Calculation:**

$$\text{Percent tin} = \frac{5.935\ (A-B)\ N}{W}$$

Where:

A = Potassium iodate solution required for sample, ml.

B = Potassium iodate solution required for blank, ml.

N = Normality of potassium iodate solution.

W = Weight of specimen, corrected for total volatiles, g.

METHOD 306.2.3

TIN AND GRAPHITE (GRAVIMETRIC METHOD)

1. SCOPE

1.1 This method is used to determine the tin and graphite content of propellants in the presence of each other.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5 g of the propellant weighed to within 0.2 mg.

3. APPARATUS

3.1 Beaker, 250 ml.

3.2 Hot plate or steam bath.

3.3 Gooch crucible.

3.4 Oven.

3.5 Watch glass.

3.6 Desiccator, containing an indicating desiccant.

4. MATERIALS

4.1 Nitric acid, 70 percent

4.2 Acetone.

5. PROCEDURE

5.1 Prepare the sample as described in Method 509.3, if required.

5.2 Prepare the Gooch crucible by washing with nitric acid and then with water and igniting at 800°C.

5.3 Place 5 g of the sample into the 250 ml beaker, and 40 ml of nitric acid, and cover with a tight fitting watch glass.

5.4 Heat on the hot plate at gentle heat (or on the steam bath) until the reaction starts, then heat for 1 hour in such a way that the temperature is approximately 95°C. Ignore the slight reaction that may seem to take place at the end of 1 hour.

5.5 Add 20 ml of water, heat to boiling and boil vigorously for 15 minutes with the watch glass in place.

5.6 Filter while hot through the tared Gooch crucible and wash thoroughly with hot water. Discard the filtrate.

CAUTION: A mixture of nitric acid and acetone produces a violent reaction. Therefore, the crucible and contents must be washed free of nitric acid and the filtrate discarded prior to subsequent washing with acetone.

5.7 Wash thoroughly with acetone and then once with water.

5.8 Dry the crucible in an oven at 350° for 40 minutes. Cool to room temperature in a desiccator and weigh.

5.9 Ignite the crucible at 800°C for 1 hour. Cool to room temperature in a desiccator and weigh.

5.10 Calculate the percentages of tin and graphite.

5.11 **Calculations:**

$$\text{Percent tin} = \frac{78.77\ (C-A)}{W}$$

$$\text{Percent graphite} = \frac{100\ (B-C)}{W}$$

Where:

A = Weight of crucible, g.

B = Weight of crucible and precipitate (ascertained in paragraph 5.8).

C = Weight of crucible and precipitate (ascertained in paragraph 5.9).

W = Weight of sample corrected for total volatiles.

METHOD 306.3.1

TIN (POLARGRAPHIC METHOD)

1. SCOPE

1.1 This method is used for determining the tin content of propellants.

2. SPECIMEN

2.1 The specimen shall consist of a portion of the propellant containing approximately 2.5 mg of tin (as determined from the detailed specifications for the propellant being tested.) Weigh the specimen to within 0.2 mg.

3. APPARATUS

3.1 Volumetric flask, 500 ml.

3.2 Volumetric flask, 250 ml.

3.3 Beakers, 50 ml.

3.4 Beakers, 100ml.

3.5 Watchglass, ribbed.

3.6 Hotplate in a well ventilated hood.

3.7 Polarograph (Sargent Recording Polarograph, Model XXI, or equivalent).

3.8 Polarographic cell, dropping mercury electrode, in constant temperature bath maintained within 0.5°C of room temperature (or any convenient temperature).

NOTE: See Kolthoff, I.M. and Lingane, J.J. Polarography, Vol I, second edition, page 353, figure XVII-1 (Interscience Publishers, Inc. NY 1952).

3.9 Beaker, 400 ml.

3.10 Microburet, 5 ml, 0.01 ml divisions.

4. MATERIALS

4.1 Tin, metallic.

4.2 Hydrochloric acid.

4.3 Nitric acid.

4.4 Sulfuric acid.

4.5 Blue litmus paper.

4.6 Ammonium chloride.

4.7 Gelatin, 0.25 aqueous solution (freshly prepared).

4.8 Nitrogen, purified, (oxygen-free) passed through water prior to introduction into the polarographic solution.

4.9 Hydrochloric acid, 6N.

5. **PROCEDURE**

5.1 Prepare a standard graph of wave height in millimeters against concentration of tin in milligrams per 50 millimeters as follows:

a. Weigh 0.5000 g of tin and place it in a 400 ml beaker. Add 250 ml of concentrated hydrochloric acid and allow it to dissolve. Transfer the solution to a 500 ml volumetric flask and dilute to mark with distilled water.

b. Transfer a 25 ml aliquot of the solution to a 250 ml volumetric flask and dilute to the mark with 6N hydrochloric acid.

NOTE: One milliliter of this solution contains 0.1 mg tin.

c. To each of five 50 ml beakers add 5 ml of concentrated HNO_3 and 2 ml concentrated H_2SO_4.

CAUTION: Any variation in the volume of sulfuric acid in the solutions being polarographed will cause variations in the half wave potential. Therefore the volume of the sulfuric acid in all solutions, both in the preparation of the standard graph and in the determination, should be kept constant at approximately 5 ml. Precautions should be taken to prevent the loss of the sulfuric acid through excess fuming.

d. Transfer aliquots of the tin solution containing 2.1, 2.3, 2.5, 2.7 and 2.9 mg of tin to the five 50 ml beakers. Treat the mixture in the beakers in the manner described in paragraphs 5.2 (c) through (j) and 5.3 (a) through (d).

e. On linear graph paper, plot the wave height in millimeters against the weight of tin in milligrams.

f. Draw a straight line which most nearly approximates the values obtained.

NOTE: This graph is valid only when the determination is made with the same capillary as that used in preparing the graph, and so long as the capillary characteristic of the dropping mercury electrode remains constant. The capillary characteristics of the electrode should therefore be checked at the time the graph is made and rechecked at intervals of about a month. If the characteristic changes by more than 0.05 units fron the original value, a new capillary should be selected and a new graph prepared.

5.2 Prepare the specimen for polarographing as follows:

a. Prepare the specimen as prescribed in Method 509.3.

b. Place the specimen in a 100 ml beaker and add 10 ml of the nitric acid and 2 ml of the sulfuric acid. Cover the beaker with a watch glass.

c. Heat on a hotplate set at LOW until the specimen is completely dissolved. Then increase the heat until the fumes of sulfur trioxide appear.

d. CAUTION: Slowly add 2 or 3 ml of concentrated nitric acid, drop by drop through the opening made by the lip of the beaker and the watchglass, and continue heating until the fumes of sulfur trioxide reappear. Repeat dropwise addition of nitric acid until the solution is clear. Cool the beaker and its contents to room temperature and remove the watchglass.

e. Cautiously add 3 ml of water, and return the beaker to the hotplate. Heat until sulfur trioxide fumes reappear. Cool the beaker and its contents to room temperature, cautiously add 3 ml of water and heat again until sulfur trioxide fumes reappear.

f. Cool the beaker and its contents to room temperature again and cautiously add an additional 3 ml of water and heat.

g. While the contents of the beaker are being heated, test for the presence of nitric acid by holding a piece of blue litmus paper in the vapors rising from the sulfuric acid solution. If the litmus paper changes color repeat step (f) until the litmus paper test indicates that all the nitric acid has been driven off. Then cool to room temperature.

h. Cautiously transfer the sulfuric acid solution to a 50 ml volumetric flask, containing 10.7 g of ammonium chloride and 30 ml of water. Add 1 ml of the gelatin solution.

i. Allow the ammonium chloride to dissolve, adding additional water if necessary. Bring the solution to room temperature and then dilute to the mark with water.

j. Transfer a portion of this solution to a polarographic cell.

5.3 Obtain a polarogram for the solution as follows:

a. Place the cell in the constant temperature bath (para 3.8).

b. Flush nitrogen through the solution for 5 to 10 minutes. Thereafter allow the gas to flow over the solution.

c. At an applied voltage of -0.35, adjust the recorder pen of the polarograph near zero. Obtain a polarogram for the -0.35 to -0.75 volt range at an appropriate sensitivity.

d. Produce a second polarogram from the same solution, and find the average wave height for the two polarograms.

5.4 Using the average of the two polarograms obtained for the propellant, read the amount of tin present in the solution from the standard graph.

5.5 Calculate the percentage of tin in the propellant.

5.6 **Calculation:**

$$\text{Percent Tin} = \frac{100A}{W}$$

Where:

A = Weight of tin, as obtained from graph, g.

W = Weight of specimen, corrected for total volatiles.

METHOD 307.1.2

CRYOLITE (SODIUM ALUMINUM FLOURIDE)

1. SCOPE

1.1 This method is used for determining the cryolite content of propellants.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5 g of the propellant, weighed to within 0.2 mg.

3. APPARATUS

3.1 Silica dish.

3.2 Muffle furnace.

3.3 Filtering crucible.

3.4 Suction filtration apparatus.

4. MATERIALS.

4.1 Paraffin wax.

4.2 Aqua regia, consisting of one volume 70 percent nitric acid and three volume 38 percent hydrochloric acid.

4.3 Precipitating reagent, prepared as follows:

a. Mix 80 g of uranyl acetate dihydrate, 48 g of 30 percent acetic acid, 390 ml of distilled water in one container, and warm to dissolve all the salts.

b. In another container, mix 240 g of zinc acetate dihydrate, 25 g of 30 percent acetic acid, 250 ml of distilled water, and warm to dissolve all the salts.

c. Mix the two solutions together and store in a borosilicate vessel.

NOTE: Sodium impurities in this reagent may cause precipitation; therefore it should be filtered immediately before being used.

4.4 Wash liquid, consisting of a saturated solution of sodium zinc uranyl acetate in 95 percent ethyl alcohol.

4.5 Diethyl ether.

5. PROCEDURE

5.1 Prepare the specimen as described in Method 509.3.

5.2 Place the specimen in the silica dish and add 10 g of molten paraffin wax. Heat gently until the wax is ignited, and allow it to burn off.

5.3 When the flame has died, place the dish in a muffle furnace at approximately 600°C until the residual carbon has been burned off. Then cool to room temperature.

5.4 Dissolve the ash in a few milliliters of aqua regia (para 4.2), then evaporate the solution until only a thoroughly dried residue remains.

5.5 Dissolve the residue in approximately 5 ml of distilled water.

CAUTION: From this point and throughout the remainder of the determination it is essential that all reagents and solution be maintained at 20 ± 1°C.

5.6 Filter 20 ml of the precipitating reagent (para 4.3) and add it to the solution in the silica dish. Stir the mixture vigorously with a thin glass rod for 15 seconds, then allow it to stand for 1 hour at 20 ± 1°C.

5.7 Filter the contents of the dish through the tared filtering crucible, with the aid of suction; wash the retained precipitate first with five 2 ml portions of the wash liquid (para 4.4) at 20 ± 1°C, and finally with 2 ml of ether.

5.8 Draw air through the crucible until the odor of ether is no longer discernible, then weigh. Calculate the percentage of cryolite in the propellant.

5.9 **Calculation:**

$$\text{Percent cryolite} = \frac{4.55A}{W}$$

Where:

A = Increase in weight of crucible (weight of sodium zinc uranyl acetate hexahydrate precipitate), g.

W = Weight of specimen, corrected for total volatiles, g.

METHOD 308.1.4

GRAPHITE AND CARBON BLACK

1. SCOPE

1.1 This method is used to determine the graphite and carbon black content of propellants containing less than 0.5 percent carbon black. Zirconium and other metals will interfere.

2. SPECIMEN

2.1 The specimen shall consist of 10 g of the propellant, weighed to within 0.5 g.

3. APPARATUS

3.1 Filtering crucible chemical porcelain, porous bottom, with fine porosity.

3.2 Beaker, 400 ml.

3.3 Steam bath.

3.4 Suction filtration apparatus.

3.5 Oven.

3.6 Dessicator containing an indicating dessicant.

3.7 Muffle furnace.

3.8 Erlenmeyrer flask, 250 ml.

3.9 Reflux condenser, water cooled.

3.10 Hotplate.

3.11 Crucible holder.

4. MATERIALS

4.1 Nitric acid.

4.2 Nitric acid solution 1:1 dilution (by volume) with water.

4.3 Acetone.

4.4 Ether.

5. PROCEDURE

5.1 Pretreat the crucible filter bottom as follows:

a. Wash the crucible filter bottom with 10 to 15 mL of the 1:1 nitric acid solution, and rinse thoroughly with water.

b. Dry in an oven for 1 hour at approximately 100°C.

c. Ignite the crucible.

5.2 Prepare the specimen of propellant in accordance with Method 509.3.

5.3 Remove organic matter from the specimen as follows:

a. Place the specimen in the beaker, and add 75 ml of the nitric acid.

b. Heat the beaker on the steam bath and when the reaction starts, remove the beaker from the bath and allow the reaction to continue until fuming ceases. If all the particles have not decomposed after the fuming ceases, reheat the beaker until decomposition is complete.

NOTE: The rate of decomposition can be controlled, if necessary, by adding small amounts of distilled water from time to time.

c. Dilute the hot solution, heat and stir until the carbon black coagulates then cool the beaker to room temperature.

d. Using a suction filtration apparatus, apply gentle suction so that the filtrate will fall from the crucible at the rate of two to three drops per second.

e. Filter the solution through the tared filter crucible, maintaining the level of the solution above the top surface of the filter. Rinse the beaker with distilled water, and transfer the rinsings to the crucible in the same manner.

CAUTION: If the solution is filtered too rapidly, or if the solution drops below the level of the top surface of the filter, the carbon black may pass through the filtrate.

f. Wash the residue in the same manner with hot distilled water to remove most of the nitric acid. Discard the filtrate.

WARNING: A mixture of nitric acid and acetone produces a violent reaction. Therefore, the crucible and filter must be completely washed free of nitric acid, and the filtrate discarded prior to subsequent washing with acetone.

g. Wash the residue with a 2:1 (by volume) mixture of ether and acetone in the same manner prescribed for filtering the solution through the crucible in paragraph 5.3 (e). Continue the solvent wash until all the organic material is dissolved, as shown by the absence of color in the washings.

h. Aspirate the crucible in the suction filtration apparatus until the odor of solvent is no longer discernible when the vacuum line is turned off.

i. Dry the crucible in the oven for 1 hour at 120 to 130°C. Cool to room temperature in a dessicator and weigh.

5.4 Remove the carbon black from the filter as follows:

a. Place the crucible in the Erlenmeyer flask. Add 5 ml of nitric acid to the crucible and 45 ml to the flask.

b. Connect the flask to the reflux condenser and boil on the hotplate for 3 hours.

c. Cool the flask to room temperature. Remove the reflux condenser, and remove the crucible, placing it in a crucible holder.

d. Attach a suction filtration apparatus to the crucible. Transfer the contents of the flask to the crucible and filter, employing strong suction. Rinse the flask thoroughly with distilled water and transfer the rinsings to the crucible in the same manner.

e. Wash the crucible thoroughly with hot distilled water to remove all traces of nitric acid. Discard the filtrate.

f. Wash the crucible and contents alternatively with distilled water and acetone a sufficient number of times to remove all the undissolved carbon black, as shown by the absence of color in the washings. Give several final rinsings with acetone and discard the filtrate.

g. Aspirate the crucible in the suction filtration apparatus until the odor of acetone is no longer discernible when the vacuum line is turned off.

h. Dry the crucible in the oven for one hour at 120 to 130°C. Cool to room temperature in a dessicator and weigh.

5.5 Determine the loss in weight of the graphite residue from the weighing of the residue containing graphite and carbon black. See para 5.3 (i). Calculate the percentage of carbon black in the propellant.

5.6 **Calculation:**

$$\text{Percent carbon black} = \frac{100\,A}{W}$$

Where:

A = Loss in weight of crucible between weighings in para 5.3 (i) and 5.4 (h), grams.

W = Original weight of the specimen, grams.

5.7 Remove the graphite from the filter as follows:

a. Ignite the crucible in the muffle furnace at 600 to 650°C until all carbonaceous matter has been burned off.

b. Remove the crucible from the furnace, cool to room termperature in a dessicator, and weigh.

5.8 Determine the loss in weight as a result of igniting the crucible, and calculate the loss as the percentage of graphite in the propellant.

5.9 **Calculation:**

$$\text{Percent graphite} = \frac{100\,A}{W}$$

Where:

A = Loss in weight of crucible between weighings in para 5.4 (h) and 5.7 (b), grams.

W = Original weight of the specimen, grams.

METHOD 309.1.2

CARBON BLACK OR GRAPHITE (GRAVIMETRIC METHOD)

1. **SCOPE**

1.1 This method is used for determining the carbon black or graphite content of propellants.

2. **SPECIMEN**

2.1 The specimen shall consist of 2 to 5 g of the propellant, weighed to within 0.2 mg.

3. **APPARATUS**

3.1 Filtering crucible chemical porcelain, porous bottom, with fine porosity.

3.2 Beaker, 400ml.

3.3 Oven.

3.4 Steam bath.

3.5 Watchglass.

3.6 Ice bath.

3.7 Suction filtration apparatus.

3.8 Dessicator containing an indicating dessicant.

3.9 Muffle furnace.

4. **MATERIALS**

4.1 Nitric acid.

4.2 Nitric acid solution, 1:1 dilution (by volume) with water.

4.3 Acetone.

4.4 Ether.

4.5 Hydrochloric acid.

5. **PROCEDURE**

5.1 Pretreat the crucible filter bottom as follows:

a. Wash the filter bottom with 10 to 15 ml of the nitric acid solution and rinse thoroughly with water.

b. Dry in an oven for 1 hour at approximately 100°C.

c. Ignite the crucible.

5.2 Prepare the specimen of propellant in accordance with Method 509.3.

5.3 Remove organic matter from the specimen as follows:

a. Place the specimen in the beaker and add 75 ml of nitric acid solution. Cover the beaker with a watchglass.

b. Heat the beaker on the steam bath. When the reaction starts, remove the beaker from the steam bath until the reaction subsides, then replace the beaker on the steam bath and allow the mixture to digest for approximately 1 hour. For metals insoluble in nitric acid, add sufficient hydrochloric acid to effect solution.

c. Remove the beaker from the bath and chill in an ice bath.

d. Add 75 ml of distilled water to the beaker and allow the beaker to stand until the major part of the carbon black or graphite has settled out.

e. Using the suction filtration apparatus, apply gentle suction so that the filtrate will fall from the crucible at the rate of two to three drops per second.

f. Filter the solution through the tared crucible, maintaining the level of the solution above the top surface of the filter. Rinse the beaker with distilled water and transfer the rinsings to the crucible in the same manner.

CAUTION: If the solution is filtered too rapidly, or if the solution drops below the surface of the filter, the carbon black or graphite may pass through with the filtrate.

g. Wash the residue in the same manner with hot distilled water to remove most of the nitric acid. Discard the filtrate.

WARNING: The mixture of nitric acid and acetone produces a violent reaction. Therefore, the crucible and filter must be completely washed of nitric acid, and the filtrate discarded prior to subsequent washing with acetone.

h. Wash the residue with a solvent containing 1 volume of acetone and 2 volumes of ether in the same manner prescribed for filtering the solution through the crucible in para (f). Continue the solvent wash until all the organic material is dissolved, as shown by the absence of color in the filtrate.

i. Gently aspirate the crucible in the suction filtration apparatus until the odor of solvent is not discernible when the vacuum line is turned off. Dry the crucible in the oven for 30 minutes at 125 ± 5°C. Cool and weigh.

5.4 Determine the percentage of carbon black as follows:

a. Ignite the crucible in the muffle furnace at 600 to 650°C until all carbonaceous matter has been burned off. Remove the crucible from the furnace, cool in a dessicator, and weigh.

b. Determine the loss in weight of the crucible after ignition in the muffle furnace and calculate this loss as the percentage of graphite or carbon black in the propellant on a volatiles-free basis.

METHOD 309.2.2

CARBON BLACK (PHOTOMETRIC METHOD)

1. SCOPE

1.1 This method is used to determine photometrically the percentage of carbon black in propellants. This method is applicable only when the calibration curve is established with identical carbon black used in manufacture of propellant. In other instances, Method 309.1 must be used.

2. SPECIMEN

2.1 The specimen shall consist of approximately 3 g of the propellant, weighed to within 0.2 mg.

3. APPARATUS

3.1 Volumetric flasks, 100 ml.

3.2 Weighing bottle, with round glass stopper.

3.3 Oven.

3.4 Desiccator containing calcium chloride.

3.5 Disintegrator, electric (Waring Blendor, or equal).

3.6 Volumetric flask, one liter.

3.7 Filtering crucible, chemical porcelain, porous bottom, of desired porosity.

3.8 Suction filtration apparatus.

3.9 Muffle furnace.

3.10 Pipet.

3.11 Wrist action shaker.

3.12 Photoelectric filter photometer with visible light source, a 540 nanometer filter and 10 mm cells.

4. MATERIALS

4.1 Carbon black representing the identical material used in the manufacture of the propellant.

4.2 Acetic acid, acetone solution, 5 percent glacial acetic acid in acetone (by volume).

4.3 Samples of all constituents indicated in the detailed specifications for the propellant, except carbon black.

4.4 Ethyl alcohol.

4.5 Nitric acid, 35 percent solution.

5. PROCEDURE

5.1 Prepare a dispersion of carbon black as follows:

a. Place approximately 0.5 g of carbon black in a weighing bottle.

b. Dry the sample in an oven at 105°C for two (2) hours.

c. Cool in a desiccator for 30 minutes.

d. Transfer approximately 0.10 g of the carbon black to the disintegrator, and add 100 ml of the acetic acid acetone solution.

e. Turn on the disintegrator until the carbon black is completely dispersed in the acetic acid acetone solution.

f. Transfer the dispersion to a one liter volumetric flask, and dilute to the mark with acetic acid acetone solution at 20°C.

5.2 Prepare a filtering crucible. Wash the filter with 10 to 15 ml of 35 percent nitric acid solution and with warm water; dry in an oven at 100°C for 1 hour; ignite the crucible, and weigh it.

5.3 Determine the exact concentration of the carbon black dispersion as follows:

a. Attach a suction filtration apparatus to the crucible.

b. Employing gentle suction, filter a 250 ml aliquot of the carbon black dispersion (para 5.1) through the crucible.

CAUTION: If the solution is filtered too rapidly, or it drops below the surface of the filter, the carbon black may pass through with the filtrate.

c. Aspirate the crucible until the odor of acetone is no longer discernible.

d. Dry the crucible in an oven at 105°C for 30 minutes, then cool in a desiccator to room temperature.

e. Weigh the crucible to determine the amount of carbon black in the 250 ml aliquot, and calculate the percentage of carbon black in the dispersion.

5.4 Prepare a standard graph of percent carbon black versus photometer readings as follows:

a. To each of four 100 ml volumetric flasks, add a total of 3 mg of the propellant components (except carbon black) in the proportion indicated in the detailed specification for the particular propellant being tested.

b. Transfer aliquots of the carbon black dispersion (para 5.1) to these flasks. Vary the size of the aliquots so that the concentrations of carbon black in these synthetic solutions are equally spaced throughout the nominal percentile range for carbon black in the propellant being tested.

c. Fill each flask to the 95 ml mark with acetic acid-acetone solution (para. 4.2). Stopper the flasks and shake with a wrist action shaker until all solid material is in solution.

d. Dilute each flask to the 100 ml mark, and mix thoroughly.

e. Using the 10 mm cell filled with a blank acetic acid-acetone solution, and a 540 nanometer filter, adjust the photometer dial reading to zero.

f. Fill the same cell or matching cells with the synthetic solutions, and obtain direct dial readings for each solution.

g. On linear graph paper, plot the percent carbon black versus the direct dial readings obtained.

5.5 Prepare the speciman as specified in Method 509.3.

5.6 Place the specimen in a 100 ml volumetric flask, and dampen it with 5 ml of ethyl alcohol to facilitate complete suspension of the propellant.

5.7 Add 90 ml of the acetic acid acetone solution (para 4.2) to the flask. Stopper the flask, and shake on a wrist action shaker until all solid material is in solution.

5.8 Make up to volume with acetic acid acetone solution, and mix thoroughly.

NOTE: Carbon black, in proportions greater than 0.1 percent, absorbs to much light at 540 nanometers to allow optimum light transmission and curve characteristics to be obtained. For propellants with carbon black concentrations higher than 0.1 percent, take appropriate aliquots of the 100 ml volume in the flask, and dilute with the 5 percent acetic acid acetone solution.

5.9 Fill a 10 mm cell with this solution; fill a matched cell with acetic acid acetone solution for the reference.

5.10 Using the photometer with a 540 nanometer, determine the direct dial reading of the propellant solution.

5.11 Using the direct dial reading obtained, determine the percent carbon black in the propellant from the prepared curve (para 5.4).

METHOD 310.3.1

POTASSIUM SALTS (FLAME SPECTROPHOTOMETRIC METHOD)

1. SCOPE

1.1 This method is used for determining the potassium sulfate and potassium nitrate contents of propellants that contain no calcium salts. This method may be used for determining the percentage of potassium salts from the salt solution prepared by Method 310.4 from propellants.

2. SPECIMEN

2.1 The specimen shall consist of approximately 1 g of the propellant, weighed to within 0.2 mg.

3. APPARATUS

3.1 Flame spectrophotometer.

3.2 Volumetric flask, 1 liter.

3.3 Beaker, 150 ml.

3.4 Cover glass, ribbed.

3.5 Steam bath in a well ventilated hood.

3.6 Hotplate.

3.7 Volumetric flask, 100 ml

TABLE I. *Standard concentrations of potassium*

Potassium concentration, ppm	Standard Solution concentration ml per liter
35	10
42	12
49	14
56	16
63	18
70	20

4. MATERIALS

4.1 Standard solution of potassium sulfate containing 3500 parts per million (ppm) of potassium, prepared by transferring 7.7998 g of analytical grade potassium sulfate to a 1 liter volumetric flask, and diluting to the mark with distilled water.

NOTE: This solution is used in preparing solutions of known potassium concentration in accordance with Table I.

4.2 Sulfuric acid.

4.3 Nitric acid, 70 percent solution.

5. **PROCEDURE**

5.1 Ascertain from the detailed specification the nominal concentration in parts per million (ppm) of potassium in the propellant being tested.

5.2 Using the standard solution (para 4.1) in accordance with Table I, prepare two potassium sulfate solutions, one having the next higher concentration than the propellant, and one having the next lower.

5.3 Prepare the specimen as specified in Method 509.3

5.4 Place the specimen in a 150 ml beaker, and add 15 ml of 70 percent nitric acid. Cover with the ribbed cover glass.

5.5 Heat on a steam bath until the specimen is completely dissolved.

NOTE: If graphite is present in the propellant, it will not dissolve.

5.6 Remove the beaker from the steam bath and add 1 ml of concentrated sulfuric acid.

5.7 Heat the beaker on a hotplate until dense fumes of sulfur trioxide are evolved.

5.8 Add more nitric acid, drop by drop, until all carbonaceous matter has decomposed.

5.9 Remove the beaker from the hotplate and cool to room temperature. Wash down the cover glass and the sides of the beaker with a fine stream of distilled water.

5.10 Return the beaker to the hotplate, and heat until the sulfur trioxide fumes have practically ceased. (The solution should not be permitted to go to dryness.)

NOTE: If a black residue starts to form on the bottom of the beaker, or if the solution darkens appreciably, add more nitric acid, drop by drop, until the solution is clear. It will be either colorless or straw colored.

5.11 Remove the beaker from the hotplate, cool to room temperature, and add 50 ml of water. If the solution is clear, proceed to para 5.12. If not, digest the solution on the steam bath for 1 hour, cool and filter into a 100 ml volumetric flask. Wash the beaker and filter with distilled water. Catch the washings in the volumetric flask and dilute to the mark.

5.12 Quantitatively transfer the solution to a 100 ml volumetric flask, and dilute to the mark with distilled water.

5.13 Fill a sample beaker with this solution.

5.14 Adjust the flame spectrophotometer in accordance with the manufacturer's directions.

a. Adjust the wavelengths to 768 nanometers.

b. Measure the flame background at this wavelength by aspirating a sample beaker of distilled water. If the flame background is greater than 1.5 transmission dial units, adjust the fuel pressure until a satisfactory flame background is obtained.

5.15 Place the sample beaker with the propellant solution in the sample positioner, and move the beaker under the capillary of the aspirator-burner by rotating the sample positioner knob.

5.16 Record the transmission of the sample. Before and after each reading, aspirate distilled water through the atomizer burner to prevent clogging.

5.17 Place the beaker containing the solution having a lower concentration of potassium than the propellant solution in the spectrophotometer. Obtain a reading for this solution and record it.

5.18 Obtain a reading for the solution having a higher concentration of potassium than the propellant solution and record it.

5.19 Prepare an intensity concentration graph on linear graph paper as follows:

a. Plot the potassium concentration of the two standard solutions in ppm against the transmission readings obtained for each solution.

b. Draw a straight line between the two points.

5.20 Using the transmission reading obtained for the specimen, read on the chart the potassium content of the propellant in ppm.

5.21 Calculate the potassium salt content of the propellant.

5.22 **Calculations:**

$$\text{Percent potassium nitrate} = \frac{0.02586A}{W}$$

$$\text{Percent potassium sulfate} = \frac{0.02229A}{W}$$

Where:

A = Potassium content of the propellant solution in ppm.

W = Weight of specimen, corrected for total volatiles, g.

METHOD 310.4.2

POTASSIUM SALTS (TETRAPHENYLBORON METHOD)

1. SCOPE

1.1 This method is used for determining the potassium sulfate or potassium nitrate content in propellants.

2. SPECIMEN

2.1 The speciman shall consist of a portion of the propellant containing approximately 75 mg of potassium salt (as determined from the detail specification for the propellant being tested). Weigh the specimen to within 0.2 mg.

3. APPARATUS

3.1 Beaker, 150 ml.

3.2 Beaker, 250 ml.

3.3 Watchglass, ribbed.

3.4 Steam bath.

3.5 Filter paper, Whatman No. 41 or equivalent.

3.6 Filtering crucible, glass, medium porosity.

3.7 Porcelain evaporating dish.

3.8 Suction filtration apparatus with provision for filtration rate adjustment.

3.9 Desiccator, containing an indicating desiccant.

4. MATERIALS

4.1 Aluminum chloride, 0.2M solution (5 g per 100 ml distilled water).

4.2 Sodium tetraphenylboron, 3% solution, prepared as follows:

a. Dissolve 9 g of sodium tetraphenylboron in 300 ml of distilled water.

b. Add 2 ml of 0.2 M aluminum chloride solution, stir, and allow to stand for 30 minutes.

c. After 30 minutes, filter the solution into a polyethylene or borosilicate glass bottle.

NOTE: On prolonged standing, the solution may become turbid. If it does, refilter before using.

4.3 Nitric acid, 70 percent solution.

4.4 Hydrochloric acid, 36-38 percent solution.

4.5 Sulfuric acid, 5 percent solution. Add 5 ml of sulfuric acid (96-98%) to 95 ml of distilled water and stir well.

5. PROCEDURE

5.1 Prepare the specimen as described in Method 509.3.

5.2 Transfer the accurately weighed specimen to a porcelain evaporating dish. Add 10-15 ml of nitric acid and cover the dish with a watchglass. In a hood, heat the dish and contents on a steam bath until the reaction starts; (CAUTION: This is an exothermic reaction) then remove the dish from the steam bath and allow it to stand until the evolution of fumes has ceased and only a gummy residue remains. If decomposition is incomplete, wash down the inner walls of the evaporating dish with nitric acid and reheat until decomposition is complete.

5.3 Remove the watchglass and wipe the underside with small pieces of damp, ashless filter paper and add these to the dish. Dry the gummy residue until only a fluffy carbonaceous deposit remains. Then heat until the carbonaceous residue is nearly burned off. (Avoid high temperatures in order to prevent fusion of the salts in the dish.)

5.4 If the propellant contains no barium salts, proceed to paragraph 5.5. If the propellant contains barium salts proceed as follows:

a. Cool the evaporating dish and contents to room temperature, rinse the inner walls with 5 ml of distilled water, and then with 5 ml of the hydrochloric acid solution. Cover the dish with a watchglass and heat the dish and contents on a steam bath for five to ten minutes.

b. Dilute the contents of the dish to approximately 25 ml with distilled water, and filter the solution through No.41 Whatman filter paper, or equivalent, into a 150 ml beaker. Wash the residue in the filter with about 50 ml of distilled water.

c. Heat the beaker and contents on a steam bath to about 95°C; then add, while stirring, 10 ml of the 5% sulfuric acid solution. Allow the solution to digest on the steam bath for one hour. Filter the solution through a filtering crucible into a 250 ml beaker, and then wash the precipitate with distilled water.

d. Heat the beaker containing the filtrate and washings and evaporate the filtrate to dryness, or until fumes of sulfur trioxide are no longer evolved.

5.5 Cool the evaporating dish and contents to room temperature. Dilute the contents of the dish to approximately 25 ml with distilled water, and filter the solution quantitatively through No. 41 Whatman filter paper, or equivalent, into a 250 ml beaker. Wash the residue in the filter with about 50 ml of distilled water and catch the washings in the beaker.

5.6 Add to the residue in the beaker, 100 ml of distilled water and 5 to 6 drops of the aluminum chloride solution. Stir the solution vigorously while adding to it about 20 ml of the sodium tetraphenlyboron solution. Allow the precipitate to settle for 5 minutes.

5.7 Filter the solution through the tared medium porosity glass filtering crucible with the aid of a suction filtration apparatus, being careful to keep a continuous flow of solution and subsequent washings (see 5.8) through the filter until washing is complete.

NOTE: The rate of filtration may be controlled by manipulating the stopcock in the suction line.

5.8 Rinse the beaker with five 20 ml portions of distilled water and pour each through the filtering crucible.

5.9 When the solution and washings have passed through the filter, dry the crucible and contents at 120 ± 2°C for 30 minutes and cool to room temperature in a desiccator.

5.10 Weigh the crucible and calculate the potassium salt content of the propellant.

5.11 **Calculations:**

$$\text{Percent potassium nitrate} = \frac{28.22\ (W_3 - W_2)}{W_1}$$

$$\text{Percent potassium sulfate} = \frac{24.32\ (W_3 - W_2)}{W_1}$$

Where:

W_1 = Weight of sample, corrected for total volatiles, g.

W_2 = Weight of empty crucible, g.

W_3 = Weight of crucible and dried precipitate, g.

METHOD 311.1.3

TOTAL LEAD (SULFATE METHOD)

1. SCOPE

1.1 This method is used for determining the percent total lead and percent lead compound in propellants containing no ions that form insoluble sulfates.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5 g of the propellant weighed to within 0.1 mg.

3. APPARATUS

3.1 Beaker (low form) 250 ml.

3.2 Watchglass, ribbed.

3.3 Hotplate in a well ventilated hood.

3.4 Steam bath.

3.5 Filtering chemical porcelain, porous bottom of desired porosity.

3.6 Suction filtration apparatus.

3.7 Muffle furnace.

3.8 Desiccator containing an indicating desiccant.

4. MATERIALS

4.1 Nitric acid, 70 percent

4.2 Sulfuric acid, 95 to 96 percent.

4.3 Sulfuric acid, 3N solution. (1 vol of acid to 18 vols. of aqueous solution, or 55 ml of acid per liter of aqueous solution).

4.4 Glacial acetic acid.

4.5 1:1 sulfuric acid.

4.6 Acetone.

4.7 Ethyl alcohol or isopropyl alcohol, 50 percent aqueous solution.

4.8 Ethyl alcohol, 95 percent.

5. **PROCEDURE**

5.1 Place the specimen in the low form beaker; add 10 ml of nitric acid solution and 5 ml of 95 percent sulfuric acid solution. Cover the beaker with the watchglass.

5.2 Heat on the steam bath until the specimen is completely dissolved.

5.3 Remove the beaker from the steam bath, and add 5 ml of nitric acid.

5.4 Heat the beaker on the hotplate until dense fumes of sulfur trioxide are evolved.

5.5 Add more nitric acid, drop by drop, until all carbonaceous matter has been decomposed, and solution remains clear on continued heating. Then cool to room temperature.

5.6 Slowly add 50 ml of distilled water, using some of the water to wash down the watchglass and the sides of the beaker (If the water is added too rapidly, excess bubbling may result).

5.7 Boil the solution vigorously for 2 to 3 minutes. Then cool to room temperature, and dilute with 15 ml of the 95 percent ethyl alcohol. Allow the solution to stand at room temperature for 2 hours.

5.8 Filter the solution through the tared filtering crucible with the aid of suction. Use five 15 to 20 ml portions of the 3N sulfuric acid solution to complete the transfer of the lead sulfate precipitate from the beaker to the crucible.

5.9 Wash the precipitate in the crucible first with two portions of 50 percent ethyl or isopropyl alcohol, then with one portion of 95 percent ethyl alcohol.

5.10 Aspirate the crucible for five minutes, then dry for 15 to 30 minutes at 110°C.

5.11 Ignite the crucible in the muffle furnace for 15 minutes at 500 to 600°C, then cool to room temperature in the desiccator.

5.12 Weigh the crucible, and calculate the percentage of lead compound in the propellant

5.13 **Calculations:**

$$\text{Percent lead compound} = \frac{100AB}{nCW}$$

$$\text{Percent total lead} = \frac{68.32A}{W}$$

Where:

A = Increase in weight of crucible, grams (weight of lead sulfate precipitate).

B = Molecular weight of lead compound in the propellant.

C = Molecular weight of lead sulfate.

W = Weight of specimen, corrected for total volatiles, grams.

n = Number of lead atoms in compound.

NOTE: Percent total volatiles may be determined on a separate sample by Method 103.3.3.

6. ALTERNATE PROCEDURE

6.1 Place the specimen in the 250 ml beaker, add 20 ml acetic acid and 70 ml of nitric acid. Cover the beaker with the watchglass.

6.2 Heat on steam bath until the sample is in solution (1/2 hour).

6.3 Remove the beaker from the steam bath and add 20 ml of 1:1 sulfuric acid.

6.4 Cover the beaker with the watchglass and heat on the hot plate until all but traces of the nitric acid have been expelled.

6.6 Remove the beaker from the hot plate, cool a few minutes and then add 1:1 ethyl alcohol dropwise until the vigorous reaction subsides.

6.6 Add 50 ml of 1:1 ethyl or isopropyl alcohol and heat on the steam bath for 10 minutes.

6.7 Cool and let the solution stand for 2 hours.

6.8 Filter through a tared medium porosity Selas or equivalent filtering crucible.

6.9 Wash the precipitate with acetone and aspirate the crucible for five minutes.

6.10 Ignite the crucible in the muffle furnace at 600°C for 1/2 hour, then cool to room temperature in the desiccator.

6.11 Weigh the crucible, and calculate the percentage of lead compound in the propellant.

6.12 **Calculation:**

$$\text{Percent lead compound} = \frac{100AB}{nCW}$$

Where:

A = Increase in weight of crucible (weight of lead sulfate percipitate).

B = Molecular weight of lead compound in the propellant.

C = Molecular weight of lead sulfate.

W = Weight of specimen, corrected for total volatiles.

n = Number of lead atoms in compound.

METHOD 311.2.2

TOTAL LEAD (CHROMATE METHOD)

1. SCOPE

1.1 This method is used for determining the percentage of total lead and the percentage of lead compunds in propellants containing no ions that form insoluble chromates.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5 g of the propellant, weighed to within 0.2 mg.

3. APPARATUS

3.1 Beakers, 250 ml

3.2 Watchglass, ribbed.

3.3 Steam bath.

3.4 Hotplate in a well-ventilated hood.

3.5 Filter paper, Whatman No. 41, or equivalent.

3.6 Filtering crucible, glass medium porosity.

3.7 Oven.

3.8 Desiccator containing an indicating desiccant.

4. MATERIALS

4.1 Nitric acid, 70 percent.

4.2 Sulfuric acid, approximately 95 percent.

4.3 Ammonium acetate 20% solution.

4.4 Potassium Dichromate 10% solution.

4.5 Glacial acetic acid.

5. PROCEDURE

5.1 Prepare the specimen as prescribed in Method 509.3

5.2 Place the specimen in the beaker and add 10 ml of the nitric acid and 5 ml of the sulfuric acid.

5.3 Heat on the steam bath until the specimen is completely dissolved.

5.4 Remove the beaker from the steam bath, and add 5ml of nitric acid.

5.5 Heat the beaker on the hotplate until dense fumes of sulfur trioxide are evolved.

5.6 Add more 70 percent nitric acid, drop by drop, until all carbonaceous matter has decomposed.

5.7 Remove the beaker from the hotplate, and cool to room temperature. Wash down the sides of the beaker with a fine stream of distilled water.

5.8 Return the beaker to the hotplate, and heat until the sulfur trioxide fumes cease. Then remove the beaker from the hotplate, and cool it to room temperature.

5.9 Add 30 ml of hot 20 percent ammonium acetate solution to the beaker. Stir, until the soluble portion of the residue in the beaker has dissolved.

5.10 Filter the solution through No. 41 Whatman filter paper into another 250 ml beaker. Wash the beaker and filter paper first with 20 ml of the hot ammonium acetate solution and then with three portions of distilled water.

5.11 To the filtrate and washings add 5 ml of glacial acetic; place the beaker on the hotplate and heat to boiling.

5.12 To the boiling solution add 20 ml of the 10 percent solution of potassium dichromate. Allow the solution to boil 5 minutes longer.

5.13 Remove the beaker from the hotplate and allow the lead chromate precipitate to settle for one hour.

5.14 Filter the contents of the beaker through the tared filtering crucible. Wash the retained precipitate with five portions of hot distilled water.

5.15 Dry the crucible in an oven 100 to 105°C until loss of weight between weighings at two hour intervals does not exceed 0.5 mg. Cool the crucible in a desiccator between weighings.

5.16 Weigh the crucible, and calculate the percentage of total lead or the percentage of lead compound in the propellant.

5.17 **Calculation:**

$$\text{Percent total lead} = \frac{64.11\,A}{W}$$

$$\text{Percent lead compound} = \frac{100AB}{nCW}$$

Where:

A = Increase in weight of crucible (weight of lead chromate precipitate).
B = Molecular weight of lead compound.
C = Molecular weight of lead chromae.
W = Weight of specimen, corrected for total volatiles.
n = Number of lead atoms in compound.

METHOD 311.3.2

TOTAL LEAD (POLAROGRAPHIC METHOD)

1. SCOPE

1.1 This method is used for determining polarographically the percentage of lead compounds in propellants.

2. SPECIMEN

2.1 The specimen shall consist of a portion of the propellant containing 10 to 15 mg of lead (as determined from the detailed specification for the propellant being tested.) Weigh the specimen to within 0.2 mg.

3. APPARATUS

3.1 Beaker, 250 ml.

3.2 Watchglass, ribbed.

3.3 Steam bath in a well ventilated hood.

3.4 Funnel, Buchner, glass with fritted disc, medium porosity.

3.5 Suction filtration apparatus.

3.6 Volumetric flask, 100 ml.

3.7 Recording polarograph (Sargent Model XXI, or equivalent).

3.8 Polarograph cell, dropping mercury electrode, in constant temperature bath maintained within 0.5°C of room (or any convenient) temperature.

4. MATERIALS

4.1 Lead nitrate solution consisting of 0.400 g of lead nitrate (ground with mortar and pestle, and dried at 100°C for 2 hours) per 250 ml of solution with 2N sodium acetate (para. 4.2).

NOTE: One ml of this solution contains 1.0 mg of lead.

4.2 Sodium acetate, 2N solution, consisting of 164 g of anhydrous sodium acetate per liter of solution.

4.3 Nitric acid, 70 percent.

4.4 Sulfuric acid, 50 percent solution.

4.5 Isopropanol.

4.6 Ethyl alcohol, 50 percent

4.7 Acetone.

4.8 Nitrogen prepurified (oxygen free) passed through water.

5. PROCEDURE

5.1 Prepare a standard graph of wave height in millimeters against concentration of lead in grams per 100 liters as follows:

a. Into three dry 100 ml volumetric flasks, pipette 10, 15, and 20 ml respectively, of lead nitrate solution (para 4.1) and then bring to the mark with 2N sodium acetate solution.

b. Tranfer each solution to a polarographic cell, and obtain a polarogram for each, as described in paragraph 5.3. In addition obtain a polarogram of the 2N sodium acetate solution used to prepare the calibrants.

c. On linear graph paper, plot the wave height in millimeters against the weight of lead in grams (0,0.010, 0.015, and 0.020 g/100 ml).

d. Draw the straight line which most nearly approximates the values obtained.

NOTE: This graph is valid only when the determination is made with the same capillary as that used in preparing the graph, and so long as the capillary characteristic of the dropping mercury electrode remains constant. The capillary characteristic of the electrode should therefore be checked at the time the graph is made, and rechecked at intervals of about a month. If the characteristic changes by more than 0.05 units from the original value, a new capillary should be selected and a new graph prepared.

5.2 Prepare the specimen for polarographing as follows:

a. Prepare the specimen as prescribed in Method 509.3.

b. Place the specimen in the 250ml beaker, and add 2 ml of the 70 percent nitric acid per gram of specimen (10 ml minimum).

c. Cover the beaker with a ribbed watchglass, and heat on the steam bath for 30 minutes.

d. Remove the beaker from the steam bath, and add 20 ml of the 50 percent sulfuric acid.

e. Cover the beaker with the ribbed watchglass, and set it about half way down into the steam bath for approximately 1 hour.

NOTE: A rubber ring around the beaker will facilitate positioning it in the steam bath.

f. Remove the beaker from the steam bath, and add isopropanol, with CAUTION drop by drop, to remove all traces of nitric acid.

NOTE: Normally 10 to 15 drops of isopropanol are sufficient.

g. When the reaction ceases, add 100 ml of 50 percent ethyl alcohol, and heat on the steam bath for 10 minutes. Remove from the steam bath and allow the lead sulfate precipitate to settle.

h. Filter the liquid in the beaker through the fritted disc glass funnel with the aid of the suction filtration apparatus; retain the bulk of the precipitate in the 250 ml beaker.

i. Add approximately 20 ml of acetone to the beaker to dissolve all organic matter.

NOTE: If necessary, warm the beaker for a few minutes on the steam bath to complete solution of organic matter.

j. *Quantitatively transfer the precipitate to the fritted glass funnel;* wash the precipitate with three 10 ml portions of acetone and two 10 ml portions of 50 percent ethyl alcohol.

k. When all of the acetone and ethyl alcohol have passed through the funnel disconnect the suction and place a clean receiving beaker in the suction filtration apparatus.

l. With the suction off, add approximately 10 ml of 2N sodium acetate to the funnel. Stir gently to facilitate dissolving the lead sulfate precipitate, then turn the suction back on. Pass 3 to 4 more 10 ml portions of 2N sodium acetate solution through the funnel to ensure complete solution of the precipitate.

m. Transfer the filtrate to a 100 ml volumetric flask, and dilute to the mark with 2N sodium acetate solution.

n. Pour an accurately measured portion of the solution into a polarographic cell.

5.3 Obtain a polarogram for the solution as follows:

a. Place the cell in the constant temperature bath (para 3.8)

b. Flush nitrogen through the solution for 5 to 10 minutes. Thereafter allow the gas to flow over the solution.

c. At an applied voltage of -0.2, adjust the recorder pen of the polarograph near zero. Obtain a polarogram for the -0.2, to -0.8 volt range at an appropriate sensitivity.

d. Produce a second polarogram from the same solution, and find the average wave height for the two polarograms.

5.4 Using the average of the two polargrams obtained for the propellant, read the amount of lead present in the solution from the standard graph.

5.5 Calculate the percentage of lead compound in the propellant.

5.6 **Calculation:**

$$\text{Percent lead compound} = \frac{100\,AB}{CWn}$$

Where:

A = Weight of lead, as obtained from standard graph, g.
B = Molecular weight of lead compound.
C = Atomic weight of lead.
W = Weight of specimen, corrected for total volatiles, g.
n = Number of lead atoms in the compound.

METHOD 311.4

TOTAL LEAD (MOLYBDATE METHOD)

1. SCOPE

1.1 This method is used for determining the percentage of lead compounds in propellants.

2. SPECIMEN

2.1 The specimen shall consist of a portion of the propellant containing at least 0.05 g of lead (as determined from the detailed specifications for the propellant being tested). Weigh the specimen to within 0.2mg.

3. APPARATUS

3.1 Boiling flask, round bottom, 200 ml.

3.2 Reflux condenser, water cooled.

3.3 Heating mantle, standard laboratory type.

3.4 Filter paper, Whatman No. 41 or equivalent.

3.5 Beaker, 500 or 600 ml.

3.6 Hotplate.

3.7 Filtering, chemical porcelain, porous bottom, medium porosity and ignited at 900°C.

3.8 Muffle furnace.

3.9 Suction filtration apparatus.

4. MATERIALS

4.1 Nitric acid, 50 percent (by volume) solution.

4.2 Ammonium cetate.

4.3 Ammonium molybdate, 5 percent solution, with 10 ml of glacial acetic acid per liter.

4.4 Ammonium nitrate, 2 percent solution.

4.5 Ammonium hydroxide.

5. PROCEDURE

5.1 Place the specimen in the round bottom flask, and add 30 ml of the 50 percent nitric acid solution.

5.2 Attach the condenser to the flask, and bring the contents of the flask to a boil by means of the heating mantle. Allow the contents of the flask to boil for 30 minutes.

5.3 Disconnect the heating mantle and condenser, and add 50 ml of distilled water to the flask. Reconnect the condenser, and boil for an additional 45 minutes.

5.4 Filter the solution in the flask through the No. 41 Whatman filter paper into the 500 or 600 ml beaker.

5.5 Add 30 g of ammonium acetate and adjust the pH of the solution to 6.5 ± 0.5 with ammonium hydroxide.

NOTE: Approximately 15 ml of ammonium hydroxide is usually required to achieve the proper pH.

5.6 Add 25 ml of the ammonium molybdate solution, and boil the solution for approximately 3 minutes. Cool to room temperature, and allow the lead molybdate precipitate to settle.

5.7 Filter the contents of the beaker through the tared Gooch crucible with the aid of suction. Wash the beaker and precipitate with approximately 100 ml of hot 2 percent ammonium nitrate solution.

5.8 Ignite the crucible at 900°C in a muffle furnace. Cool to room temperature.

5.9 Weigh the crucible, and calculate the percentage of lead compound in the propellant.

5.10 **Calculation:**

$$\text{Percent lead compound} = \frac{100AB}{nCW}$$

Where:

A = Increase in weight of crucible (weight of lead molybdate precipitate).

B = Molecular weight of lead compound.

C = Molecular weight of lead molybdate.

W = Weight of specimen, corrected for total volatiles.

n = Numer of lead atoms in compound.

METHOD 311.5.1

LEAD (ATOMIC ABSORPTION)

1. SCOPE

1.1 This is a general method to determine lead salts in propellants containing lead concentrations of 0.2 percent or greater. It measures the lead content in parts per million (ppm) and converts this value to a percentage of lead salt.

2. SPECIMEN

2.1 The specimen should be large enough to contain 4 - 5 mg of lead. Large grains or sheets shall be cut or sliced as in method 509.3. The specimen shall be weighed within 0.2 mg in a 100 ml volumetric flask. If necessary, the specimen can be weighed into a 100 ml tall form beaker.

NOTE: Do not use a specimen larger than 2.0 grams.

3. APPARATUS

3.1 Atomic absorption spectrophotometer with lead hollow cathode tube.

3.2 Volumetric flasks, 100, 250, l000ml.

3.3 Steam bath in a ventilated hood.

3.4 Hot plate in a ventilated hood.

3.5 Pipettes 3, 4, 5, and 6 ml.

3.6 Beakers, 100 ml, tall form, graduated (if needed).

4. MATERIALS

4.1 A stock solution of lead perchlorate is prepared by dissolving 250 mg of lead metal in 5 ml of concentrated perchloric acid in a 250 ml volumetric flask. After warming the contents of the flask slightly to insure all the lead dissolves, cool the resulting solution thoroughly and dilute to the mark with methanol water solution.

4.2 Prepare a matrix solution of methanol water by first transferring 100 ml of distilled water into a 1000 ml volumetric flask. Dilute to the mark with methanol and mix well.

NOTE: Prepare enough methanol water solution to cover that which is needed for the specimens, standards and blanks.

4.3 Nitric acid, 70 percent.

4.4 Perchloric acid, 70 percent.

4.5 Methanol, reagent grade.

5. **PROCEDURE**

5.1 Add to the specimen in a 100 ml volumetric flask (or in 100 ml beaker if this was used), 20 ml of 70 percent nitric acid. Cover with a watch glass if a beaker was used.

5.2 Heat on a ventilated steam bath until the specimen is completely dissolved.

5.3 After the specimen is dissolved, heat slowly to the boiling point. Boil for about 10 minutes or until the evolution of brown fumes ceases.

NOTE: Using a volumetric flask for boiling small specimens is very convenient and avoids any loss of specimen due to splattering. However, the flasks do undergo some small distortion after being heated. A set of flasks should be set aside for such purposes.

5.4 Remove the specimen from the hot plate, cool thoroughly, and add 2 ml of 70 percent perchloric acid.

NOTE: The amount of 70 percent perchloric acid to be added depends on the specimen weight. The amount of acid to be added is as follows: 0.5 g of specimen or less, add 2 ml, 0.5 to 1.0 g of specimen, add 3 ml, 1.0 to 2.0 g of specimen, add 5 ml.

NOTE: Perchloric acid can be used safely as specified in this procedure. It should not, however, be brought in contact with finely divided aluminum silicon, and easily oxidizable organic matter. The hood where the specimen solution is heated should be thoroughly free from organic materials and should be cleaned after use. Also, do not allow specimens being heated with perchloric acid to go to dryness.

5.5 Return the specimen to the hot plate and heat to white fumes of perchloric acid (nitric acid is gone).

5.6 Cool the sample thoroughly, dilute to the mark with methanol water solution, and mix well.

NOTE: If a beaker was used, transfer the residue with methanol water solution to a 100 ml volumetric flask and then dilute to the mark with methanol water solution. If the specimen contains graphite or carbon black, the solutions will have to be filtered.

5.7 Prepare working standards by pipetting successively 3, 4, 5 and 6 ml of the standard lead perchlorate solution into a series of four 100 ml volumetric flasks. Add to each flask as much 70 percent perchloric acid as was added to the specimen flask. Immediately dilute to the mark with methanol water solution. This will give standards of 30, 40, 50 and 60 ppm of lead.

5.8 Prepare a blank in a 100 ml volumetric flask. Use as much 70 percent perchloric acid as was needed for the specimen and dilute to the mark with methanol water solution.

5.9 The blank, specimen and standard are then analyzed by atomic absorption (following instrument instruction manual and standard safety procedures) using either the 2170 or 2833 Angstrom analytical wavelengths. Use air as the oxidizer and hydrogen as the fuel.

5.10 Obtain the absorbance of the standard and specimen as follows:

a. Convert absorption to transmittance by subtracting the absorption from 100.

b. Change transmittance to absorbance.

c. Subtract any absorbance due to the blank from each of the standards and from the specimen.

5.11 On linear graph paper plot absorbance versus concentration (ppm) for the standards. From the resulting curve (which should be linear or nearly linear) determine the concentration of the lead salt in the specimen.

5.12 Calculate the lead content of the propellant and the lead salt content.

5.13 **Calculations:**

$$\text{Percent Lead} = \frac{A}{100\ W}$$

Where:

A = Lead content of the propellant specimen solution in parts per million.

W = Weight of the specimen in grams, corrected for total volatiles.

Percent Lead Salt = Percent Lead x G

Where:

G = Gravimetric factor of the salt.

METHOD 312.1.1

MAGNESIUM SALTS (FLAME SPECTROPHOTOMETRIC METHOD)

1. SCOPE

1.1 This method is used for determining the magnesium salt content (as an approximately 1 percent impurity) in the potassium perchlorate used in M7 propellant. It measures the magnesium content in parts per million (ppm), and converts this value to percentage of magnesium salts.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5.0 g of the propellant, weighed to within 0.2 mg.

3. APPARATUS

3.1 Flame spectrophotometer (Beckman Instruments, Inc., Model DU with Flame Attachment, Model 9200, and Regulator, Model 9200, or equivalent).

3.2 Beaker, 250 ml.

3.3 Volumetric flask, 2 liter.

3.4 Volumetric flasks, 1 liter.

3.5 Buret, 50 ml.

3.6 Volumetric flask, 500 ml

3.7 Beaker, 150 ml.

3.8 Cover glass, ribbed.

3.9 Steam bath in a well ventilated hood.

3.10 Hotplate.

3.11 Volumetric flask, 100 ml.

4. MATERIALS

4.1 Master magnesium solution containing 486.5 ppm magnesium, prepared as follows:

a. Quantitatively transfer 0.973 g of magnesium metal to a 250 ml beaker, and add 50 ml of distilled water.

b. Add a few drops of 50 percent (1:1) sulfuric acid solution. Wait until the reaction caused by these first drops has ended, then continue to add the sulfuric acid solution dropwise until no further reaction occurs.

c. Quantitatively transfer this solution to a 2 liter volumetric flask, and dilute to the mark with distilled water.

4.2 Standard magnesium solution, 12.17 ppm, prepared as follows: Quantitatively transfer 3.861 g of potassium perchlorate to a 1 liter volumetric flask, and using a 50 ml buret, quantitatively add 25.0 ml of the master magnesium solution. Dilute to the mark with distilled water, and mix thorougly.

4.3 Standard magnesium solution, 12.95 ppm, prepared as follows: Quantitatively transfer 3.861 g of potassium perchlorate to a 1 liter volumetric flask, and using the 50 ml buret, quantitatively add 26.66 ml of the master magnesium solution. Dilute to the mark with distilled water and mix thoroughly.

4.4 Magnesium calibrating solution, prepared as follows: Transfer 25 ml of master magnesium solution to a 500 ml volumetric flask. Dilute to the mark and mix thoroughly.

4.5 Nitric acid, 70 percent solution.

4.6 Sulfuric acid, concentrated.

5. PROCEDURE

5.1 Prepare the specimen as specified in Method 509.3.

5.2 Place the specimen in a 150 ml beaker, and add 30 ml of 70 percent nitric acid and 2 ml of concentrated sulfuric acid. Cover with a ribbed cover glass.

5.3 Heat the beaker on a steam bath until the specimen is dissolved.

NOTE: If graphite or carbon black, or both, are present, they will not dissolve at this time.

5.4 Transfer the beaker to a hotplate, and heat gently until dense fumes of sulfur trioxide are evolved.

5.5 Add more 70 percent nitric acid drop by drop, until all carbonaceous matter has disappeared.

5.6 Remove the beaker from the hotplate, and cool to room temperature. Wash down the cover glass and the sides of the beaker with a fine stream of distilled water.

5.7 Return the beaker to the hotplate. After the sulfur trioxide fumes reappear, continue to heat the solution for 5 minutes.

NOTE: If a black residue starts to form on the bottom of the beaker, or if the solution darkens appreciably, add more nitric acid, drop by drop, until the solution is clear. It will be either colorless or strawcolored.

5.8 At the end of 5 minutes, remove the beaker from the hotplate and cool to room temperature.

5.9 Quantitatively transfer the solution to a 100 ml volumetric flask, dilute to the mark with distilled water, and mix thoroughly.

5.10 Fill a 5 ml sample beaker with this solution.

5.11 Fill similar sample beakers with the standard magnesium solutions, 12.17 ppm and 12.95 ppm (see paras 4.2 and 4.3).

5.12 Adjust the flame spectrophotometer as follows:

NOTE: The details concerning instrumentation given here apply to the Beckman spectrophotometer (para 3.1). If a different flame spectrophotometer is used, follow the manufacturer's instructions.

a. Adjust the oxygen pressure for the specific atomizer burner being used; adjust the acetylene pressure to 4 ± 1 psi; light the burner.

NOTE: 1 psi = 6.9 kPa

b. Set the phototube load resistor switch in the number 3 position (incorporating a 10,000 megohm resistor in the circuit).

c. Set the selector switch at 0.1.

d. Set the sensitivity control at one half turn from its counterclock wise limit.

e. Pull the phototube selector knob so that the blue sensitive phototube is in position.

f. With shutter closed, rotate the dark current control to zero the meter needle.

g. Adjust the wavelength setting to 371 nanometer and the slit to approximately 0.2 mm.

Note: To adjust the wavelength setting accurately, aspirate the magnesium calibrating solution (para 4.4) into the flame, open the shutter, and readjust the wavelength dial until the maximum reading is obtained on the transmission dial with the meter needle at zero.

h. Close the shutter, and check the meter needle. If it is more than 0.2 divisions away from zero, rotate the dark current control until it is back to zero.

NOTE: The meter needle should be similarly checked, and if necessary, reset before and after each subsequent reading.

5.13 Place the sample beaker containing the propellant solution in the sample positioner, and move the beaker under the capillary of the aspirator burner by rotating the sample positioner knob.

NOTE: When correctly positioned, the beaker will be tilted, and the capillary tube will project into its lowest corner. The capillary tube should not touch the beaker; if it does, bend the sample positioner to correct the condition.

5.14 Open the shutter of the spectrophotometer and adjust the transmission dial until the meter is at zero. Record the transmission dial reading.

NOTE: After each reading, aspirate a small quantity of distilled - water through the atomizer burner to prevent clogging.

5.15 Place the beaker containing the 12.17 ppm standard magnesium solution in the spectrophotometer. Readjust the sensitivity and slit width, if necessary, to obtain a transmission dial

reading of 50 ± 5 when the 12.17 ppm magnesium solution is being aspirated into the flame, and record this reading.

5.16 Obtain a reading for the 12.95 standard magnesium solution and record it.

5.17 Prepare an intensity concentration graph on linear graph paper as follows:

a. Plot the magnesium concentrations of the two standard solutions in ppm against the transmission dial readings obtained for each solution.

b. Draw a straight line between the two points.

5.18 Using the transmission dial reading obtained for the specimen, read on the graph the magnesium content of the propellant in ppm.

5.19 Calculate the magnesium salt content of the propellant.

5.20 **Calculation:**

Percent magnesium salts = 0.006208Y

Where:

Y = Magnesium content of specimen in ppm.

METHOD 313.1

INORGANIC NITRATE IN NITROCELLULOSE BASE PROPELLANTS (COLORIMETRIC METHOD)

1. SCOPE

1.1 This method is used for determining the potassium nitrate and barium nitrate content of nitrocellulose base propellants. Other inorganic nitrates, chlorates, nitroquanidine, RDX, and HMX interfere.

2. SPECIMEN

2.1 The specimen shall consist of approximately 0.3 or 0.5 g of the propellant, weighed to within 0.2 mg. No special preparation of the specimen is necessary.

3. APPARATUS

3.1 Beakers, 250ml.

3.2 Pipets.

3.3 Cylinder, graduate, 10 ml.

3.4 Volumetric flasks, 25 ml, 250 ml, and 1 liter.

3.5 Erlenmeyer flask with ground glass stopper, 125 ml.

3.6 Oven.

3.7 Filtering crucible, glass, fritted disc, fine porosity, 30 ml capacity.

3.8 Suction flasks, 250 ml, and 500 ml.

3.9 Safety trap for suction flask.

3.10 Filter paper, 14 cm, Whatman No. 42 or equivalent.

3.11 Funnel.

3.12 Hot plate.

3.13 Spectrophotometer (Beckman Instruments Inc., Model B; or equivalent).

4. MATERIALS

4.1 Potassium nitrate, dried for 2 hours at 135 to 150°C.

4.2 Standard potassium nitrate solution (1 ml - 0.10 mg of NO_3). Dissolve 0.1630 g of potassium nitrate in distilled water and dilute to 1 liter in a volumetric flask.

4.3 Sodium hydroxide, approximately 0.1 N solution. Dissolve 8.2 g of sodium hydroxide pellets (minimum 97 percent NaOH) in 2 liters of distilled water.

4.4 Sulfuric acid, 95 to 98 percent.

4.5 Sulfuric acid (10 to 3). Add 1000 ml of sulfuric acid to 300 ml of distilled water and cool to room temperature.

4.6 Ferrous sulfate solution. Dissolve 2 g of $FeSO_4 \cdot 7H_2O$ in 30 ml of distilled water containing a few drops of sulfuric acid. This sulfuric acid is necessary to prevent air-oxidation of the ferrous ion. Add 100 ml of sulfuric acid all at one time and cool to room temperature. Prepare fresh daily.

4.7 Acetone.

4.8 Acetone saturated with potassium nitrate. Grind potassium nitrate to a powder in a mortar, dry in an oven at 135 to 150°C., cool, place 5 g into a dry 2 liter bottle, add 2 liters of acetone, shake, and allow to stand overnight or longer. Filter through a dry 14 cm No. 42 Whatman Filter paper (do not tear the edges).

4.9 Filter aid. Diatomaceous earth reagent grade.

4.10 Wash diatomaceous earth with about 200 ml of distilled water and pour the suspension into a Buchner funnel. Filter with suction, and wash several times with distilled water and twice with acetone. Allow air to pass through the the diatomaceous earth for several minutes, transfer to a beaker, dry at 110 to 120°C for 2 or more hours and store in a stoppered bottle.

5. PROCEDURE

5.1 Prepare a calibration curve as follows:

a. Pipet 15, 30, and 45 ml aliquots of standard potassium nitrate solution into 250 ml beakers and add 1.5 ml of 0.1N sodium hydroxide solution. Carry along a reagent blank prepared by adding 1.5 ml of distilled water.

b. Evaporate to dryness on the hot plate.

c. Cool, add 3.0 ml of distilled water with a pipet, and swirl to dissolve the salts.

d. Cool to 10 to 15°C in an ice and water bath, add 10 ml of sulfuric acid by means of a 10 ml graduated cylinder and allow to stand in the ice and water bath for 5 minute.

e. Remove the beakers from the ice and water bath and add 10 ml of ferrous sulfate solution measured with a 10 ml graduate cylinder while swirling.

f. Adjust the temperature to 22 ± 2°C.

g. Decant into 25 ml volumetric flasks that have been rinsed with sulfuric acid (10 to 3) and wash the beakers with sufficient sulfuric acid (10 to 3) at 22 ± 2°C to bring the volumes in the volumetric flasks up to the mark.

h. Shake, and measure the absorbance in 10 minutes to 2 hours at 520 nanometers with a spectrophotometer that has been set to zero absorbance with the reagent blank contained in a cell similar to that containing the solution.

i. Plot mg of N03 against absorbance.

5.2 Dry a 125 ml Erlenmeyer flask with a ground glass stopper by heating at 110 to 120°C . Insert the stopper and allow to cool.

5.3 Transfer a weighed portion of the sample to the flask. For 0 to 0.4 percent NO_3 use a 0.5 mg sample, for more than 0.4 percent NO_3 use a 0.3 g sample. The NO_3 content of potassium and barium nitrates is 61.34 percent and 47.45 percent respectively.

5.4 Add 25 ml of acetone saturated with potassium nitrate, insert the stopper and allow to stand overnight at room temperature. Do not swirl during the solution process since this may cause particles of propellant to adhere to the sides of the flask. Carry along a blank through the entire procedure, including the overnight standing.

5.5 Add 0.2 g of the treated diatomaceous earth and swirl.

5.6 Place a glass filtering crucible into the 500 ml suction flask, and wash with water.

5.7 Fill the crucible with acetone and allow to drain.

5.8 Swirl the solution of the sample, filter, and wash the Erlenmeyer flask and filtering crucible with acetone (saturated with potassium nitrate) contained in a wash bottle.

5.9 Dry the outside of the crucible by rubbing with a cloth saturated with acetone.

5.10 Place the holder and filtering crucible into a clean 250 ml suction flask.

5.11 Add several portions of distilled water at 95 to 100°C to the original Erlenmeyer flask, transfer to the crucible, and filter. The total volume of water used should be 100 to 125 ml.

5.12 If less than 1.4 percent NO_3 is present, wash the filtrate into a 250 ml beaker. If more than 1.4 percent NO_3 is present, wash into a 250 ml volumetric flask, dilute to the mark, and pipet an aliquot containing 2.5 to 4.5 mg of NO_3 into a 250 ml beaker.

5.13 Add 1.5 ml of 0.1N sodium hydroxide solution.

5.14 Proceed as described in 5.1 (b) to 5.1 (h). In making the readings, set the spectrophotometer to zero absorbance with the blank that has been carried through the entire procedure.

5.15 *Calculate the percent* NO_3.

5.16 **Calculation:**

$$\text{Percent } NO_3 = \frac{A}{10W}$$

Where:

A = Weight of NO_3 as read from curve, mg.

W = Weight of specimen, corrected for total volatiles, represented by aliquot taken, g.

5.18 Calculate the percent of the inorganic nitrate salt.

5.19 **Calculations:**

Percent potassium nitrate = 1.630 x percent NO_3

Percent barium nitrate = 2.108 x percent NO_3

5.20 For the determination of potassium and barium nitrates when both are present in the propellant, determine the NO_3 as described above, and then determine the barium nitrate by precipitating the barium as barium sulfate as specified in Method 304.1. Calculate the percent potassium nitrate.

5.21 **Calculation:**

Percent potassium nitrate = 1.630 (C – 0.4745 D)

Where:

C = Total percent NO_3.

D = Percent barium nitrate.

METHOD 314.1

ALUMINUM (GRAVIMETRIC METHOD)

1. SCOPE

1.1 Aluminum in casting powder or cast propellants is determined gravimetrically. Any other elements or compounds which are insoluble in the acetic acid-acetone mixture or in dimethyl formamide will interfere. Zirconium or zirconium oxide will remain with aluminum and additional steps will be necessary to effect further separation. Graphite or carbon black, if present in a propellant, will also interfere and it will be necessary to correct the aluminum value by subtracting the percent graphite or carbon black as found by independent testing. Graphite contents of 0.05 percent or less are not considered interferences.

1.2 standard deviation of this method between laboratories is 0.08 percent and within laboratories is 0.04 percent.

2. SPECIMEN

2.1 The specimen shall consist of 5 g of the propellant weighed to within 0.2 mg. Prepare the specimen as described in 509.3 if required.

3. APPARATUS

3.1 Beaker, 250 ml.

3.2 Stirring rod.

3.3 Watch glass.

3.4 Steam bath.

3.5 Filtering crucible, glass, fritted disc, medium porosity.

3.6 Oven.

3.7 Desiccator with desiccant.

4. MATERIALS

4.1 Dimethyl formamide.

4.2 Acetic acid-acetone solution prepared by mixing one volume glacial acetic acid, to two volumes of acetone.

5. PROCEDURE

5.1 Transfer the accurately weighed specimen to a 250 ml beaker.

5.2 Add approximately 50 ml of dimethyl formamide or 150 ml of the acetic acid-acetone solution to the beaker.

5.3 Insert a stirring rod into the beaker, cover with a watch glass and place it on a steam bath.

5.4 Digest on the steam bath with frequent stirring until the organic matter is dissolved.

5.5 Transfer beaker contents to a tared medium porosity, filtering crucible.

5.6 Wash the beaker and residue with approximately 25 ml of dimethyl formamide or acetic acid-acetone solution, and also transfer to tared crucible.

5.7 Wash the residue in the filtering crucible with approximately 20 ml of acetone.

5.8 Aspirate filtering crucible to remove all traces of acetone.

5.9 Dry in a 100 to 105°C oven for one hour.

5.10 Remove filtering crucible from oven, cool in a desiccator and weigh. Calculate the percent aluminum as follows:

5.11 **Calculations:**

$$\text{Percent aluminium} = \frac{(B - A) \times 100}{W}$$

Where:

B = Weight of crucible plus residue, g

A = Tare weight of crucible, g

W = Weight of sample, g

When it is known that other materials are present which are insoluble in the acetic acid-acetone mixture, corrections may be made as follows:

$$\text{Percent aluminum} = \frac{(B - A) \times 100}{W} - C$$

Where:

C = Percent of interfering materials present.

METHOD 315.1

ALUMINUM AND ZIRCONIUM

1. SCOPE

1.1 This method is used for the quantitative determination of aluminum and zirconium when they occur with each other. Aluminum and zirconium are determined together by a gravimetric method. After the aluminum and zirconium are weighed together, the aluminum is dissolved in sodium hydroxide solution and the zirconium is filtered off and weighed. The aluminum is determined by subtracting the percent zirconium from the combined percentages of aluminum zirconium. Limitation and Interferences. Any material which is insoluble in the solvent systems will interfere. Graphite will interfere and if present may be determined and an appropriate correction applied.

2. SPECIMEN

2.1 Solid cast propellants shall be comminuted by cutting, grinding, etc., to particles no larger than 1/8 inch on greatest dimension. Solid propellant shavings from a dry machined grain may be used directly for the determination.

3. MATERIALS.

3.1 Solvent.

3.1.1 Dimethyl formamide (DMF).

3.1.2 Acetone-acetic acid solution. (One (1) part of volume of acetic acid (glacial), to two (2) parts by volume of acetone).

3.2 Sodium hydroxide, 20% solution.

4. PROCEDURE

4.1 Weigh approximately 2 grams of sample to nearest 0.1 mg and tansfer to a 250 ml beaker.

4.2 Add 50 ml of DMF or 150 ml of acetone acetic acid solution to the beaker.

4.3 Insert a stirring rod in the beaker, cover with a watch glass, and place on steam bath.

4.4 Digest on the steam bath with frequent stirring until the organic material is dissolved.

4.5 Filter beaker contents through a tared Gooch crucible containing a fiber glass filter disc or a tared medium porosity filter crucible.

4.6 Wash beaker and residue with 25 ml of DMF or acetone-acetic acid solution depending upon which was originally used.

4.7 Give aluminum and zirconium powder or strands in the crucible a final wash with 50 ml acetone. Aspirate crucible with air to remove all traces of acetone.

4.8 Dry in a 100 to 105°C oven for one hour.

4.9 Remove crucible from oven, cool in a desiccator, and weigh. Record as weight "B".

4.10 The residue in the crucible (aluminum, zirconium, and any interfering materials) is quantitatively transferred to a 400 ml beaker with the aid of a water wash bottle.

4.11 Add 50 ml of 20% sodium hydroxide to the aluminum and zirconium in the beaker.

4.12 When the rate of reaction subsides, wash down the side of the beaker with a wash bottl

4.13 Place the beaker on a steam plate and heat until there is no further reaction.

4.14 Filter the contents of the beaker through a tared Gooch crucible containing a fiber glass disc or a tared medium porosity filtering crucible.

4.15 Wash beaker and residue thoroughly with water.

4.16 Dry crucible in a 100 to 105°C oven for one hour.

4.17 Remove crucible from oven, cool in a desiccator, weigh and record as weight "F".

4.18 **Calculations:**

a. Percent aluminum plus zirconium = $\frac{(B - A) \times 100}{W} - C$

Percent zirconium = $\frac{(F - E) \times 100}{W} - C$

Percent aluminum = $G - H$

B = Weight of crucible plus Al and Zr residue in grams

A = Tare weight of crucible in grams

W = Sample weight in grams

C = Percent of interfering materials present

F = Weight of crucible plus residue in grams (see 4.17)

E = Tare weight of crucible in grams

G = Percent of aluminum and zirconium

H = Percent zirconium

METHOD 316.1.1

METALS (ATOMIC ABSORPTION)

1. SCOPE

1.1 This method may be used for determining lead, barium, copper, potassium, sodium and other metal ions in most propellants. It is not suitable for formulations containing ions which form insoluble products, eg, barium in the presence of sulfate.

2. SPECIMEN

2.1 The specimen shall consist of sufficient propellant to contain approximately 15 mg lead (or 30 mg barium, 3 mg copper, 1.5 mg potassium, 0.8 mg sodium, or other ion as required.) The specimen shall be weighed to within + 0.2 mg.

NOTE: The specimen weights and concentrations of standards given here are guides to the analyst. Since the sensitivity of the instrument can be varied by such things as burner height, wavelength, burner selection, fuel system, etc, it may be necessary at times to use specimen weights and standard solution concentrations other than those specified.

3. APPARATUS

3.1 Flask, 125 or 250 ml to fit condensers.

3.2 Condensers, water cooled.

3.3 Volumetric flasks.

3.4 Atomic absorption spectrophotometer.

4. MATERIALS

4.1 Nitric acid, 1:1 by volume.

4.2 Standards containing 20 to 100 ppm lead, 50 to 200 ppm barium, 5 to 20 ppm copper, 2 to 8 ppm potassium, 1 to 4 ppm sodium, or other ions as required. Standards shall contain 4 ml 1:1 nitric acid/250 ml.

5. PROCEDURE

5.1 Place the specimen in a flask and add 4 ml 1:1 nitric acid from a pipet. Boil under a reflux condenser until the propellant is decomposed (15 to 45 minutes). Transfer to a 250 ml volumetric flask and dilute to the mark with water. Filter a portion of the solution through a dry filter paper if solid particles are present.

5.2 Determine the concentration of lead (or other cation) in the solution by running specimen and standards on the atomic absorption spectrophotometer in accordance with the manufacturer's instructions. If necessary, aspirate acetone occasionally to prevent buildup of organic material in the capillary.

NOTE: When the general method given in 5.1 is not applicable, use one of the following variations or any other suitable method of specimen dissolution. In ail cases prepare standards having the same solvent composition as the specimen.

Variations.

a. To remove all organic matter, digest the specimen with concentrated nitric acid, add 1 ml concentrated perchloric acid and heat on a hot plate (without condenser) until white fumes of perchloric acid are formed. Dilute as required.

NOTE: Use all proper safety precautions when using perchloric acid.

b. Dissolve the specimen (containing less than 150 mg nitrocellulose) in 15 ml dimethyl formamide in a 100 ml volumetric flask, add 1 ml 1N nitric acid and dilute to volume with methanol. Include nitrocellulose in standards.

c. For lead in the presence of sulfate, digest as in 5.1. After the specimen is decomposed add 175 ml water and 10 g ammonium chloride and boil under reflux for 15 minutes. Dilute to 250 ml and continue as usual. Add ammonium chloride to standards.

d. For specimens too large to digest as in 5.1, digest on a steam bath with the minimum volume of concentrated nitric acid (about 2 ml per gram) to speed the digestion. Add water and boil to dissolve residue. This method is not recommended for determining lead, which is partly converted to an insoluble form by concentrated nitric acid. The function of the condenser in 5.1 is control of the acid concentration.

METHOD 317.1.1

SODIUM, CALCIUM, BARIUM, AND POTASSIUM (ATOMIC ABSORPTION METHOD)

1. SCOPE

1.1 This method is used for determining the sodium, calcium, barium, and potasium content of propellants. The dilutions described are for the routine determination of salts in the following ranges: sodium sulfate, 0 to 0.10%; calcium carbonate, 0 to 1.25%; barium nitrate, 0.5 to 4.5%; potassium sulfate or nitrate, 0 to 1.5%. For higher precision work, the concentration of the sample solution should be such as to give an absorbance reading of preferably 0.2 to 0.5; also, the standards should closely bracket the sample.

2. SPECIMEN

2.1 The specimen shall consist of approximately 1.00 g of the propellant weighed to within 0.2 mg.

3. APPARATUS

3.1 Atomic absorption specrophotometer (Perkin-Elmer Model 303 atomic absorption spectrophotometer, or equivalent).

NOTE: The instrument settings recommended for the Perkin-Elmer Model 303 atomic absorption spectrophotometer are as follows:

Sodium - wavelength, 295; scale, 1: meter response, 1; range, visual; slit, 3 filter out; source, hollow cathode sodium lamp (15 mA) fuel, acetylene; full flow, 9.0; air flow, 9.0, (pressure at burner regulator should be 30 psig).

Calcium - wavelength, 212; scale, 1; meter response, 1; range, visual; slit, 4; filter, out; source, hollow cathode calcium lamp (15 mA); fuel, acetylene; fuel flow, 9.0 air flow, 9.0 (pressure at the burner regulator should be 30 psig).

Barium - wavelength, 277; scale, 5; meter response, 1; range, visual; slit, 3; filter, out; source, hollow cathode barium lamp (20 mA); fuel, acetylene; fuel flow, 9.0; air flow, 9.0 (pressure at burner regulator should be 30 psig).

Potassium - wavelength 383; scale, 1; meter response, 1; range, visual, slit, 4; filter, in; source, hollow cathode potassium lamp (26 mA); fuel, acetylene; fuel flow, 9.0; air flow, 9.0 (pressure at the burner regulator should be 30 psig).

NOTE: 1 psi = 6.9 kPa

3.2 Beakers, 150 ml.

3.3 Volumetric flasks, 100 ml.

3.4 Pipet, 20 ml.

4. MATERIALS

4.1 Hydrochloric acid, 38 percent.

4.2 Perchloric acid, 70 percent.

4.3 Nitric acid, 70 percent.

4.4 Sodium stock solution (0.05 mg of sodium per ml). Dissolve 0.1271 g of sodium chloride in water and dilute to 1 liter in a volumetric flask.

4.5 Calcium stock solution (0.5 mg of calcium per ml). Transfer 1.2490 g of calcium carbonate to a 250 ml beaker, add 150 ml of water and 5 ml of concentrated hydrochloric acid (slowly), warm until dissolved, cool, and dilute to 1 liter in a volumetric flask.

4.6 Barium stock solution (2.5 mg of barium per ml). Dissolve 4.7575 g of barium nitrate in water and dilute to 1 liter in a volumetric flask.

4.7 Potassium stock solution (0.15 mg of potassium per ml). Dissolve 0.2865 g of potassium chloride in water and dilute to 1 liter in a volumetric flask.

5. PROCEDURE

5.1 Prepare calibration curves for sodium, calcium, barium, and potassium as follows:

a. Sodium - Transfer 1.00, 2.00, 4.00 and 6.00 ml of sodium stock solution to 100 ml volumetric flask, and dilute to volume. This gives a range of 0.05, 0.10,. 0.20, and 0.30 mg of sodium per 100 ml. Perform the atomic absorption measurements and plot mg of sodium per 100 ml vs absorbance.

b. Calcium - Transfer 2.00, 5.00, 8.00 and 10.00 ml of calcium stock solution to 100 ml volumetric flasks and dilute to volume. This gives a range of 1.00, 2.50, 4.00 and 5.00 mg of calcium per 100 ml. Perform the atomic absorption measurements and plot mg of calcium per 100 ml vs absorbance.

c. Barium - Transfer 2.00, 5.00, 8.00, and 10.00 ml of barium stock solution to 100 ml volumetric flasks and dilute to volume. This gives a range of 5.0, 12.5, 20.0 and 25.0 mg of barium per 100 ml. Perform the atomic absorption measurements and plot mg of barium per 100 ml vs absorbance.

d. Potassium - Transfer 2.50, 5.00, 8.00 and 10.00 ml of potassium stock solution to 100 ml volumetric flasks and dilute to volume. This gives a range of 0.375, 0.75, 1.20, and 1.50 mg of potassium per 100 ml. Perform the atomic absorption measurements and plot mg of potassium per 100 ml vs absorbance.

NOTE: New calibration curves should be prepared each time a sample is run.

5.2 Prepare the sample for analysis as follows:

Transfer approximately 1.00 g of sample to a 150 ml beaker and add 10 ml of nitric acid and 3 ml of perchloric acid. Carry along a blank throughout the entire procedure. Warm on a hot plate until the propellant is dissolved, and then evaporate to fumes of perchloric acid. Continue the fuming with occasional swirling until not more than 1 ml of liquid remains. Cool. (If the sample contains tin, add about 25 ml of water, filter off the metastannic acid through a Whatman No. 42 filter paper, and wash with water).

Transfer to a 100 ml volumetric flask and dilute to volume. Use this solution for the determination of sodium, calcium, and barium. For the determination of potassium, pipet a 20 ml aliquot into a 100 ml volumetric flask, and dilute to volume.

NOTE: Use proper safety precaution.

5.3 Perform the analysis of the salts as follows:

a. Sodium – perform the atomic absorption measurements and convert the readings to mg of sodium per 100 ml by referring to the calibration curve. Deduct the blank. Calculate the percent of sodium sulfate in the propellant as follows:

$$\text{Percent sodium sulfate} = \frac{\text{mg of Na (per 100 ml)}}{\text{g of sample} \times 10 \times 0.3237} = \frac{0.3089 \times \text{mg of Na (per 100 ml)}}{\text{g of sample}}$$

b. Calcium – perform the atomic absorption measurements and convert the readings to mg of calcium per 100 ml by referring to the calibration curve. Deduct the blank. Calculate the percent of calcium carbonate in the propellant as follows:

$$\text{Percent calcium carbonate} = \frac{\text{mg of Ca (per 100 ml)}}{\text{gm of sample} \times 10 \times 0.4004} = \frac{0.2498 \times \text{mg of Ca (per 100 ml)}}{\text{g of sample}}$$

c. Barium – perform the atomic absorption measurement and convert the readings to mg of barium per 100 ml by referring to the calibration curve. Deduct the blank. Calculate the percent of barium nitrate in the propellant as follows:

$$\text{Percent barium nitrate} = \frac{\text{mg of Ba (per 100 ml)}}{\text{g of sample} \times 10 \times 0.5255} = \frac{0.1903 \times \text{mg of Ba (per 100 ml)}}{\text{g of sample}}$$

d. Potassium – perform the atomic absorption measurements on the diluted sample and convert the readings to mg of potassium per 100 ml by referring to the calibration curve. Deduct the blank. Calculate the percent of potassium sulfate or potassium nitrate in the propellant as follows:

$$\text{Percent potassium sulfate} = \frac{\text{mg of K (per 100 ml)} \times 5}{\text{g of sample} \times 10 \times 0.448} = \frac{1.114 \times \text{mg of K (per 100 ml)}}{\text{g of sample}}$$

$$\text{Percent potassium nitrate} = \frac{\text{mg of K (per 100 ml)} \times 5}{\text{g of sample} \times 10 \times 0.3867} = \frac{1.293 \times \text{mg of K (per 100 ml)}}{\text{g of sample}}$$

METHOD 403.1.3

VACUUM STABILITY TESTS (90 and 100°C)

1. SCOPE

1.1 This method is used for determining the stability of single base and double base propellants on the basis of the volume of gas liberated on heating the propellant under vacuum. This method may also be used to determine the rate of gas evolution as well as the volume of condensable gases. Single base propellants are heated to 100°C; double base propellants are heated to 90°C.

2. SPECIMEN

2.1 The specimen shall consist of 5.00 g of the propellant.

3. APPARATUS

3.1 Constant temperature reflux bath, consisting of a solution of ethyl alcohol and water (specific gravity, 0.98) for a 90 ± 0.5°C test, or a solution of glycerin and water (specific gravity, 1.05) for a 100 ± 0.5°C test. (A thermostatically controlled bath or heating block can be substituted.)

NOTE: Check the temperature of the bath by inserting a thermometer to the bottom of the empty heating tube (figure 1) immersed in the bath. Adjust the temperature of the bath by adding one or the other of the constituents of the solution.

3.2 Vacuum stability measuring apparatus (figure 1).

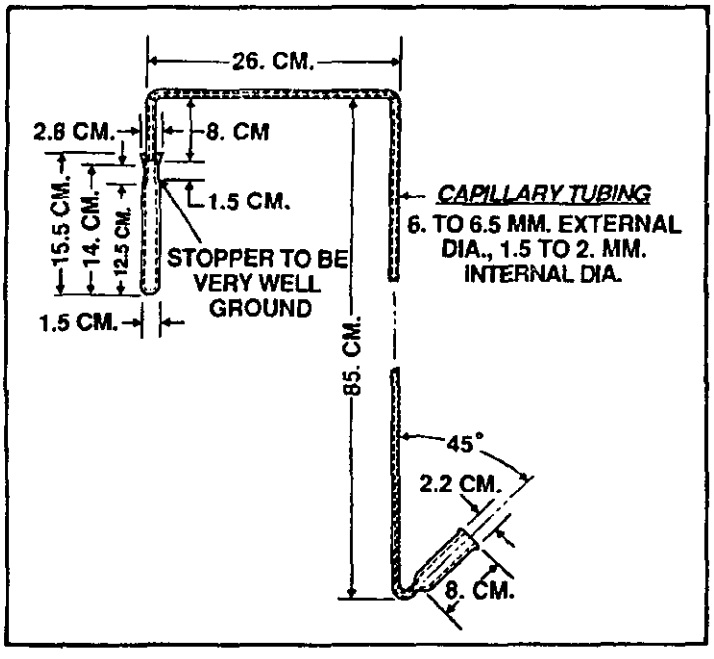


Figure 1. *Apparatus for Vacuum Stability Test.*

3.3 Vacuum pump.

4. PROCEDURE

4.1 Standardize the vacuum stability measuring apparatus (figure 1) as follows:

a. Determine the volume of the heating tube by filling it with mercury from a buret until the mercury reaches the level at which it will contact the ground glass joint of the capillary tube.

b. Determine the total length, in mm, of the capillary tube by measuring the length of each of the three parts of the capillary tube.

c. Determine the unit capacity of the capillary by placing exactly 10 g of mercury in its cup, and manipulating the tube so that all the mercury passes into the long (85 cm) section of the capillary. Be sure that the mercury remains as a continuous column. Measure the length of the mercury column at three positions in the long section of the capillary, and average the three measurements.

Calculate the unit capacity of the capillary, using the following formula:

$$C = \frac{W}{13.54L}$$

Where:

C = Unit capacity of capillary, cm^3 per mm.

W = Weight of mercury g.

L = Average length of mercury column, mm.

NOTE: Density of mercury = 13.54 g cm^3 at 21 - 24°C.

4.2 Prepare the specimen by grinding or by rasping, until it is reduced to approximately 12 mesh.

NOTE: Solvent propellants should be dried for 6 hours in a vacuum oven at 55°C before testing. Solventless propellants can be tested without drying.

4.3 Place the specimen in the heating tube (figure 1).

4.4 Coat the ground glass joint of the capillary tube with a light film of petroleum jelly and make an airtight connection between the heating tube and the capillary by pressing the tube up against the capillary with a twisting motion.

4.5 Mount the apparatus on a rack so that the long section of the capillary is nearly vertical, and so that the cup at the bottom rests on a solid support.

4.6 Fill the cup with 7.0 ml of mercury, and connect a vacuum line to the mouth of the cup.

4.7 Evacuate the capillary to a pressure of approximately 5 mm of mercury (absolute).

NOTE: Evacuation will be facilitated by tilting the apparatus until the capillary opening in the bottom of the cup is free of mercury.

4.8 When the pressure has been reduced to 5mm of mercury, remove the vacuum line and allow the mercury to enter the capillary. Record the following data:

a. The total length in mm of the capillary tube minus the vertical height of the column of mercury in the cup before heating (B_1).

b. The height of mercury column above surface of mercury pool at beginning of test (H_1).

c. The temperature ($^{\circ}C$) of room at beginning of test (t_1).

d. The barometric pressure in millimeters of mercury at beginning of test (P_1).

4.9 Immerse the heating tube in the constant temperature bath (par 3.1), being careful not to loosen the connection between the heating tube and the capillary. Heat the tube for 40 hours.

4.10 Remove the tube from the bath, cool to ambient temperature and record the following data.

a. The total length of the capillary tube minus vertical height of mercury column in the cup after heating (B).

b. The height of mercury column above the surface of mercury pool at the end of the test (H).

c. The temperature ($^{\circ}C$) of room at end of test (t).

d. The barometric pressure in millimeters of mercury at end of test (P).

4.11 Calculate the volume of gas (at standard temperature and pressure) liberated during test, as follows:

$$CM^3 \text{ gas} = [A + C(B - H)] \frac{273(P - H)}{760\ (273 + t)} - [A + C(B_1 - H_1)] \frac{273(P_1 - H_1)}{760\ (273 + t_1)}$$

Where:

A = the volume of the tube minus the volume of the sample and the volume of the sample is the weight of the sample divided by the density of the sample.

B = is the total length in mm of the capillary tube minus the vertical height of the column in mercury in the cup at the end of the test.

B_1 = is the total length in mm of the capillary tube minus the vertical height of the column of mercury in the cup before heating.

C = is the determined unit capacity of the capillary tubing in cm^3 per mm.

P = is the barometer reading at the end of the test.

P_1 = is the barometer reading when the test is started.

H = the height of mercury column above the surface of mercury pool at the end of test.

H_1 = the height of mercury column above the surface of mercury pool at beginning of test.

4.12 If it is desired to obtain rate data or the volume of condensable gases, modify the procedure as follows:

a. Rate data. Measure the height of the mercury column at convenient intervals of time with the heating tube in place, and calculate the volume of gas at standard temperature and pressure (STP). Plot cubic centimeters of gas versus time.

b. Condensable gases. At the end of 40 hours measure the height of the mercury column, with the heating tube in situ, and calculate the volume of gas at STP.

METHOD 404.1.2

HEAT TESTS (120 and 134.5°C)

1. SCOPE

1.1 This method is used for estimating the stability of nitrocellulose as well as those propellants which react in a similar manner when subjected to a specified temperature, in the presence of indicator paper.

2. SPECIMEN

2.1 The specimen shall consist of approximately 2.5 g of the propellant or the nitrocellulose.

NOTE: Tests are conducted simultaneously on five specimens at 120°C. However, when a 134.5 °C test is specified for nitrocellulose, only two specimens are tested.

3. APPARATUS

3.1 Constant temperature reflux bath, such as a solution of glycerin and water, the temperature of which is adjusted by varying its specific gravity. Alternatively, the apparatus may consist of a metal block, e.g., copper or aluminum. Either apparatus must be capable of maintaining the desired temperature ± 0.5°C. The inner diameter of each thermowell in the apparatus shall be 19 ± 0.5mm.

NOTE: Check the temperature by insterting a thermometer or thermocouple tube in the apparatus, so that the bulb is about 12.5 mm above the bottom of the tube. For a temperature of 120 ± 0.5°C, the specific gravity of the reflux bath is approximately 1.21; for 134.5 ± 0.5°C, the specific gravity is 1.24.

3.2 Test tubes of borosilicate glass, approximately 15 mm id; 18 mm od; and 290 mm length.

3.3 Standardized methyl violet test paper, cut into pieces 20 mm by 70 mm.

3.4 Corks, containing breather holes 4 mm in diameter (or notches of equivalent area).

3.5 Thermometer, total immersion. Scale divisions shall not be greater than 0.2°C.

4. PROCEDURE

4.1 Weigh out each propellant specimen, using whole grains where possible. If it is necessary to cut any grains in preparing a specimen, cut them lengthwise. Transfer to test tubes.

4.2 Dry nitrocellulose specimens, weigh them, and press them into the bottom 2 inches of the test tube.

NOTE: Dry the nitrocellulose on paper trays for 2 hours at 38 to 42°C, or for one to 1 1/2 hours at 48 to 52°C. If preferred, dry it overnight at room temperature with further drying for 30 minutes at 38 to 42°C.

4.3 Into each tube place a piece of the test paper (para 3.3) vertically so that the lower end of the paper is 25mm from the specimen.

4.4 Place a cork (par 3.4) in each tube, and set the tubes in the bath at the specified temperature.

NOTE: No more than 6 to 7 mm of the tubes should project above the bath.

4.5 Test specimens as follows:

a. Ascertain the minimum time requirement for the heat test from the detail specification.

b. When 5 minutes less than the specified time has elapsed, examine the test papers in the tubes to see if they have changed completely to salmon pink. This is done by lifting the tubes half way out of the bath, and quicky replacing it. When the test paper in any tube has changed color completely, the test is considered complete.

c. If none of the papers have changed completely continue the heating, and recheck the tubes at 5 minute intervals. Record the time to completion of the test. With some propellants, a small band of green or brown may appear on the paper. In general, these extraneous colors may be ignored.

d. Heating of the tubes may be continued to determine whether a specimen will explode in less than 5 hours.

4.6 Test nitrocellulose specimens by examining the test paper after the first 20 minutes in the bath, and thereafter at 5 minute intervals until the completion of the test. Examine the papers as described in paragraph 4.5; discontinue the test when the salmon pink end point is attained in any of the papers. Record the test time. (For example, if the violet paper is not completely changed in 25 minutes, but is completely changed in 30 minutes, record the time of the test as 30 minutes).

METHOD 406.1.2

TALIANI TEST

1. SCOPE

1.1 This method is used for determining the stability of propellants by subjecting them to a specified temperature and atmosphere. Unless otherwise specified, a temperature of 110°C and a nitrogen atmosphere should be used.

2. SPECIMEN

2.1 The specimen shall consist of 1.000 ± 0.001 g of the propellant, which has been dried previously for 16 hours in a desiccator containing an indicating desiccant (duplicate specimens shall be processed for each test).

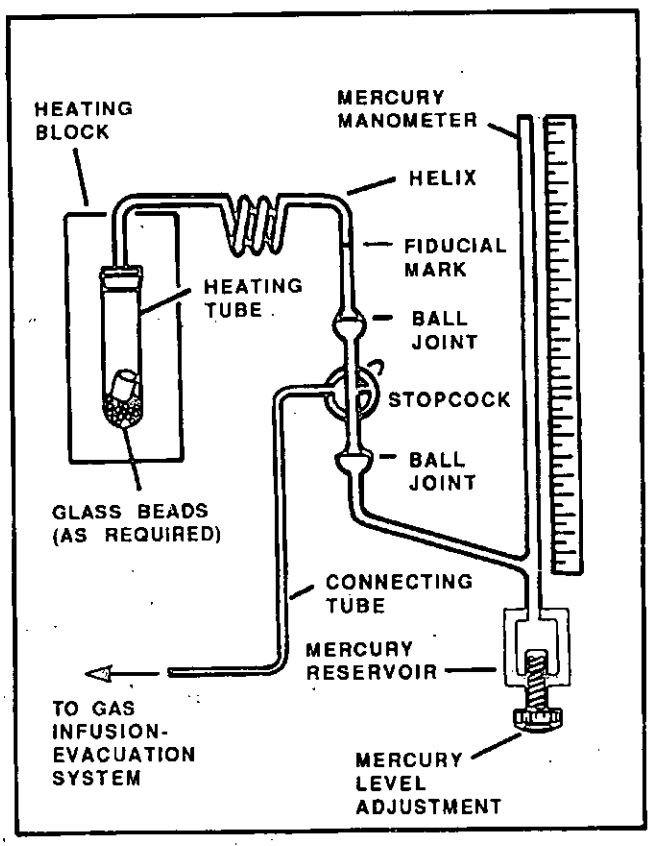


Figure 1. *Taliani test apparatus.*

3. APPARATUS

3.1 Taliani test apparatus (figure 1), consisting of the following:

a. Heating block, maintained at required temperature to within ± 0.1°C.

b. Helix, consisting of a coiled 2mm capillary having a volume of approximately 0.75 ml.

c. Connecting tube, containing a three way stopcock.

d. Gas infusion-evacuating system, consisting of a vacuum pump with a modulating control, and a gas supply with a flow control (pressure gage, needle valve, and bubble counter containing dibutylphthalate). Connect the vacuum line and gas supply to the connecting tube (item C) by a two way stopcock.

e. Manometer (with mercury level adjusting device).

f. Heating tubes, 6 ml.

3.2 Buret.

4. PROCEDURE

4.1 Set up the apparatus as shown in figure 1, using silicone stopcock grease for all glass to glass joints. Adjust the mercury level in the manometer so that it is just below the stopcock.

4.2 Standardize the apparatus as follows:

a. Make a fiducial (reference) mark on the helix just above the ball joint.

b. Remove the helix from the apparatus, and determine its volume from the heating-tube end to the fiducial mark by filling it with mercury or water (clean, distilled) from a buret. Also determine the volumes of the heating tubes to be used in the test.

c. Adjust the total volume of the heating tube and the helix (up to the fiducial mark) to exactly 6 ml by placing an appropriate number of 3mm glass beads into the heating tube.

d. Reconnect the helix to the apparatus.

NOTE: The average volume of the beads in a lot can be calculated by placing 100 beads (ten at a time) in a buret partially filled with softened water, noting the water displacement, and dividing by 100. Also check the uniformity of the lot by noting the displacement of each ten beads.

4.3 Prepare the propellant specimen by grinding or rasping to a 10 to 40 mesh.

4.4 Transfer duplicate specimens to the heating tubes, connect the tube to the helix, and heat it in the heating block.

4.5 Adjust the three way stopcock in the connecting tube so that the helix and heating tube are connected to the gas infusion evacuation apparatus.

4.6 Evacuate the tube and helix to a pressure of 5 mm of mercury. Then allow gas to enter the tube and helix at such a rate that bubbles will form in the bubble counter (para 3.1 (d)) too rapidly to be counted but slow enough that they will not agitate the liquid.

4.7 Repeat the evacuation and gas infusion (step 4.6) four times more. At the end of the fifth infusion, adjust the stopcock to seal the helix and heating tube. Disconnect the infusion-evacuation system.

NOTE: The gas in the system should be at approximately atmospheric pressure.

4.8 Allow the tube and helix to remain sealed for 15 minutes, while continuing the heating.

4.9 At the end of 15 minutes, release the pressure from the helix by opening the stopcock, and quickly closing it again.

4.10 With the stopcock turned so that the helix is sealed and the manometer is open to atmosphere, raise the level of the mercury until the stopcock is full of mercury. Then turn the stopcock to close the system to atmosphere and open the manometer to the helix. With the stopcock in this position, adjust the mercury leveling device until the mercury rises to the fiducial mark. Note the reading on the manometer. (This reading is the zero reference point from which all further readings are measured.) Also record the barometer reading.

4.11 After 30 minutes, readjust the mercury level to the fiducial mark, and record the corresponding manometer readings. Also record the barometer reading.

4.12 Determine the absolute pressure of the system by adding any changes in barometric pressure to the new manometer reading, and subtracting the zero reference readings (para. 4.10).

4.13 Repeat the readjustment of the mercury level and record the manometer readings every 30 minutes until the mercury has risen 150 mm above the zero reference point, or for a maximum of 6 hours.

NOTE: The pressure for duplicate tubes of a propellant lot should agree within 4 mm in the 0 to 50 mm range, within 6 mm in the 50 to 100 mm range, and within 8 mm above 100 mm.

4.14 Average the readings for the two specimens.

4.15 Prepare a graph, if required, on a linear graph paper with time in minutes on the abscissa and the average pressure on the ordinate.

4.16 Report the desired data or report the slope at 100 mm and at 100 minutes, and the time to 100 mm.

5. CALCULATE AND REPORTING

5.1 Average the readings where duplicate samples are used.

5.2 Plot a graph of time in minutes versus pressure in mm of mercury and draw the best straight line or two lines, if necessary, through the points. If the plotted graph is curved, the slope is computed from the best straight line drawn tangent to the curve.

OR

Select a point above and below positions where slope is desired and geometrically calculate slope of line joining the two point.

$$\text{SLOPE} = \frac{\text{Difference in pressure from lower to upper point in mm mercury}}{\text{Difference in time from lower to upper point in minutes}}$$

Geometrically determine the time to 100mm pressure based on the slope at the pressure.

5.3 Report the following data:

1. Time in minutes to reach 100-mm pressure.
2. Slope of line at 100-mm pressure.
3. Slope of line at 100 minutes.

5.4 Figures 2, 3 and 4 are examples of typical stability curves.

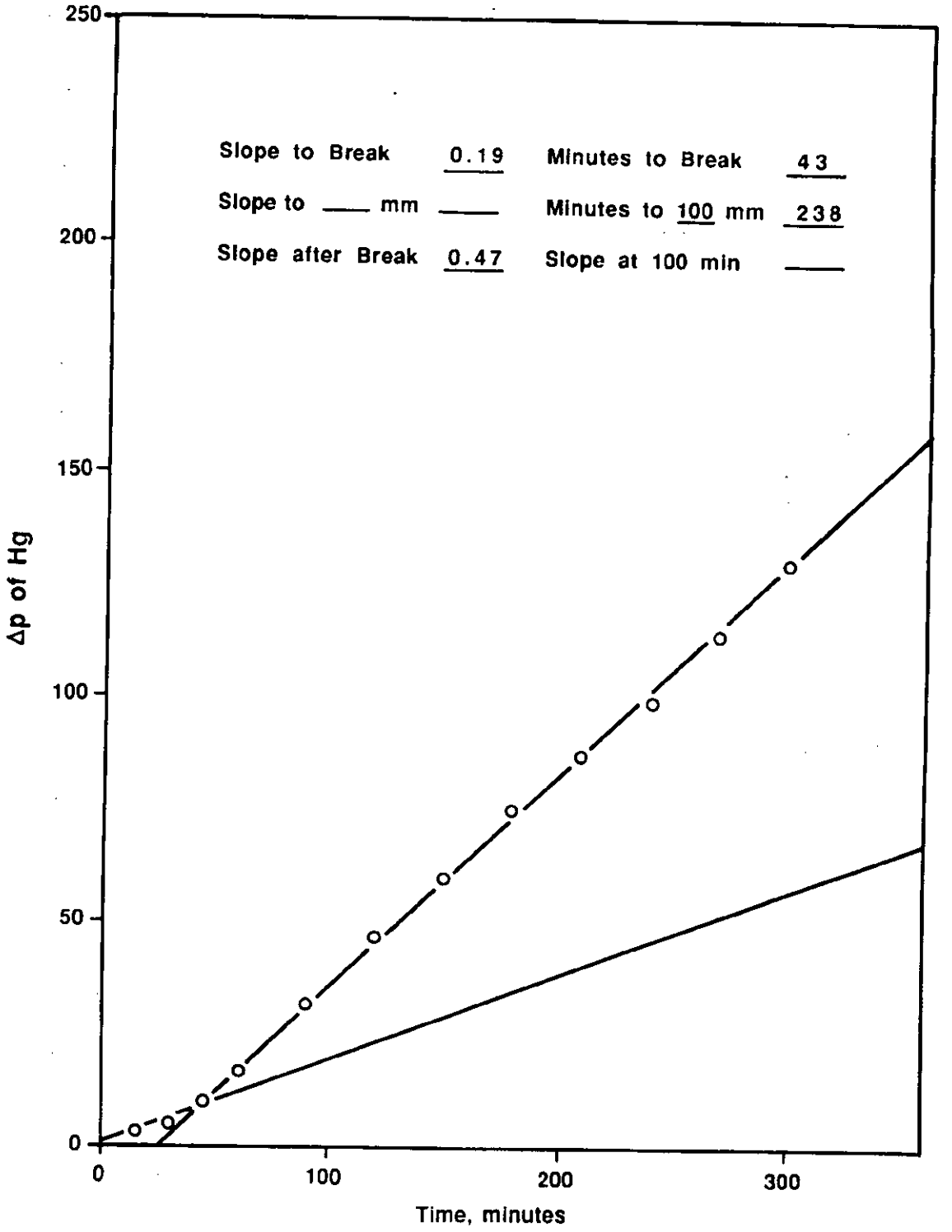


Figure 2. *Taliani graph indicating a break in slope.*

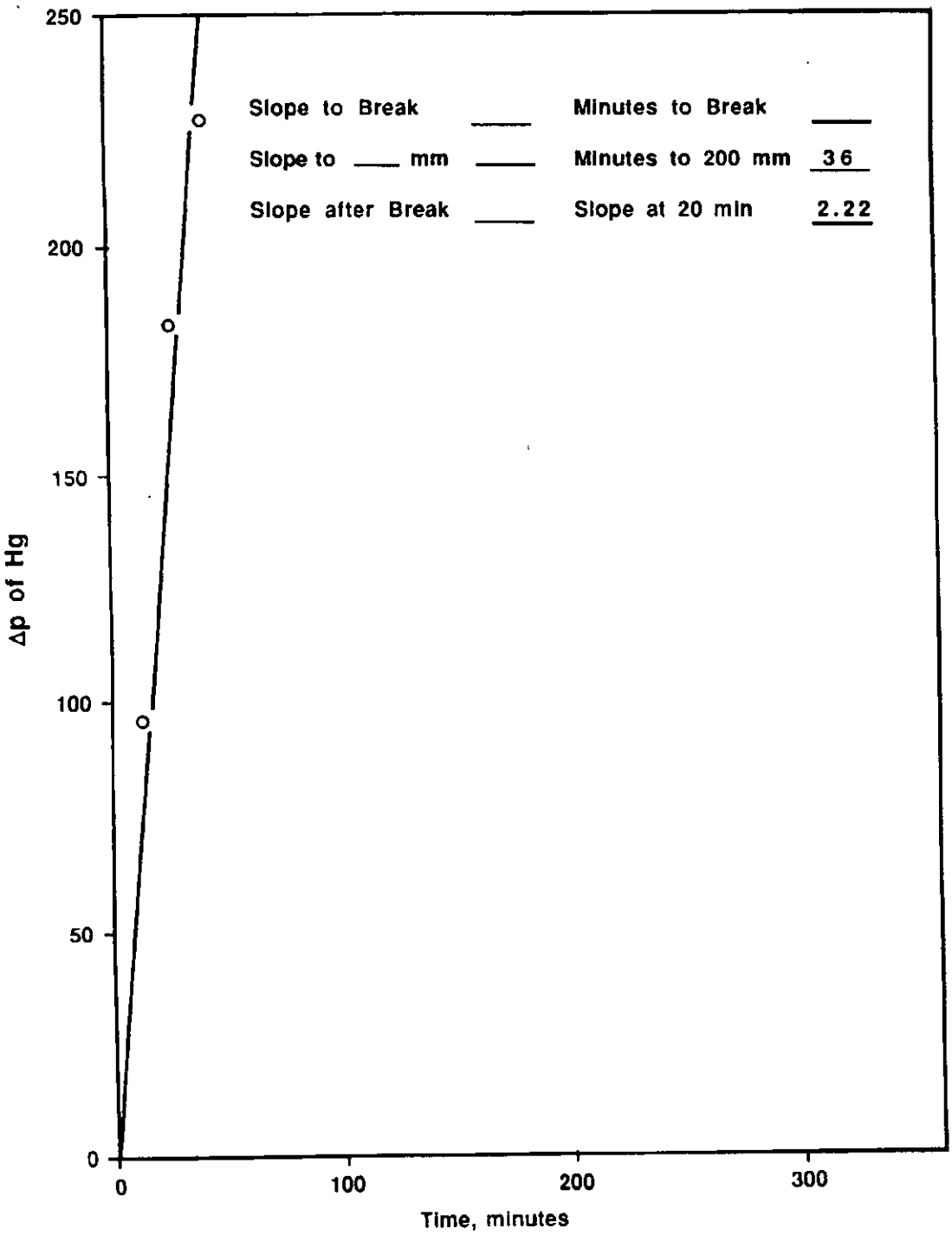


Figure 3. *Taliani graph indicating a sharp slope and sample instability.*

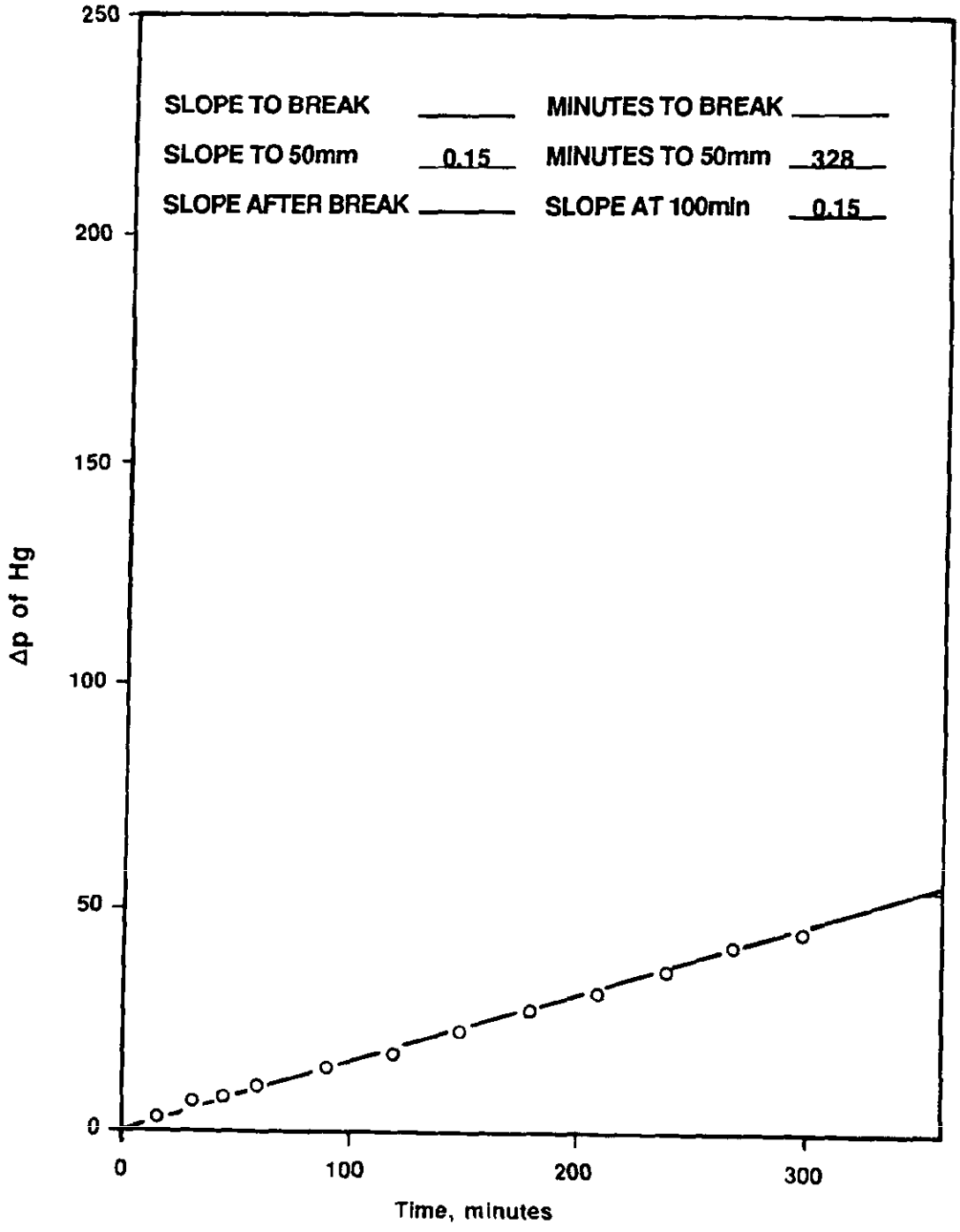


Figure 4. *Taliani graph indicating a low slope and sample stability.*

METHOD 407.1

SURVEILLANCE TEST (65.5°C)

1. SCOPE

1.1 In general, this method is intended for the evaluation of the stability of small arm propellants, artillery propellants as well as rocket propellants.

2. SPECIMEN

2.1 For small grain propellants. Use a 45 gram portion of the sample.

2.2 For propellant for 10 inch or larger cannon. Use a test sample of five (5) propellant grains or as many as can be inserted in the bottle.

2.3 For rocket propellants - small diameter sticks. Cut a sufficient number of 3 inch lengths to obtain a 45 gram sample.

2.4 For rocket propellant - large diameter sticks (up to and including 1 3/8 inches). Cut a sufficient amount from the length to obtain a 45 gram sample.

2.5 For rocket propellant - large cylindrical sticks greater then 1 3/8 inches. Cut a longitudinal section through the center, 1 inch wide on the grain surface, 1 3/8 inch in depth and of sufficient length of obtain a 45 gram sample.

2.6 For rocket propellant - larger cruciform sticks. Cut a longitudinal section from one arm, 3/4 inch wide on the exterior grain surface and 3/4 inch deep on the recession and of sufficient length to obtain a 45 gram sample.

NOTE: Include lateral inhibitor if present.

2.7 For sheet powders. Cut sufficient lengths, 2 1/2 inches wide to obtain a 45 gram sample.

NOTE: Coil the sample before placing it into test bottle.

3. APPARATUS

3.1 An 8 ounce glass stoppered bottle having a wide mouth with a velvet ground mushroom stopper which provides an essentially air-tight seal. The bottle should be etched or ground on the side so as to be suitable for labeling and must be made from a special resistance glass which has practically no color and an alkalinity of not more than 0.02% (calculated as potassium hydroxide). Determine the alkalinity of the glass by placing a 10 gram sample of ground glass in a boroxsilicate glass flask, adding 20 mL of N/20 hydrochloric acid, allowing to stand for 24 hours, and titrating with N/20 sodium hydroxide, using phenolphthalein indicator.

NOTE: The bottles may be obtained from the Wheaton Glass and Plastic Co., Millville, NJ (or equivalent source).

4. PROCEDURE

4.1 Using the sample prepared as described in paragraph 2 above, place about 45 grams of the sample in an 8 ounce glass stoppered bottle.

4.2 Place the bottle and contents in a chamber maintained at 65.5 ± 1.0°C., the air in which is preferably maintained in constant circulation.

4.3 Reseat the stopper after the bottle and contents have been heated for 24 hours.

4.4 Make daily observations of the appearance of the bottle and contents. Note the number of days required to cause the liberation of visible reddish fumes of oxides of nitrogen.

METHOD 408.1.1

REACTIVITY TEST (90 and 100°C)

1. SCOPE

1.1 This method is used to determine the reactivity of propellants with contact material.

2. SPECIMEN

2.1 The specimen shall consist of 5 g of the propellant and 5 g of the contact material. A 2.5 g portion of the materials is tested as received except in the case of solvent containing contact materials (paints, adhesive, etc.) which would in normal usage be in the dry state. In this case the materials are air dried on glass plates and removed in the form of films for testing. The remaining portion of the propellant and contact material are reduced to a practicable finess for intimacy of contact. Propellants are rasped or milled to a fineness of passing through 12 mesh screening sieve.

3. APPARATUS

3.1 The apparatus used in this method is identical with that used in Method 403.1.3.

4. MATERIALS

4.1 Contact materials as specified in the applicable method or specification.

5. PROCEDURE

5.1 Standardize the vacuum stability measuring apparatus as described in Method 403.1.

5.2 Place weighed portion of 2.5 g of the propellant in one heating tube, and 2.5 g of contact material in a second heating tube.

5.3 In a third tube place a 5 g portion of a 50/50 mixture of the contact material and propellant.

5.4 Determine the volume of gas evolved as specified in Method 403.1.

5.5 Determine the amount of gas produced by the mixture of contact material and the propellants in excess of the amount of gas evolved by the materials themselves, as follows:

$$R = C - (A + B)$$

Where:

C = amount of gas evolved by the 50/50 mixture of the contact material and the propellant.

A = amount of gas evolved by the propellant.

B = amount of gas evolved by the contact material.

R = extent of reactivity, or volume of gas generated by the mixture in excess of the controls.

5.6 Report the reactivity from the following table:

Gas volume due to reactivity/reactivity rating	
From 0.0 to 3.0 cubic centimeter	(Negligible)
From 3.0 to 5.0 cubic centimeters	Moderate
More than 5.0 cubic centimeters	Excessive

NOTE: The empirical adjective rating of reactivity was devised as a criterion for the purpose of reporting and classifying data. With the complete data available, the investigator will evaluate its significance as it applies to his particular problem. In general, the first condition (less than zero) occurs when the amount of gas generated by the controls is in excess of that generated by the mixture. Since the Vacuum Stability Test is sensitive only to the first place, minus values of low order (0.10 - 0.30) may be accepted as essentially indicative of no reactivity. Minus values of higher order may indicate a stabilizing of blanketing effect produced by the contact materials upon the propellant and should be taken into account by the investigator in evaluation of the data. Since the test is severe, reactivity up to and includifng slight is considered acceptable. Use of a moderately reactive material should be justified by further testing with modifications of existing procedures to more closely approximate the intended use; or a less reactive substitute material may be sought. This latter action is normally taken upon establishment of excessive reactivity.

METHOD 409.1.1

NITROGEN OXIDES EVOLUTION PROFILE (NEP) TEST

1. SCOPE

1.1 This method established the procedure to obtain an NEP (nitrogen oxides evolution profile) of a single-base cannon propellant with the prototype AADCO propellant stability analyzer. The NEP value obtained from the profile is a measure of the chemical stability of the propellant. The NEP values are indirectly affected by the quantity of stabilizer (diphenylamine) present and measures the effectiveness of the stabilizer.

2. SPECIMEN

2.1 The specimen shall consist of approximately 1.0 gram of propellant (whole or crushed grains) weighed within 0.1 g.

3. APPARATUS

3.1 AADCO Propellant Stability Analyzer (figure 1 and 2), Model 580.

4. MATERIAL

4.1 Nitrogen (carrier gas).

4.2 Air, compressed (for pneumatic actuators and drive train)

4.3 Oxygen (gas for ozonator).

4.4 Span gas (or calibration gas), 300 to 400 ppm nitric oxide (NO) of known concentration.

4.5 Recorder, 10 inch, 10 mv full scale.

5. PROCEDURE

5.1 Test Conditions

a. Function Switch	Auto operation
b. Furnace (or oven) temperature	140 ± 0.3°C
c. Detector temperature	See note below
d. Sample holder temperature (initial)	40°C
e. Sample holder temperature during operation	139.5°C in less than 5 min & maintain 140 ± 0.5°C
f. Switching valve variac setting at rear of instrument	60 (140°C)
g. Thermal converter	ON
h. Carrier gas (N_2) pressure	40 psig
i. Carrier gas (N_2) rotameter	4.5 (150 cm^3/min)
j. Oxygen pressure	25 psig
k. Oxygen rotameter	4.5 (150 cm^3/min)
l. Air, compressed	55 psig
m. Span gas pressure (for calibration)	40 psig

n. Span gas rotameter (for calibration)	4.5 (150 cm^3/min)
o. Sample carriage drive train	Auto
p. Recorder input	10 mV
q. Recorder chart speed	0.25 in/min
r. Recorder range-calibration	50
large propellant grains	50
small propellant grains	20
s. Analysis time	30 min (or as required)

NOTE: Detector temperature is factory set at subambient temperature. Level is not important but should remain relatively constant during testing.

NOTE: 1 psi = 6.9 kPa

5.2 Verify that carrier gas pressure and flow are in accordance with conditions above. Carrier gas should remain on while instrument is on.

5.3 Verify that the oven, detector and sample holder are stable at the above temperatures. (The sample holder operating conditions can be verified by operating the instrument through a time cycle with no sample present.)

5.4 Verify th at the thermal converter is on. (Approximately 2 hours are required for the convertor to reach the operating temperature and stabilize).

5.5 Check switching valve variac setting in back of instrument.

5.6 Turn on oxygen supply to ozonator. Verify pressure and rotameter settings.

5.7 Switch on ozonator. Wait a minimum of 5 minutes before operating detector.

5.8 Verify that compressed air to sample holder drive mechanism is on and at 55 psig.

5.9 Sample carriage drive train switch must be in Auto position.

5.10 Place function switch on face of instrument in Auto Operation position.

5.11 Set recorder conditions as specified above. With recorder range switch on instrument at 50, zero recorder with span gas off.

5.12 Turn on span gas and set pressure and rotameter setting (flow rate) idential to those of the carrier gas. Carrier gas can be left on.

5.13 Using the calibration knob on the recorder, calibrate the recorder so the maximum pen response corresponds to the nitric oxide (NO) in the span gas and so that full scale recorder response will represent 500 ppm NO (or NOx for sample.)

5.14 After calibrating the instrument (or recorder), turn off span gas and allow pen to return to zero.

5.15 Set analysis time.

5.16 Place the weighed sample of propellant in one of the thin walled sample tubes with the provided screened plugs at each end to insure sample containment.

5.17 Replace the blank sample tube in the sample holder with the one containing the test sample.

5.18 Seat the sample tube securely against the bottom wall of the holder for rapid heat transfer.

5.19 Move the self locking leaf bolt to the lock position to set the sample tube ends against the Teflon seals which are center pierced for passage of inert carrier gas.

5.20 Press the START button.

5.21 The unit will automatically sequence as follows:

a. The sample carriage will drive the sample holder into the preheated oven.

b. The gas switching valve will rotate and direct preheated carrier gas through the sample tube.

c. The sample holder will be rapidly heated to the preset temperature (140°C) and maintained through the interactions of its own heater and heat radiating from the inside oven walls.

d. NOx evolved from the heated sample is carried by the inert carrier gas through the thermal converter where all oxides of nitrogen are converted to NO.

e. The NO passes into the chemiluminescent detector and reacts with ozone to produce a signal which represents the quantity of NO_x in the stream.

f. The concentration of NO_x vs time is continuously monitored by the recorder to produce an NEP.

g. Upon conclusion of the cycle, all functions revert to their original status.

h. The sample heater cuts off.

i. The gas switching valve directs ambient carrier gas through the sample holder.

j. After 30 second COOL period, the sample holder is retrieved automatically from the oven a READY light comes on, and the sonic buzzer notifies the operation that the cycle is completed.

5.22 After the sample holder temperature has decreased to less than 40°C, remove and replace the sample tube with a tube containing the next test sample or with an empty (or blank) tube.

NOTE: The sample holder temperature cool-down may be hastened by turning on the fan located immediately below the sample holder. The fan should be off during sample testing.

5.23 When testing is completed, turn off recorder, turn off ozonator, turn off oxygen at main cylinder valve (for Safety), turn off compressed air, switch drive mechanism to MANUAL, shut off span gas cylinder valve to prevent loss of span gas, and leave carrier gas on.

5.24 Determine and record the NEP Value "A" as shown in Figure 3.

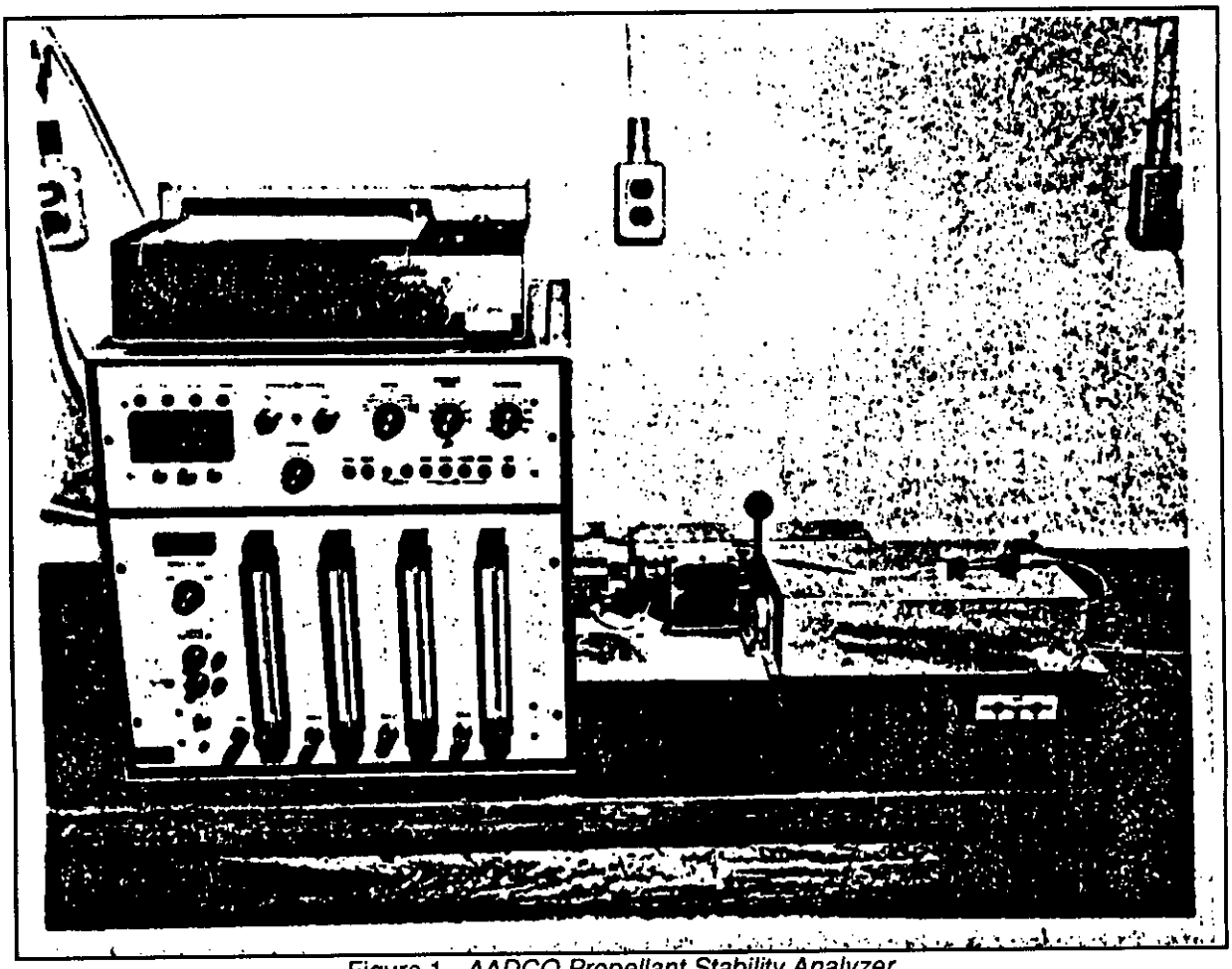


Figure 1. *AADCO Propellant Stability Analyzer.*

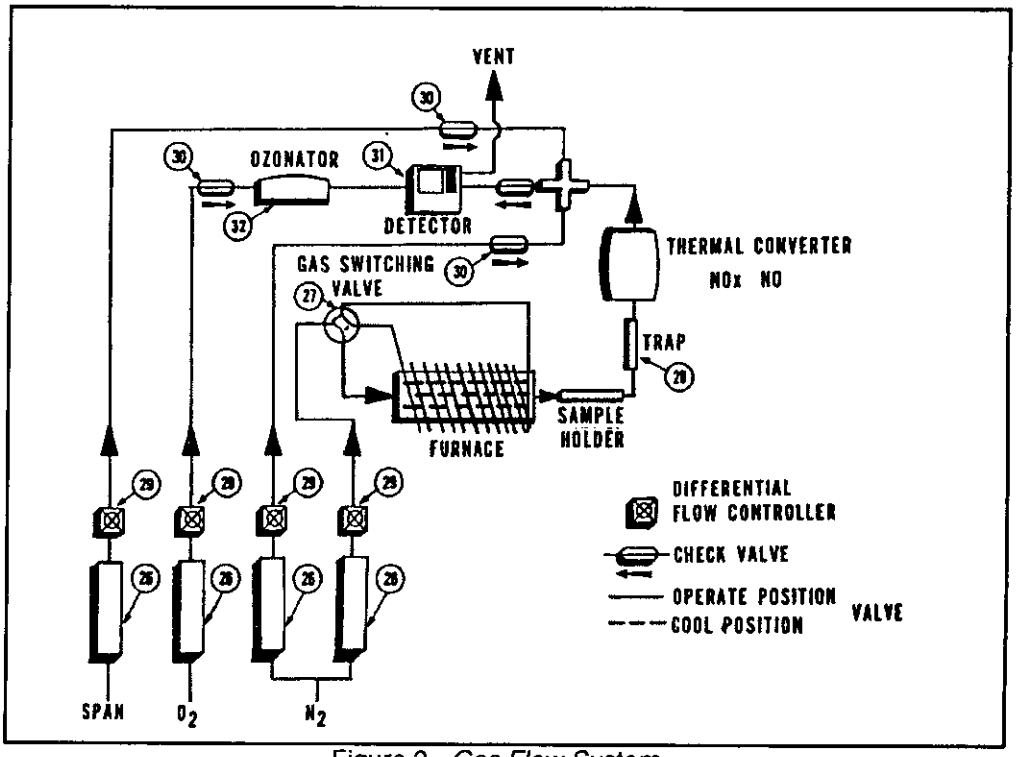


Figure 2. *Gas Flow System.*

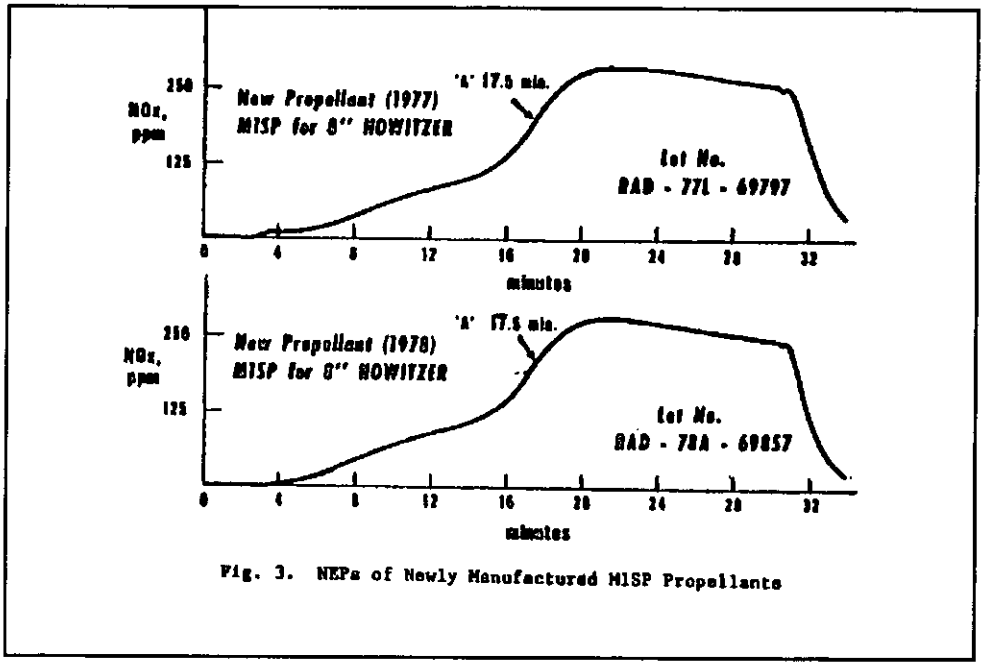


Fig. 3. NEPs of Newly Manufactured M1SP Propellants

Figure 3. *NEPs of Newly Manufactured M1SP Propellants.*

METHOD 501.1.3

DUST AND FOREIGN MATERIAL

1. SCOPE

1.1 This method is used for determining the dust and foreign material content of propellants whose surface is not disintegrated by water.

2. SPECIMEN

2.1 The specimen shall consist of two portions of approximately 50 grams each of propellant as received, taken for a 1 quart sample reserved for the dust determination. Each portion should be weighed to within 1 g.

3. APPARATUS

3.1 Test assembly (figure 1) consisting of two 750 ml Erlenmeyer flasks (A and A_1), for holding duplicate samples, a 500 ml bottle (B) filled with glass wool to filter air, a 1 liter suction flask (C) used as a pressure regulator, and a glass tube (D) used as a pressure indicator.

3.2 Filter crucibles, glass or porcelain, of desired porosity.

3.3 Oven.

3.4 Desiccator containing an indicating desiccant.

4. PROCEDURE

4.1 Carefully transfer (to prevent loss or alteration of the dust content) the accurately weighed 50 g portions of the propellant to each of two Erlenmeyer flasks (figure 1) containing 200 ml of distilled water.

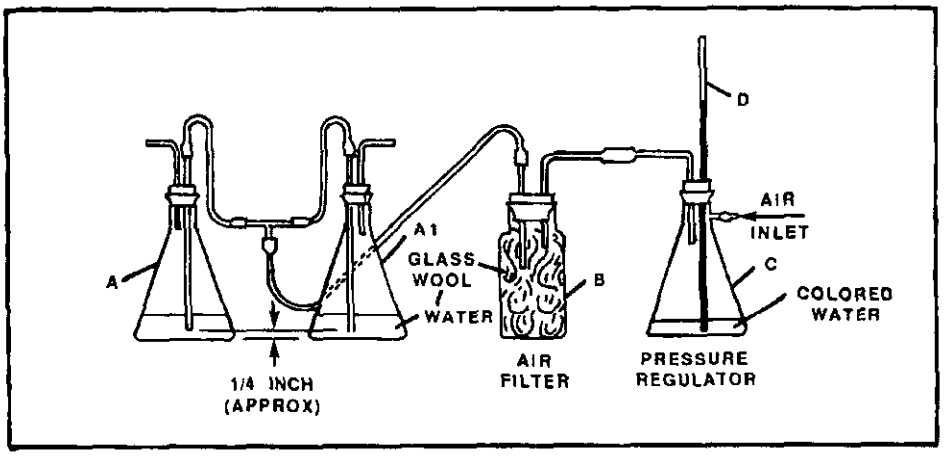


Figure 1. *Test assembly.*

NOTE: If small grain propellant is being tested, add two drops of wetting agent (Nikal N.S., Antara Products, New York, 14, New York or equivalent to the distilled water.

4.2 Assembly the test assembly shown in figure 1.

4.3 Connect a low pressure air supply to the air inlet assembly, and adjust the air pressure to raise the water in the pressure indicator tube to 26 inches above the surface of the liquid. Allow the air to agitate the propellant mixtures for 10 minutes. Swirl the contents of the flasks occasionally.

4.4 At the end of 10 minutes, shut off the air supply. Remove the stoppers from the Erlenmeyer flasks, and wash down the air inlet tubes with distilled water, collecting the washings in the flasks.

4.5 Swirl the flasks, and quickly decant the liquid into separate one liter beakers.

4.6 Add 150 ml of distilled water to the propellant in the flasks, and repeat the swirling and decantation until no more dust particles are visible on the liquid.

NOTE: A total of 650 to 800 ml of water is normally required.

4.7 Filter the dust particles from the liquids, using filtering crucibles.

4.8 Dry the crucibles in an oven at 100°C for one hour. Cool in a desiccator, and weigh.

4.9 Calculate the percentage of dust and foreign matter in each specimen.

4.10 **Calculation:**

$$\text{Percent dust and foreign matters} = \frac{100A}{W}$$

Where:

A = Increase in weight of the crucible, g

W = Weight of specimen, g

4.11 Report the average percentage of two specimens as the percentage of dust and foreign matter in the propellant.

METHOD 502.1.1

BULK DENSITY

1. SCOPE

1.1 This method is used to determine the bulk gravimetric density of propellants by utilizing a duPont densimeter.

NOTE: The bulk (gravimetric) density of the propellant is defined as equal to the apparant specific gravity multiplied by 1000. The apparent specific gravity is the ratio of the weight of a given volume of propellant to the weight of the same volume of water at a temperature of 70°F (21.1°C).

2. SPECIMEN

2.1 The specimen shall consist of approximately 400 g of the propellant, as received.

3. APPARATUS

3.1 DuPont Densimeter (figure 1) or Triple Beam Platform Balance.

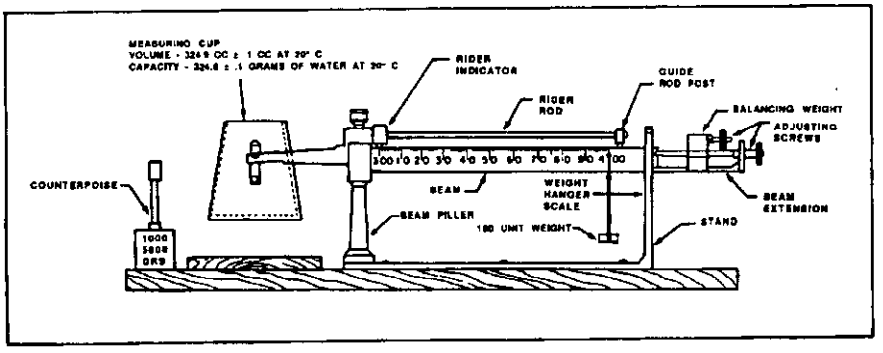


Figure 1. *DuPont densimeter.*

3.2 Flowing Cup for DuPont Densimeter.

NOTE: The hopper opening should be 1/2 inch. However, a 3/8 inch opening may be used but must be reported in the analysis statement.

4. PROCEDURE

4.1 Store the propellant at the temperature of the test for 24 to 36 hours prior to testing.

NOTE: The temperature range is critical in this determination.

4.2 Close the hopper valve, and fill the hopper level with 350 to 400 ml of the propellant.

4.3 Quickly open the valve completely, permitting the propellant to fill the cup until it just overflows. Close the valve.

4.4 Remove the hopper. Run a straight edge across the top of the cup to strike off the excess, then tap the cup gently to settle the contents and prevent spilling.

4.5 Place the cup on the balance of the densimeter, and adjust the balance weight. The reading on the scale beam is the bulk (gravimetric) density for the propellant.

NOTE: If the temperature of the propellant is not 70°F, add 0.001 to the reading for every 2° above 70°F, subtract 0.001 for every 2° below 70°F.

METHOD 502.2.1

BULK DENSITY (POUNDS PER CUBIC FOOT)

1. SCOPE

1.1 This method is used to determine gravimetrically (in pounds per cubic foot) the bulk density of propellants.

2. SPECIMEN

2.1 The specimen shall consist of approximately 450 cc of the propellant.

3. APPARATUS

3.1 Cylinder, approximately 6 inches long and 2 5/16 inches ID.

NOTE: A 1000 ml graduate severed at the 400 ml mark has been found suitable.

3.2 Counterpoise, equal in weight to the cylinder.

4. PROCEDURE

4.1 Allow the specimen to attain approximately room temperature.

4.2 Weigh the empty cylinder on a trip balance, and record the weight.

4.3 Fill the cylinder with distilled water, weigh on the balance, and record the weight. Empty the cylinder and dry.

4.4 Fill the cylinder completely with the propellant, permitting the propellant to overflow, run a straight edge across the top to strike off the excess, then tap the cylinder gently to settle the contents and prevent spilling in handling.

4.5 Weigh the filled cylinder on the balance and record the weight.

4.6 Calculate the bulk density.

4.7 **Calculation:**

$$\text{Bulk density (lbs. per cu. ft)} = \frac{62.5A}{B}$$

Where:

A = Weight of specimen, g.

B = Weight of water, g.

METHOD 502.3.1

PACKING DENSITY

1. SCOPE

1.1 This method is used for determining the packing density of base grain powder for cast rocket propellant.

2. SPECIMEN

2.1 The specimen shall consist of approximately 545 grams of base grain powder.

2.2 The size of the base grain powder for the apparatus contained herein are for base grain powders having the following dimensions:

	Dia (in)	Height (in)
Type I	0.030 ± .003	0.030 ± .003
Type II	0.350 ± .002	0.035 ± .003

3. APPARATUS

3.1 A standard packing density determination assembly, figure 1. Figures 2 through 7 present details of all components for this assembly.

3.2 A base leveling plate, figure 8, or equivalent.

3.3 A brass bar, figure 9.

3.4 An aluminum spillage pan (Fed spec RR-P-54) or equivalent. Substitute must be non-sparking metal.

3.5 A circular spirit level, Sargent-Welch, Catalog No. S-4436, or equal)

3.6 Spouted container, such as a Griffin beaker, low form, 600 ml Teflon, FEP. (Nalgene Catalog No. 1500-0600), or equal.

4. CONDITIONING

4.1 The sample of base grain powder as well as all the apparatus specified in paragraph 3 shall be conditioned to a constant temperature of 70 ± 5°F (21.1 ± 2.8°C) for 18-24 hours. The base grain powder does not have to be conditioned for humidity provided the moisture content of the sample is between 0.1 and 3.0 percent and the test is made in a room having a relative humidity between 30 and 80 percent.

5. PROCEDURE

5.1 The empty 500 ml container shall be tared.

5.2 The apparatus for standard packing density determination shall be assembled as shown in figure 1.

5.3 The spillage pan shall be grounded to a cold water pipe with a grounding cable.

5.4 The base leveling plate shall be placed inside the spillage pan.

5.5 The circular spirit level shall be placed on the base leveling plate. The leveling screws shall be adjusted until the plate is level and solid.

5.6 The standard packing density determination assembly, figure 1, shall be placed on the base level plate in the seat provided therein. A ground cable shall be attached to the hopper.

5.7 The spouted container shall be tared and approximately 545 grams of propellant weighed out.

5.8 The propellant shall be dumped into the hopper in one motion. When all the propellant has run through the column, all parts of the apparatus above the 500 ml cylinder shall be removed. This shall be accomplished by holding the bottom cylinder firmly and lifting off the other sections as units. The excess propellant, shall be struck off by using the brass bar with a 1/4 inch edge held flush with the top of the cylinder and with a slow constant movement across the cylinder top toward the operator. The excess propellant shall be removed with the brass bar. The cylinder shall be removed from the base plate and any propellant that may be clinging to the sides of the container brushed off.

5.9 The propellant and cylinder shall be weighed and the weight recorded.

5.10 The screen loading density shall be reported in grams per cubic centimeter. It shall be determined by subtracting the tared weight of the container from the gross weight of base grain powder and container.

This difference in weight, in grams, shall be divided by the volume in cubic centimeters, of the container. The volume of the container shall be determined from its dimensions stamped on the bottom. The volume shall be determined by using the formula in 5.11.

5.11 **Calculation:**

$$V = \pi r^2 h$$

Where:

V = Volume, cubic centimeters

r = radius, centimeters

h = Height, centimeters

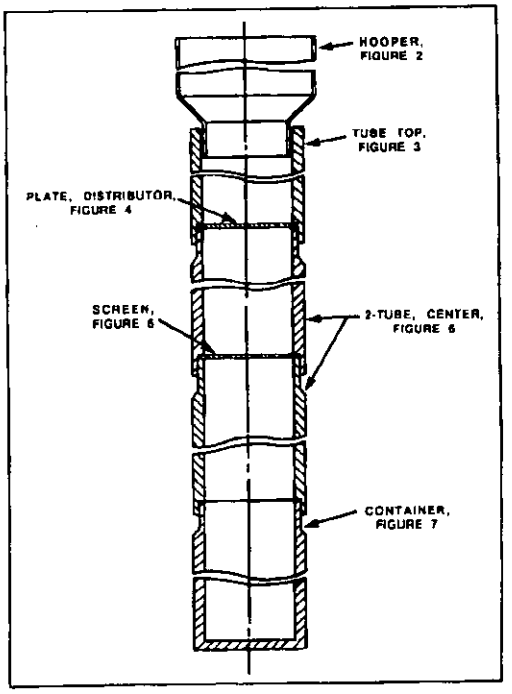


Figure 1. *Standard packing density determination, assembly.*

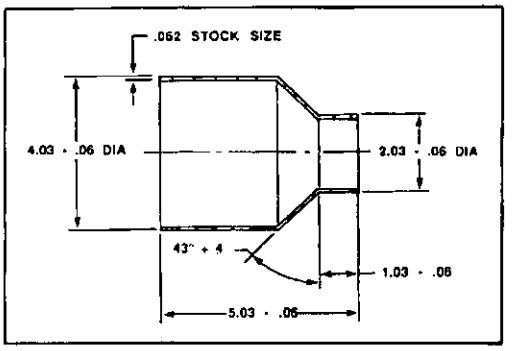


Figure 2. *Hopper.*

NOTES:
1. SPEC MIL-A-2250 applies.
2. Material - brass, any type, except soft.
3. Surface finish √125 all over.
4. This item may be made from an optional No. of pieces. (See note 5)
5. Braze construction permitted.

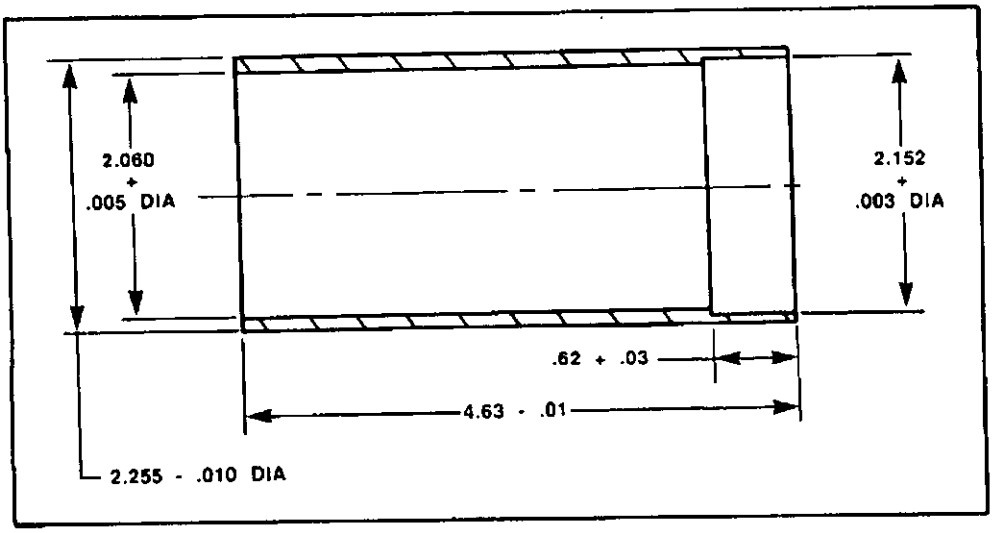


Figure 3. *Top Tube.*

NOTE:
1. SPEC MIL-A-2550 applies.
2. Material - Brass, any type, except soft.
3. Surface finish √125 all over.

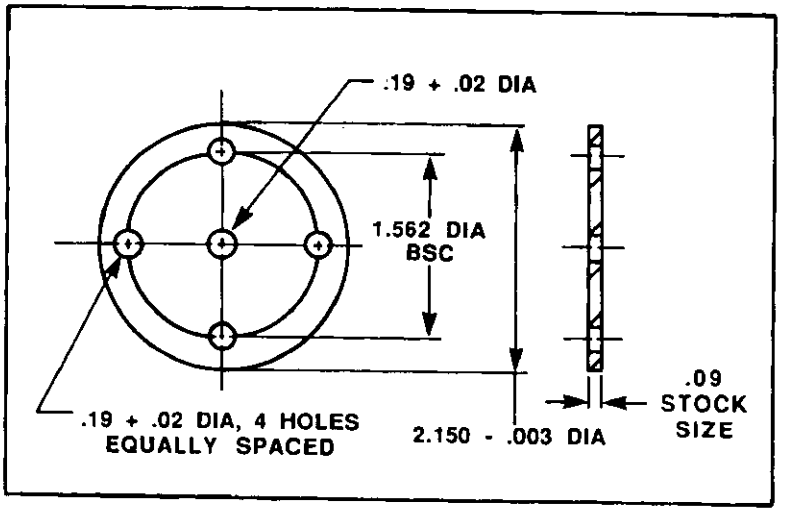


Figure 4. *Distributor Plate.*

NOTE:
1. SPEC MIL-A-2550 applies.
2. Material - Brass, any type, except soft
3. Surface finish √125 all over.

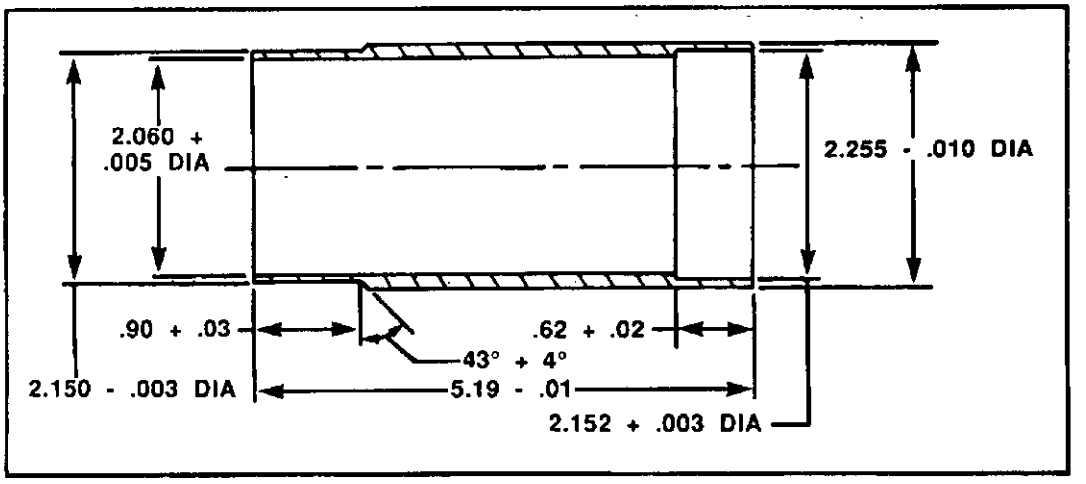


Figure 5. *Center Tube.*

NOTE:
1. SPEC MIL-A-2550 applies.
2. Material - Brass, any type, except soft.
3. Surface finish √125 all over.

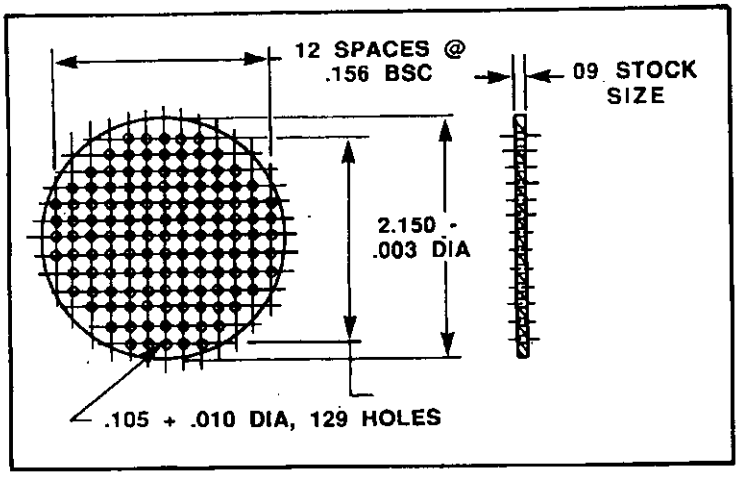


Figure 6. *Screen.*

NOTE:
1. SPEC MIL-A-2550 applies.
2. Material - Brass, any type, except soft.
3. Surface finish √125 all over.

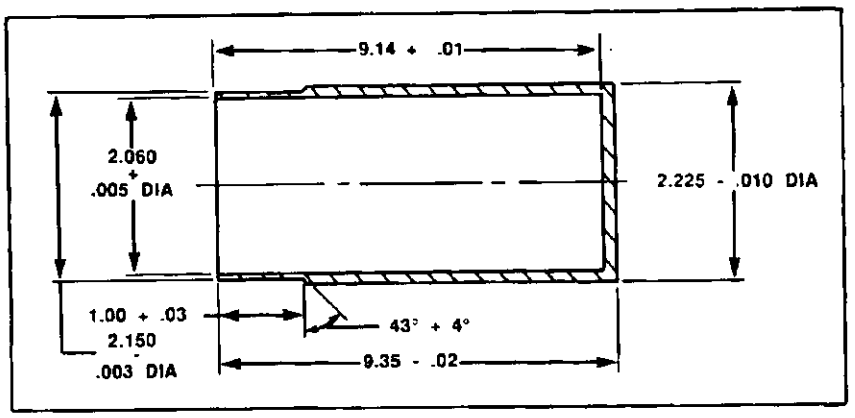


Figure 7. *Container.*

NOTE:
1. SPEC MIL-A-2550 applies.
2. Material - Brass, any type, except soft.
3. Surface finish √125 all over.
4. Optional two piece braze construction permissible.
5. The dimensions should be determined at 70 ± 5°F.
6. The exact internal diameter and internal length shall be stamped on bottom of container.

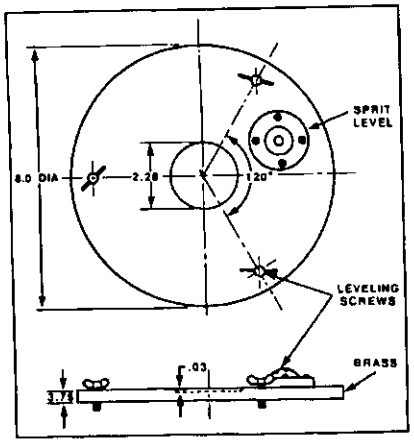


Figure 8. *Base Leveling Plate.*

NOTE:
1. SPEC MIL-A-2550 applies.
2. Material - Brass, any type, except soft.
3. Surface finish √125 all over.

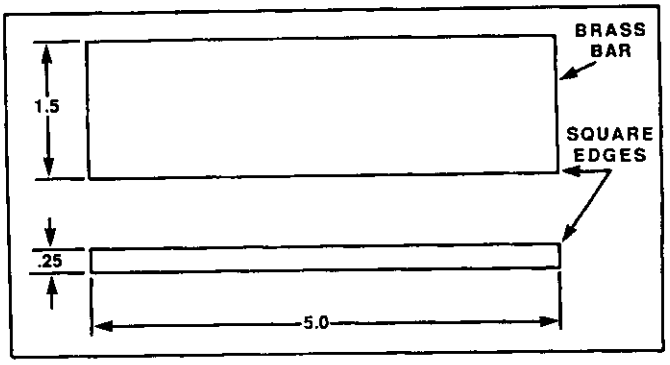


Figure 9. *Brasss Bar.*

NOTE:
1. SPEC MIL-A-2550 applies.
2. Material - Brass, any type, except soft.
3. Surface finish √125 all over.

METHOD 503.1.3

HYGROSCOPICITY, SMALL ARMS PROPELLANTS

1. SCOPE

1.1 The hygroscopicity is estimated by determining the amount of moisture gained or lost when propellant is exposed to high and low relative humidities.

2. SPECIMEN

2.1 Two specimens shall be analyzed; each shall consist of 10 to 15 g of the propellant, weighed to within 0.2 mg.

3. APPARATUS

3.1 Two glass weighing bottles with ground glass covers.

3.2 Desiccator containing sulfuric acid-water solution (59.2 ± 0.5 weight percent) for producing a 20 percent relative humidity at 30°C.

3.3 Desiccator containing sulfuric acid-water solution (18.6 ± 0.5 weight percent) for producing a 90 percent relative humidity at 30°C.

3.4 Oven.

3.5 Desiccator containing an indicating desiccant.

4. PROCEDURE

4.1 Process the two specimens as follows:

a. Place the specimens in separate glass weighing bottles.

b. Place one bottle (minus glass cover) in the desiccator containing the 20 percent humidity-producing solution.

c. Place the other bottle (minus glass cover) in the desiccator containing the 90 percent humidity-producing solution.

d. Place both desiccators in an oven maintained at a constant temperature of 30 ± 2°C.

4.2 Remove the bottles from the oven after 2 days, cover each bottle with its ground glass cover, cool in a desiccator containing the indicating desiccant, and weigh.

4.3 Reweigh the bottles at 2 day intervals until the change in weight (of each bottle) between the weighings is no greater than 0.2 mg.

NOTE: This process usually takes 6 or 7 days.

4.4 Determine the percentage of moisture lost or absorbed by each specimen in its respective storage (relative humidity) condition.

4.5 **Calculation:**

$$\text{Percent hygroscopic moisture} = \frac{100A}{W}$$

Where:

A = loss or gain in weight of weighing bottle and contents at relative humidity (storage condition) used.

W = original weight of specimen used.

4.6 Calculate the hygroscopicity of the propellant by adding the percentages derived in para 4.4 & 4.5.

METHOD 503.2.2

HYGROSCOPICITY, CANNON PROPELLANTS (EQUILIBRIUM METHOD)

1. **SCOPE**

1.1 This hygroscopicity of cannon propellant is estimated by determining the amount of moisture that will be absorbed if the dry propellant is exposed to high humidity.

2. **SPECIMEN**

2.1 Two specimens shall be analyzed; each shall consist of approximately 100 g of the propellant, weighed to within 0.2 mg.

3. **APPARATUS**

3.1 Two glass weighing bottles with ground glass covers.

3.2 Desiccator, 10 liter capacity, containing one liter of sulfuric acid-water solution (18.6 ± 0.5 weight percent) for producing a 90 percent relative humidity at 30°C.

3.3 Desiccator containing an indicating desiccant.

3.4 Oven.

4. **PROCEDURE**

4.1 Process the two specimens as follows:

a. Place the specimens in separate glass weighing bottles.

b. Place each bottle (minus glass cover) in the desiccator containing the 90 percent humidity-producing solution.

c. Place the desiccator in an oven maintained at a constant temperature of 30 ± 2°C.

4.2 Remove the bottles from the oven after 4 days, cover each bottle with its ground glass cover, cool to room temperature in a desiccator containing the indicating desiccant, and weigh.

4.3 Reweigh the bottles each day until the change in weight (of each bottle) between weighings is no greater than 0.2 mg.

4.4 Analyze a sample of the propellant to determine the total moisture content of the propellant as received. Any appropriate moisture method may be used.

4.5 Calculate the hygroscopicity of the propellant.

4.6 **Calculation:**

% hygroscopic moisture = A + B

Where:

A = percentage increase in weight of specimen subjected to 90 % relative humidity.

B = percentage of moisture in the propellant as received.

METHOD 504.1.1

DIMENSIONS OF GRAINS

1. SCOPE

1.1 This method is used for determining the dimensions of granular propellant (figure 1).

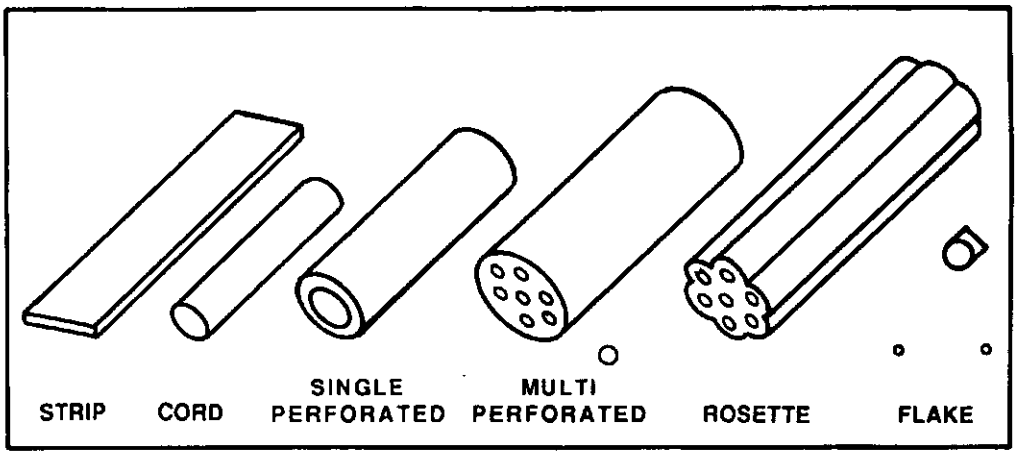


Figure 1. *Forms of propellant grains.*

2. SPECIMEN

2.1 The specimen shall consist of approximately 30 grains of propellant selected at random.

3. APPARATUS

3.2 Micrometer.

3.2 Cutting tool (razor blade or hacksaw).

3.3 Magnifying instrument, such as a microscope or optical comparator, giving suitable magnification (20-25X is usually satisfactory) and equipped with crosshairs, horizontal scale, and vernier screw scale capable of measurement to at least 0.001 inch.

NOTE: The optical comparator must be used with reflected light, in the same manner as the microscope.

4. PROCEDURE

4.1 Length. Measure the length of grains, using the micrometer. Calculate and report the average of these lengths.

NOTE: When the ends of the propellant grains are irregular, determine the average length as closely as possible.

4.2 Grain diameter, perforation diameter, and web thickness. Prepare and measure the grains as follows:

a. With the cutting tool, cut each grain partly through from opposite sides of the approximate midpoint of the grain, and break the grain in two.

NOTE: Multiperforated propellant should be cut so that when broken the narrow ridge left along the line of breakage will pass through the centers of three perforations on the diameter of the grain.

b. Using petroleum jelly or double stick adhesive tape to hold the grains in position, mount one of the halves of each grain on a glass slide so that the broken end of the grain is face up. Mount the slide on the stage of the microscope so that the line of measurement aligns with the edge of the stage.

c. Using the vernier adjustment, measure (in a continuous series of readings along the diameter of the grain) the thickness of the webs, the diameters of the perforations, and the diameter of the grain. Record the individual measurements, and determine the average diameters of the grains and the perforations.

4.3 Length to diameter ratio. Using the average length of the grain (para 4.1) and the average diameter of the grain (para 4.2), calculate the ratio between these averages.

4.4 Length and diameter uniformity. Using the dimensions determined in paragraphs 4.1 and 4.2 calculate the mean variation of the individual dimensions from the mean dimension, and report the variation as a percentage of the mean dimension.

4.5 Grain diameter to perforation diameter ratio. Using the averages from paragraph 4.2, calculate the ratio between the average diameter of the grains and the average diameter of the perforations.

4.6 Web measurements (type 1). Determine the relationship between web dimensions as follows:

a. Using the web measurements obtained in paragrah 4.2, calculate the average thickness of the outer webs (Wo, figure 2) and of the inner webs (Wi).

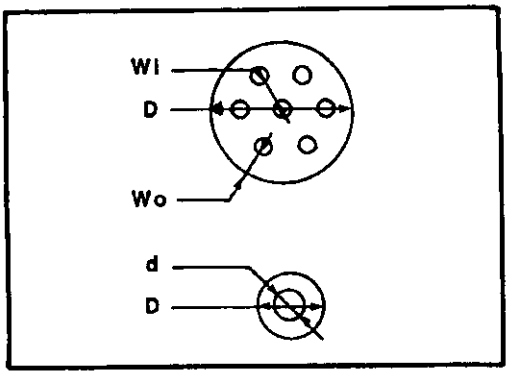


Figure 2. *Propellant grain cross section dimensions.*

b. Using these average web thicknesses (Wo and Wi), calculate the average web thickness (Wa).

c. Determine the difference between the average inner and outer web thicknesses (Wi and Wo), and calculate the difference in terms of the average web thicknesses (Wa):

d. **Calculation:**

$$\text{Percent Difference} = \frac{100\,(W_o - W_i)}{Wa} \quad \text{or} \quad \frac{100\,(W_i - W_o)}{Wa}$$

4.7 Web measurements (type II). Determine the relationship between web dimensions as follows:

a. Using the web measurements obtained in para 4.2, determine the median thickness of all webs.

b. Calculate the average thickness of all webs above the median, and of all webs below the median.

c. Calculate the percentage by which each of the averages differ from the average of all web measurements (Wa).

4.8 **Web calculation (W_c):**

$$W_c = \frac{D - (X - 1)\,d}{X}$$

Where:

D = outside diameter of grain

X = the number of webs measured in 4.2

d = the diameter of the perforation determined in para 4.2

W_c = the calculation web

METHOD 504.2.1

DIMENSIONS OF GRAINS AFTER QUICK SHRINKAGE (SINGLE BASE PROPELLANTS)

1. SCOPE

1.1 This method is used for determining the dimensions of grains of single-base propellants that have been pretreated in a vacuum oven and dried.

2. SPECIMEN

2.1 The specimen shall consist of at least 60 g of the propellant.

3. APPARATUS

3.1 Vacuum oven

3.2 Drying oven.

4. PROCEDURE

4.1 Air-dry the specimen for approximately 24 hours at a temperature of 30 ± 2°C.

4.2 Heat the specimen for approximately 12 hours in a vacuum oven set at 55 ± 2°C, with vacuum maintained at 25 inches of mercury (635 mmHg)

NOTE: 1 inch of Hg (15.6°C) = 3.4 kPa

4.3 Dry the specimen in an oven set at 100 ± 2°C for four hours.

4.4 Cool the specimen in the open air to room temperature.

4.5 Measure the propellant grains and calculate the relationship between these dimensions in accordance with procedures described in Method 504.1.1

METHOD 504.3

DIMENSIONS OF SHEET PROPELLANT (INCREMENT PROPELLANT)

1. SCOPE

1.1 This method is used for determining the dimensions of propellant sheets, including the lengths of sides, thicknesses, perforation diameters, and distances between perforations.

2. SPECIMEN

2.1 The specimen shall consist of two sheets from each of several increments of the propellant selected at random.

NOTE: Use the same sheets for all measurements and calculations.

3. APPARATUS

3.1 Scale, steel.

3.2 Micrometer.

3.3 Microscope, 25 diameters magnification, equipped with cross hairs, and having a horizontal scale and vernier screw scale capable of accurate measurement to at least 0.001 inch.

4. PROCEDURE

4.1 Length of side. Select one of the sheets from each increment, and measure the lengths of all sides of each sheet, using the steel scale. Calculate and report the average length of all sides measured.

4.2 Thickness. Select two sheets from each increment, and measure the thicknesses, using the micrometer. Calculate and report the average of these thicknesses.

4.3 Diameter of perforation. Select one of the sheets from each increment, and using the microscope, measure the diameter of the perforations along two axes at right angles to each other. Calculate and report the average diameter of the perforations.

4.4 Distance between perforations. Select one of the sheets from each increment, and using the microscope, measure the distance between the centers of double-perforated increments or the distance between the center of the central perforation and each corner perforation of multiperforation increments.

NOTE: The distance between centers may be calculated by adding the width of the web between the perforations to one-half of the sum of the diameters of the two perforations.

METHOD 504.4

CASTING POWDER DIMENSIONS

1. SCOPE

1.1 This method is used for determining the dimensions of casting powder granules through a microscope with a calibrated ocular scale or with a moving stage micrometer.

1.2 Measurements are made on granule cut length and diameter. Cut length is that distance between the two points of entry of the cutting blade. The cut length differs from the overall length of the grain due to tails caused by a cut that is not perpendicular to the axis of the grain.

1.3 The approximate limitations for the instruments used to measure casting powder granule dimensions are listed in Table 1. Casting powder granules greater than one half inch in length or diameter can be measured with a micrometer. Granule dimensions of one inch or greater can be measured by rule with 1/64 inch (0.015625 inches) divisions or by a caliper with 0.039 inch per division.

2. SPECIMEN

2.1 A random sample of 100 granules shall be selected from a lot of casting powder. The sample shall be mixed into a composite sample.

3. APPARATUS

3.1 Micro slides. Sciglaso, 75 x 25 mm or equivalent.

3.2 Microscope. Several types are capable of being used. Should have suitable scale eyepiece or mechanical stage. Magnifications and range of measurements as shown in Table 1.

3.3 Micro-Projector. Bausch & Lomb Illuminator Triple Purpose, Type 42-63-58, or equivalent.

3.4 Optical Comparator. Table or Pedestal Measuring Instrument, Magnification and range of measurements as shown in Table 1.

4. CALIBRATION OF OCULAR SCALE

4.1 Microscope. Calibrated Ocular Scale. Mount the calibrated micro slide on the stage of the microscope. Adjust the microscope to the magnification range per granule limitations shown in Table 1.

4.2 Calibrate the ocular scale in accordance with the following procedure.

4.2.1 While looking through the ocular eyepiece, position the micro slide in the field of view with its calibrated markings parallel to but not overlapping those of the ocular scale.

4.2.2 Accurately align one end of the micro slide scale with the beginning of the ocular scale. View the alignment several times to minimize error.

4.2.3 Then find the last visible line on the ocular scale which exactly coincides with a line on the micro slide.

4.2.4 The number of lines on the ocular scale that coincide with the calibrated micro slide is dependent upon the magnification.

4.2.5 Carefully count and record the number of ocular scale divisions that exist between the two alignments.

4.2.6 Calculate the value for each division on the ocular scale, calibration factor (F), as follows:

$$\text{Factor} = \frac{\text{(No. of div.) (Value per div. of micro slide)}}{\text{(No. of div. of ocular scale)}}$$

5. PROCEDURE

5.1 Randomly select a minimum of 40 granules from a composite sample of the casting powder lot. Cover one side of two micro slides with pressure sensitive tape or petroleum jelly. One of the taped slides mount a minimum of 20 granules lengthwise for length measurements. On the second taped side mount a minimum of 20 granules for diameter measurement. Place one of the slides on the microscope stage using surface illumination. Position the first granule to be measured directly beneath the ocular micrometer scale. Focus carefully on the surface of the granule and record the number of divisions the granule length or diameter covers on the ocular scale. Repeat this procedure on the remaining granules. Calculate the lengths (L) and diameters (D) of the granules as follows and record:

$$L \text{ or } D = N \times F$$

Where:

N = Number of divisions observed on the ocular scale.

F = Factor to which the ocular scale is calibrated.

L/D = Length to diameter ratio

Where:

L = Average length of the granules.

D = Average diameter of the granules.

5.2 Microscope. Mechanical Measuring Stage. Randomly select a minimum of 20 granules from a composite sample of the casting powder lot. Place a glass microscope slide in the slide holder of the microscope stage. Arrange the granules in a lengthwise position for length measurements. Use surface illumination on the microscope stage. Focus carefully on the surface of the first granule to be measured. Line up the reticule in the eyepiece with one of the edges of the granule by moving the stage with one of the micrometer dials. Record the dial reading. Next, move the stage again with the same dial until the reticule is lined up with the other edge of the granule. Record this dial reading. The difference between the two dial readings is the granule length. Record lengths.

A second 20 granule minimum portion of the powder lot is randomly chosen for the diameter measurement. The granules are arranged on end on the microscope slide. If they are too small to set on end by themselves, they can be set in vaseline or on some pressure sensitive tape. The diameters are then measured in the same manner. Record diameters.

5.3 Micro Projector. The micro projector is calibrated by placing a piece of wire, 0.035 inches diameter, on the stage of the micro projector. Raise or lower the micro projector to a position where the shadow of the wire covers thirty five divisions on the graph paper, eg., K & E No. 359-14, giving the equivalent of 0.001 inch per division as the calibration factor. The micro projector set at this position is ready to measure the casting powder dimension in the range as shown in Table 1.

Randomly select a minimum of 20 granules of casting powder from a composite sample representing a lot. Place the granules, lengthwise, upon the slide coated with oil to prevent granule movement. Place the slide in position on the projector stage and position the shadow of the first granule to be measured upon the graph paper. If necessary make small adjustments to the micro project focus lens to clearly define the granule shadow fringe. Adjust the graph paper so that one axis coincides with one side of the projected shadow. Read the length and diameter of the granule in inches as indicated on the graph paper scale and record to three significant figures. Repeat measurements on the remaining granules without making changes in position of the projector or graph paper. Record lengths and diameters.

5.4 Optical Comparator. Perform the maintenance and operation of the optical comparator in accordance with references 2a and 2b. Calibrate the instrument with the appropriate wire dimensions, magnification setting, and the chart paper scale, in accordance with granule dimension limits as shown in Table 1.

Randomly select a minimum of 20 granules from a composite sample of casting powder representing a lot. Line them up end to end on the stage of the comparator. In measuring each granule, first select the end which has the best cut and align its projected shadow with the reference line on the projector screen. Measure granule length from reference line to cut length (L) by the metric measuring stage or calibrated graph paper. Measure the vertical distance which best represents the granule diameter (D). Proceed to measure and record the same dimensions on the remaining granules.

5.5 **Calculations:**

a. Calculate average length and diameter

b. Calculate L/D ratio

c. Calculate the standard deviation of length and diameter

$$s = \frac{\Sigma(x_i - x)^2}{n-1}$$

Where:

s = standard deviation.

Σ = Sum of squared differences.

x_i= Individual value.

x = Average of individual values.

n = number of individual values.

5.6 References:

a. Microscope calibration. Photomicrography, pages 146-148, D. Van Nostrand Company, Inc. Princeton, NJ.

b. Optical Comparator.

(1) "Precision Measurement in the Metal Working Industry", Volume Two, Syracuse University, Syracuse, New York.

(2) "Setting up and operating Instructions for PC-14 Optical Comparators". Jones and Lamson Machine Company, Springfield, Vermont.

(3) Catalog No. 401, Charts for Optical Comparators", Jones and Lamson Company, Springfield, VT.

TABLE 1. Granule measurements instrument limitations

Instrument	Magnification	Calibration wire (inches)	Length or diameter Granule size, inches Min	Max
Micrometer Microscope	10	(calibrated micro slides or mechanical measuring stage)	0.500	1.000
	28		0.043	0.0430
	35		0.010	0.100
	50			
	60		0.0086	0.0430
	100		0.0043	0.0215
	430		0.0001	0.0050
MicroProjector	100	0.035	0.001	0.150
Optical-Comparator	10	1.000	0.001	1.00
	20	0.500	0.0005	0.500
	31.25	0.320	0.0003	0.320
	50	0.200	0.0002	0.200
	62.5	0.160	0.0002	0.160
	100	0.100	0.0001	0.100
	125	0.080	0.00008	0.080

METHOD 504.5.1

GRAIN DIMENSIONS OF FLAKE PROPELLANT

1. SCOPE

1.1 This method is used for determining the dimensions of flake propellant using a microscope with calibrated eyepiece.

2. SPECIMEN

2.1 The specimen shall consist of approximately sixty (60) grains (flakes) of propellant selected at random.

3. APPARATUS

3.1 Magnifying intrument, such as microscope or optical comparator, giving suitable magnification (20 to 25X is usually satisfactory) and equipped with crosshairs, horizontal scale, and vernier screw capable of measurement to at least 0.0001 inch.

NOTE: The optical comparator must be used with reflected light, in the same manner as the microscope.

3.2 Double coated tape (scotch brand double stick tape, 1/2 x 250, cat. no. 136 or equivalent).

3.3 Fine tipped forceps.

3.4 Microscope slides.

4. PROCEDURE

4.1 Length (thickness).

a. Place a strip of double coated tape on microscope slide.

b. Using a fine tipped forcep, place thirty (30) grains of flake propellant one at a time on edge (i.e, the smooth or cut surfaces are positioned vertically). The flakes are evenly spaced in a row.

c. Measure between the smoothly cut edges midway of each flake. (Care must be taken not to measure jagged edges or shadows which may be around the cut edges of the flake). A–B (see figure 1) indicates the location of the measurements.

4.2 Diameter.

a. Prepare a slide with double coated tape as for the length determination.

b. Using fine tipped forceps position thirty (30) grains of flake propellant on the tape with their flat surfaces horizontal.

c. Measure the diameter of each flake. (Avoid measuring round (jagged) edges or shadows appearing at the circumference). C-D figures 1 indicates the location of measurements.

5.0 CALCULATION

5.1 Determine the average value for the 30 length and 30 diameter measurements.

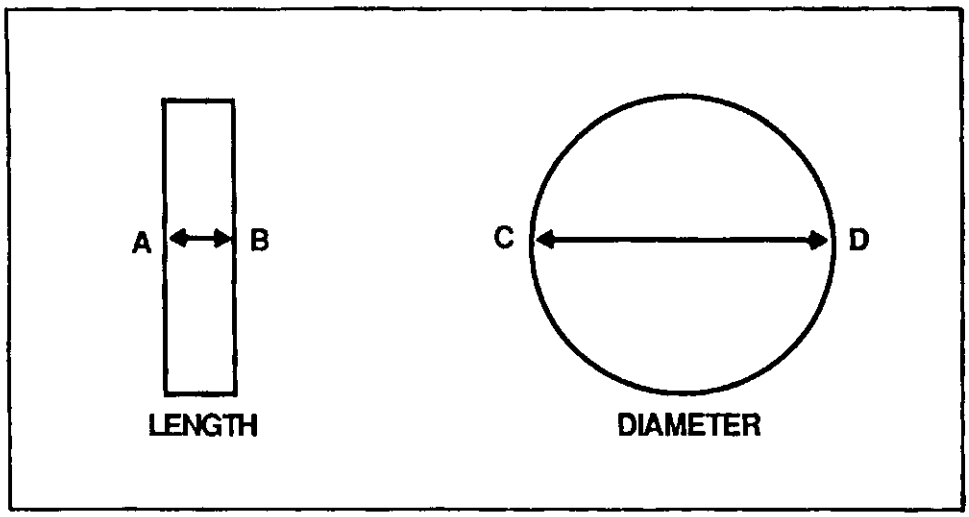


Figure 1. *Dimensions of Flake Cross Section.*

METHOD 504.6.1

DIMENSIONS OF GRAINS (IMAGE ANALYZER)

1. SCOPE

1.1 This method is used for determining the dimensions of granular propellant (figure 1).

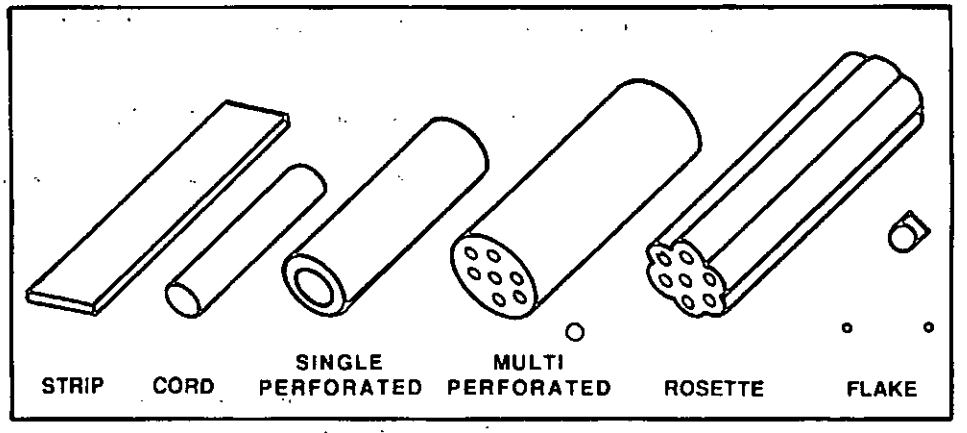


Figure 1. *Forms of propellant grains.*

2. SPECIMEN

2.1 The sample shall consist of a minimum of 30 grains of propellant selected at random.

3. APPARATUS

3.1 Micrometer, capable of measuring to 0.001 inch or better.

3.2 Cutting tool (razor blade or hacksaw).

3.3 Magnifying instrument consisting of one of the following (or equivalent).

a. Microscope or optical comparator with suitable magnification (20 - 30x is usually satisfactory) and equipped with cross hairs, horizontal scale, and vernier screw scale capable of measurement to at least 0.001 inch.

NOTE: The optical comparator must be used with reflected light, in the same manner as the microscope.

b. An image analyzer with closed circuit television (TV) system such as the Leitz Simplex measuring microscope, distributed by the Leitz Co.,Rockleigh, NJ which contains the following parts or subassemblies (or equivalent).

(1) Microscope base (part no. 900-202) with post (part no. 812-920), measuring stage (part no. 812-319), Simplex tv tube (part no. 900-206), objectives (1X, 2X, 3X or as required), non-focusing eye-pieces (6.3X, 10X or as required), and surface illuminator.

(2) ITP 113A Tele-microscope II monitor (part no. 916-000).

(3) ITP 142A electronic micrometer (part no. 916-050), capable of measuring to 0.001 inch.

(4) ITP 148A Tele-microscope II closed circuit TV (part no. 916-019).

(5) ITP 150C-29mm image rotator (part no. 916-063) with ITP 125B control unit (part no. 916-062).

(6) Hewlett-Packard HP9810 or HP9825 desk computer (or equivalent).

(7) Calibrated microscope stage micrometer (for instrument calibration), 0.200 inch minimum scale length with 0.01 inch divisions.

3.4 Microscope glass slides.

4. PROCEDURE

4.1 Length. Measure and record the length of grains to 0.001 inch using the micrometer. Calculate, record, and report the average and standard deviation of these lengths.

4.2 Grain diameter, perforation diameter, and web thickness. Prepare and measure the grains as follows:

a. With a cutting tool, cut each grain partly through from opposite sides at the approximate length midpoint of the grain, and break the grain into two sections.

NOTE: Multiperforated propellant should be cut so that when broken the narrow ridge left along the line of breakage will pass through the centers of three perforations on the diameter of the grain.

b. Using petroleum jelly or double coated tape to hold grains in position, mount one of the halves of each grain on a side so that the broken end of the grain is face up for obtaining measurements.

c. Mount the slide containing the prepared grains on the microscope stage so that the line of measurement aligns with measuring device: eyepiece scale, vernier adjustment or measuring lines on the TV monitor.

d. After selections of magnification, calibrate the equipment using the calibrated microscope stage micrometer. Recalibration will be required if either eyepiece or objective is changed.

NOTE: If the Simplex measuring microscope with closed circuit TV system is used, select eyepieces and objective combination to provide the largest possible image of the grain cross section on the TV monitor without exceeding 2/3 of the screen width.

e. Measure (in continuous series of readings along the diameter of the grain) the thicknesses of the webs, the diameters of the perforations, and the diameter of the grain to 0.001 inch. Record the individual measurements or enter into the programmed computer (if applicable), and determine the average and standard deviation of the diameters of the grains and the perforations.

4.3 Length to diameter ratio. Using the average length of the grain (para 4.1) and the average diameter of the grain (para 4.2), calculate and report the ratio between these averages.

4.4 Length and diameter uniformity. Using the dimensions determined in paragraph 4.1 and 4.2 calculate and report length and diameter uniformity according to the equation below:

a. **Calculation:**

$$\text{Uniformity} = \frac{(\text{Std dev})\ (100)}{\text{Average Value}}$$

4.5 Grain diameter to perforation diameter ratio. Using the averages from para 4.2, calculate and report the ratio between the average diameter of the grains and the average diameter of the perforations.

4.6 Web measurements (type I). Determine and report the relationship between web dimensions as follows:

a. Using the web measurements obtained in para 4.2 calculate the average thickness of the outer webs (Wo, figure 2) and of the inner webs (Wi).

b. Using these average web thicknesses (Wo and WI), calculate the average web thickness (Wa).

c. Determine the difference between the average inner and outer web thickness (Wi and Wo), and calculate and report the percent difference in terms of the average web thicknesses (Wa).

d. **Calculation:**

$$\text{Percent difference} = \frac{100\ (W_o - W_i)}{Wa} \quad \text{or} \quad \frac{100\ (W_i - W_o)}{Wa}$$

4.7 Web measurements (type II). Determine and report the web uniformity as follows:

a. Using the web measurements obtained in paragraph 4.2 determine the average thickness and standard deviation of all webs.

b. Determine the web uniformity according to the equation below.

c. **Calculation:**

$$\text{Web uniformity} = \frac{(\text{Std dev})\ (100)}{\text{Average web thickness}}$$

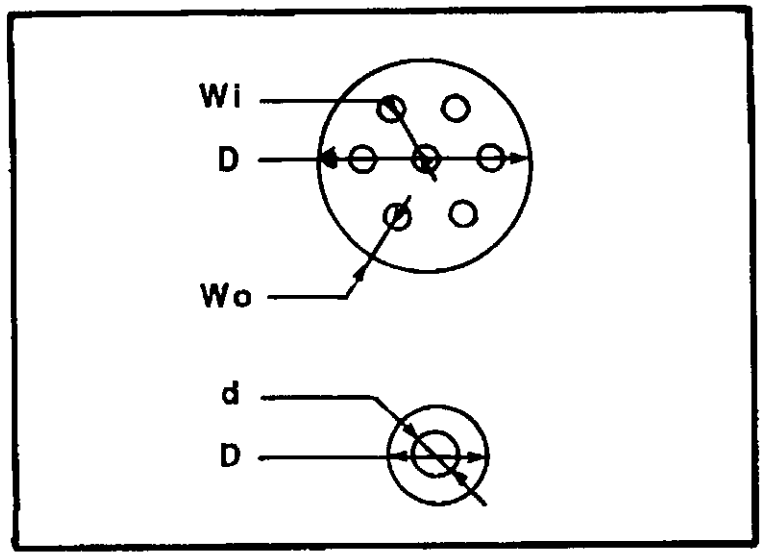


Figure 2. *Propellant grain cross section dimensions.*

METHOD 505.1

COMPRESSIBILITY OF GRAINS

1. SCOPE

1.1 This method is used for determining the percentage of compressibility of propellant grains. It consists of removing both ends of several grains, compressing the center portions until disintegration begins, and calculating the average percentage of compression.

2. SPECIMEN

2.1 The specimens shall consist of ten grains that are representative of the sample. They must be normal in shape, and must contain no obvious flaws.

NOTE: A total of 30 grains should be tested where results are indeterminate.

3. APPARATUS

3.1 Propellant holding device.

CAUTION: The holding device must not score or otherwise leave any visible marks on the central portion of the grain.

3.2 Hand-operated press with parallel jaw surfaces (hydraulic or equal).

3.3 Micrometer caliper (0.25 inch diameter jaws).

3.4 Hacksaw.

3.5 Abrasive (sandpaper, or equivalent).

4. PROCEDURE

4.1 Cut off the ends of each grain so that the length of the central portion is equal (within 0.01 inch) to the diameter of the grain, and so that the ends are perpendicular to the side within 2 degrees. Use the following procedure:

a. Using a micrometer caliper, measure the diameter of the grain.

b. Grip the end to be discarded in the holding device, and cut the grain straight across, using the hacksaw.

c. When both ends have been cut off, grip the central portion with the fingers and slowly rub the end of the grain against an abrasive surface, such as sandpaper.

NOTE: Cutting may be done with a lathe. The cutting tool, however, must not become so warm that it cannot be held with comfort against the back of the hand. Any burr remaining on the grain must be removed by means of an abrasive or a file.

4.2 Allow the grains to reach room temperature within the range of 60 and 100°F (15.6 to 37.8°C). (A temperature of 70 to 80°C is recommended).

4.3 Measure the length of each grain to the nearest 0.001 inch, using the micrometer caliper.

4.4 Center the ends of the grain on the jaws of the press, and slowly compress the grain between the parallel surfaces, increasing the load slowly, until the first crack appears.

NOTE: Cracks can be detected by directing a light beam across the surface of the grain so that the beam is perpendicular to the crack. The first crack, which will appear as a dark line, will probably be in the first light colored area to form as the pressure is increased.

4.5 When the first crack appears, release the pressure, and immediately measure the compressed length to the nearest 0.001 inch.

4.6 Calculate the average compressibility of the grains.

4.7 **Calculation:**

$$\text{Percent compressibility} = \frac{100\,(A - B)}{A}$$

Where:

A = Average length of uncompressed grains.

B = Average length of compressed grains.

METHOD 506.1

GRANULATION

1. SCOPE

1.1 This method is used for determining the percentages of the various size granules comprising a sample of propellant.

2. SPECIMEN

2.1 The specimen shall consist of 50 g of the propellant.

3. APPARATUS

3.1 Set of U.S. Standard sieves with receiving pan.

3.2 Mechanical shaker, geared to produce 300 ± 15 gyrations and 150 ± 10 taps of a striker per minute.

4. PROCEDURE

4.1 Superimpose the sieves of the meshes required by the propellant specification, and attach the receiving pan to the bottom.

4.2 Place the 50 g specimen in the top sieve, mount the assembly on the shaker, and operate the shaker for 5 minutes.

4.3 At the end of 5 minutes, weigh the granules retained in each sieve and in the pan and calculate the percentages of each.

METHOD 507.1

DENSITY OF LOADING

1. **SCOPE**

1.1 This method is used for determining the density of propellant as loaded in cartridge cases.

2. **APPARATUS**

2.1 Funnel.

3. **PROCEDURE**

3.1 With the cartridge case in a vertical position, fill the case with a propellant charge of the weight and at the velocity required by the applicable specification.

NOTE: In the absence of specific requirements, pour the propellant very slowly through the funnel mounted so that the bottom end of the funnel stem is 2 inches from the mouth of the cartridge case, being careful that the propellant strikes the side of the case as little as possible.

3.2 Note the volume of the propellant in the case; empty the case, and weigh the propellant charge.

3.3 Fill the cartridge case with a volume of water at $70 \pm 2^{\circ}F$ ($21.1 \pm 1.1^{\circ}C$) equal to the volume of the charge.

3.4 Divide the propellant weight (in grams) by the volume of water (in milliliters), and report the result as the density of the propellant charge.

METHOD 508.1.3

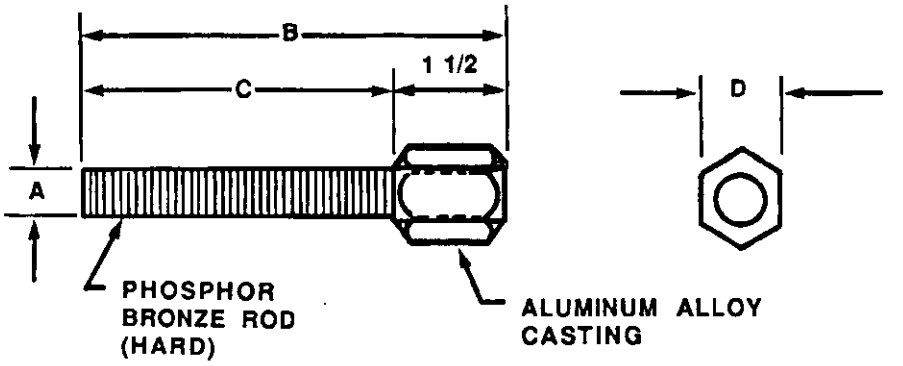
AIRSPACE

1. SCOPE

1.1 This method is used for determining the airspace (in linear inches) for a specific cartridge after a weighed charge has been poured into the case.

2. APPARATUS

2.1 Airspace gage (figure 1) appropriate size for ammunition caliber, preferably made from aluminum. All the dimensions are in inches. The graduations are read with a magnifying glass that may be attached to the gage. The apparatus as used for small caliber ammunition is shown in figure 2.



SPACE GRADUATIONS (0.008 WIDE, 0.01 DEEP) 0.05 APART

FILL WITH BLACK ENAMEL

CALIBER	A	B	C	D
.22	13/64	2 1/2	1	5/8
30 (CARBINE)	19/64	3	1 1/2	3/4
.30	19/64	3 3/4	2 1/4	3/4
.45	27/64	2 1/2	1	1
.50	29/64	5 1/2	4	1
.60	9/16	5 1/2	4	1

Figure 1. *Airspace gage.*

3. **PROCEDURE**

3.1 Set the cartridge case in a vertical position.

3.2 With the stem of the funnel 2 inches above the open end of the case, very slowly pour the weighed propellant charge through the funnel into the case, being careful that the propellant strikes the sides of the case and funnel as little as possible.

3.3 With the cartridge case still in a vertical position, carefully insert the air space gage into the mouth of the case until it rests lightly on the propellant charge. Note the depth of insertion indicated by the graduations on the side of the gage. Use a magnifying glass to read the graduations.

3.4 Determine the seating depth of the bullet.

3.5 Subract the bullet seating depth from the airspace gage reading; the difference is the airpsace (in linear inches).

NOTE: The reported airspace should be based upon the average of at least three determinations.

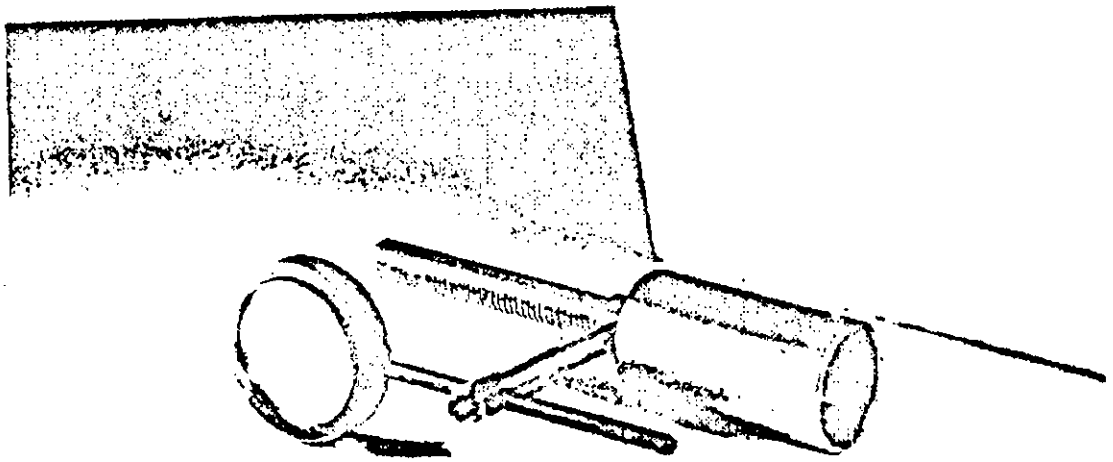


Figure 2. *Typical airspace gage used for smaller caliber ammunition.*

METHOD 509.3

PREPARATION OF PROPELLANT SAMPLES

1. SCOPE

1.1 This method is used for preparing sheet and granular propellant for analysis.

WARNING: Procedures involving grinding should not be used for propellants containing potentially hazardous oxidants, such as chlorates and perchlorates.

2. SPECIMEN

2.1 The specimen shall consist of a portion of propellant selected in accordance with the applicable propellant specification, and weighed in accordance with the test method used.

3. APPARATUS

3.1 Laboratory mill (Wiley, Standard Model No. 2G, or equivalent), equipped with a shield and an explosion-proof motor (class 2).

3.2 Beryllium alloy shears or a razor blade.

3.3 Powder cutter (modified papercutter, preferably with a beryllium alloy blade).

3.4 Glass bottle, stoppered.

4. PROCEDURE

4.1 Sheet propellant. Cut sheet propellant into pieces approximately 1/8 inch square, using razor blade or shears. Place cut propellant immediately in a stoppered glass bottle.

NOTE: If grinding of sheet propellant is specified, the propellant must be brittle. Soft and pliable sheet can be made brittle by chilling the propellant container in an ice bath. Grind sheet propellant as prescribed for small grains (para 4.2).

4.2 Small grain propellant. Grind small grain propellant (0.2 g or less) in the laboratory mill as follows:

a. Prepare the mill for grinding by placing the 20 mesh screen between the grinding chamber and the receiving container, and firmly clamping the rotor cover plate in position.

b. Place the shield in proper position.

c. With motor running, grind a few grains at a time, checking the temperature of the machine between grindings.

WARNING: Allow sufficient time for the rotor and blades to cool before grinding additional samples of the propellant.

d. Place ground propellant immediately in a stoppered glass bottle.

4.3 Large grain propellant. Cut large-grain propellant (grains larger than 0.2g) into slices approximately 0.17 mm thick, using the powder cutter. Cut these slices into pieces approximately 1/8 inch square. Place cut propellant immediately in a stoppered glass bottle.

NOTE: For solvent extractive matter determination, grind the slices as prescribed for small grains (para 4.2).

METHOD 510.1.1

SPECIFIC GRAVITY (PYCNOMETER METHOD)

1. SCOPE

1.1 This method is used for determining the specific gravity of propellants by comparing the density of the propellant with the density of water at 15.6°C using a pycnometer.

NOTE: This method contains instructions for analyzing propellants with water insoluble components. Propellants containing water soluble components can be analyzed by substituting for the water medium an appropriate liquid medium in which the propellant components exhibit little or no solubility. However, the specific gravity of the substitute medium at 15.6 / 15.6°C must be known or determined.

2. SPECIMEN

2.1 The specimen shall consist of approximately 10 g of the propellant, weighed to the nearest milligram.

3. APPARATUS

3.1 Pycnometer, 50 ml.

3.2 Source of vacuum

3.3 Rubber tubing (suitable for vacuum line use).

4. PROCEDURE

4.1 Determine the weight of the pycnometer filled with distilled water at 15.6°C as follows:

a. Cool the pycnometer by filling it with recently boiled distilled water that has been cooled to approximately 10°C.

b. Empty the pycnometer, and refill it with more of the cooled boiled distilled water.

c. Insert the thermometer into the pycnometer, using a slow steady motion so as not to trap air bubbles, and so that the capillary in the side arm is full of water, and the level of the water is flush with the ground top of the side arm. Remove any excess water with a piece of filter paper.

d. Allow the pycnometer to stand at room temperature until the thermometer reads exactly 15.6°C. During this period, wipe the assembly dry several times with absorbent paper to remove condensation.

NOTE: Avoid direct contact of the hands with the assembly.

e. When the thermometer reads exactly 15.6°C, place the overflow on the capillary side arm. Wipe the entire assembly dry, paying particular attention to the depression at the rim of the thermometer joint. Weigh the assembly to the nearest milligram.

4.2 Repeat step 4.1 until two weighings agree within 3 mg. Use the average of these two values for the weight of the pycnometer and water.

4.3 Determine the weight of the pycnometer containing the specimen and distilled water at 15.6°C as follows:

a. Place the specimen in the empty pycnometer and add hot. (preferably boiling) distilled water until the pycnometer is approximately three fourths full.

b. Maintain the elevated temperature of the pycnometer contents by immersing the assembly in a vessel containing hot water.

c. Using a rubber tube, connect the neck of the pycnometer to a source of vacuum at approximately 20 inches of mercury (508 mmHg).

d. With vacuum applied, intermittently close off the side arm opening with a finger until no more air is removable from the grain perforations. Disconnect the tubing.

NOTE: If desired, the air bubbles may be removed from the grain perforations by placing the pycnometer and contents in a vacuum desiccator.

e. Carefully fill the pycnometer with additional hot water, and chill the pycnometer and contents to approximately 10°C.

f. Cautiously insert the thermometer into the pycnometer, using a slow steady motion so as not to trap air bubbles, and so that the capillary in the side arm is full of water, and the level of the water is flush with the ground top of the side arm. Remove excess water with a piece of filter paper.

g. Allow the pycnometer to stand at room temperature until the thermometer reads exactly 15.6°C. During this period, wipe the assembly dry several times with absorbent paper to remove condensation.

h. When the thermometer reads exactly 15.6°C place the overflow cap on the capillary side arm. Wipe the assembly dry, with particular attention to the rim of the thermometer joint. Weigh the assembly to the nearest milligram.

4.4 Calculate the specific gravity of the specimen.

4.5 **Calculation:**

$$\text{Specific gravity at } 15.6/15.6^{\circ}\text{C} = \frac{AF}{A + B - D}$$

A = Weight of specimen.

B = Weight of pycnometer and medium.

D = Weight of pycnometer, specimen, and medium.

F = Specific gravity of medium at 15.6/15.6°C.

METHOD 510.2.1

SPECIFIC GRAVITY OF LIQUIDS (WESTPHAL METHOD)

1. SCOPE

1.1 This method is used for determining the specific gravity of liquids by comparing the density of the liquid with the density of water at 20°C, using a Westphal balance.

2. SPECIMEN

2.1 The specimen shall consist of approximately 200 ml of the liquid, or sufficient liquid to fill the cylinder.

3. APPARATUS

3.1 Glass cylinder, approximate diameter 25mm, length 150mm, or equivalent container suitable for use with Westphal balance.

3.2 Ice bath (or other suitable coolant).

3.3 Westphal balance.

4. PROCEDURE

4.1 Shake or stir the specimen thoroughly to ensure a uniform consistency, and transfer it to the glass cylinder.

4.2 Place a thermometer in the cylinder, and suspend the assembly in an ice bath until the thermometer reads approximately 19°C.

4.3 Remove the cylinder from the ice bath and place the cylinder on a Westphal balance. When the thermometer reads 20.0 ± 0.5°C adjust the balance, and record the reading.

4.4 Conduct the standard specific gravity determination of water at the same temperature, and compare the value obtained with the value for specific gravity of water at 20°C cited in the standard tables. (The difference between the two values is the correction factor).

4.5 Algebraically add the correction factor to the value obtained in para 4.3 for the specific gravity of the liquid at 20 /20°C.

METHOD 510.3.1

DENSITY (AIR PYCNOMETER METHOD)

1. SCOPE

1.1 This method is used for determining the density of propellants by comparing the density of the propellant with the density of air, using a pycnometer.

2. SPECIMEN

2.1 The specimen shall consist of approximately 25 g of sample weighed to the nearest 0.01 g.

3. APPARATUS

3.1 Air pycnometer (Beckman Model 980 or equivalent). Simplified schematic diagram shown in Figure 1.

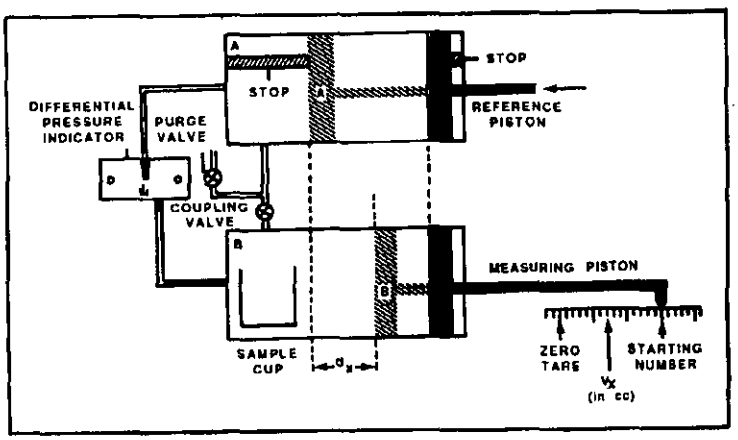


Figure 1. *Simplified schematic diagram.*

4. MATERIALS

4.1 Solid objects of known volume for calibration of the pycnometer.

5. PROCEDURE

5.1 Determine the volume of the weighed specimen as directed by the operating instructions supplied with the air pycnometer.

5.2 Calculate the density of the sample.

5.3 **Calculation:**

$$\text{Density} = \frac{M}{W}$$

Where: M = Weight of the specimen, g.
V = Volume of the specimen, ml.

METHOD 511.1

GRAINS PER POUND

1. SCOPE

1.1 This method is used for calculating the number of grains per pound of granular propellant.

TABLE 1. Grain count

Single grains, grams	Grains to be weighed
0.001 to 1.0	200
1.0 to 5.0	100
5.0 to 10.0	50
10.0 to 20.0	25
20.0 to 40.0	10

2. PROCEDURE

2.1 Weigh a single grain of the propellant to the nearest milligram.

2.2 On the basis of the single grain weight, count out the number of grains prescribed in Table 1.

2.3 Weigh the grains to the nearest milligram.

2.4 Calculate the number of grains per pound of propellant.

2.5 **Calculation:**

$$\text{Grains per pound} = \frac{453.6A}{W}$$

Where:

A = Number of grains weighed.

W = Weight of number of grains weighed, grams.

METHOD 601.1.1

TITANOUS CHLORIDE (0.2N STANDARD SOLUTION)

1. SCOPE

1.1 This method is used for the preparation of a 0.2N standard solution of titanous chloride, using as a base either a titanous chloride solution or titanium hydride.

2. APPARATUS

2.1 Storage system (figure 1) consisting essentially of:

a. Solution bottle, clear borosilicate glass painted black.

b. Kipp generator for maintaining a protective atmosphere of carbon dioxide.

NOTE: A cylinder of inert gas may be used. However, a special pressure release valve must be installed so that the pressure on the buret and on the storage bottle is approximately equal to prevent gassing of the solution in the buret.

c. Buret, 50 ml.

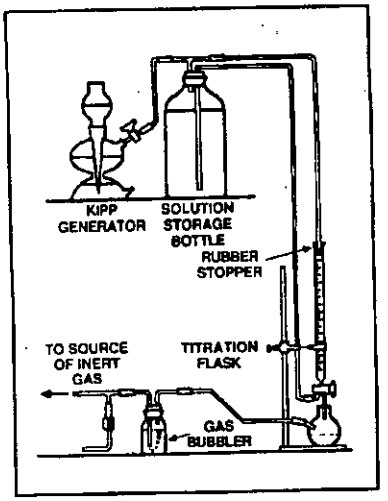


Figure 1. *Storage system.*

2.2 Titration flask, (figure 2).

2.3 Filter paper, Whatman No. 41, fluted.

2.4 Hotplate in a well ventilated hood.

3. MATERIALS

3.1 Titanous chloride, 20 percent solution or titanium hydride.

3.2 Hydrochloric acid, 38 percent solution.

3.3 Inert gas (carbon dioxide or nitrogen), highest purity, oxygen-free.

3.4 Potassium dichromate, National Bureau of Standards Sample No. 136, dried for two hours at 100°C.

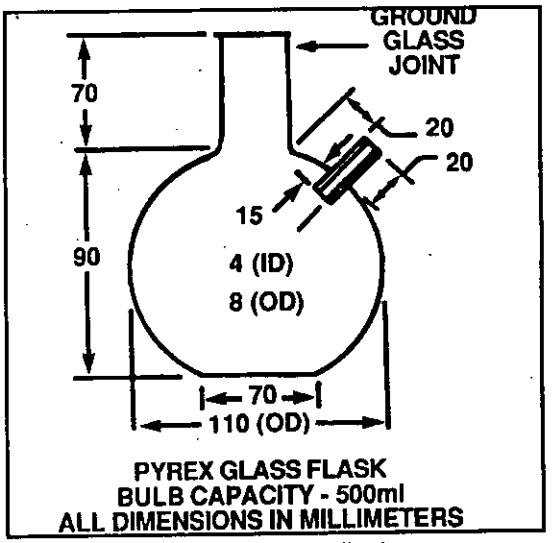


Figure 2. *Titration flask.*

3.5 Sulfuric acid, 10 percent solution.

3.6 Barium diphenylamine sulfonate indicator solution, as specified in Method 708.1.

NOTE: Sodium diphenylbenzidine sulfonate indicator solution, specified in Method 707.1, may be used as an alternative, and will produce essentially the same end-point color in the titration process. However, in case of dispute, use the barium diphenylamine sulfonate solution.

3.7 Ammonium thiocyanate indicator solution, 20 percent, as specified in Method 706.1

4. PROCEDURE

4.1 Prepare the 0.2N solution from 20 percent titanous chloride solution as follows:

NOTE: The proportions given in the following procedure will yeild one liter of solution. Normally 18 liters are prepared at one time.

a. Mix 150 ml of the 20 percent titanous chloride solution with 100 ml of 38 percent hydrochloric acid. Dilute to 1 liter with distilled water.

b. Mix the solution thoroughly by passing a current of oxygen free inert gas through it.

c. If necessary, filter the solution through No. 41 Whatman filter paper until the filtrate is completely clear.

d. Agitate the solution thoroughly with the inert gas for a few minutes, and store the solution in the black bottle. Maintain the inert atmosphere during storage, using the apparatus shown in figure 1.

4.2 Prepare the 0.2 N solution from titanium hydride as follows:

a. For each liter of solution required, warm l00ml of 38 percent hydrochloric acid to 70 to 80°C on a hotplate in a well ventilated hood.

b. For each liter of solution required use 12 g of titanium hydride.

CAUTION: This reaction must be conducted in a hood. Add the titanium hydride to the acid in small portions to avoid excessive frothing. Remove all sources of heat since hydrogen is evolve which is flammable and explosive. External heat is unnecessary since the heat of the reaction will maintain the desired temperature.

c. Add approximately 250 ml of oxygen free distilled water, and mix the solution thoroughly for 5 to 10 minutes by passing a current of oxygen free inert gas through it.

d. Filter the solution through the filter paper until the filtrate is completely clear.

g. Add 100 ml of the 38 percent hydrochloric acid dilute the solution to one liter with oxygen free distilled water.

f. Agitate the solution with the inert gas, and store as described in para 4.1.

4.3 Standardize the solution as follows:

a. Attach the source of inert gas to the titration flask, and allow the gas to flow for 5 minutes to displace the air in the flask. Continue the flow of gas through the flask throughout the entire titration procedure.

b. Transfer to the titration flask 0.3 to 0.4 g of potassium dichromate, weighed to within 0.2 mg and dissolve in 100 ml of distilled water.

c. Add 50 ml of 10 percent sulfuric acid solution.

d. Titrate the solution with the 0.2N titanous chloride solution, until near the end point, as shown by the change in color to green.

NOTE: The change in color is from brownish purple to purple, and to a distinct green.

e. Add five drops of the barium diphenylamine sulfonate indicator solution, and continue the titration until the end point is reached, as shown by the appearance of a light green color, which does not change to a light blue color for at least 30 seconds.

NOTE: The light green color will change to light blue upon standing.

4.4 Make a blank determination to correct for the presence of iron as follows:

a. Add 5 ml of the 20 percent ammonium thiocyanate indicator solution to the flask. If iron is present, a ferric thiocyanate complex will form and the solution will change from light blue to deep red.

b. Back titrate the ferric thiocyanate complex with the 0.2N titanous chloride until the light blue color reappears.

4.5 Determine the milliliters of titanous chloride solution required to complete both the titration and the back titration. Add the two values and apply buret and temperature corrections.

4.6 Calculate the normality of the titanous chloride solution.

4.7 **Calculation:**

$$\text{Normality of titanous chloride} = \frac{A}{0.04904\ B}$$

Where:

A = Potassium dichromate, g.

B = Titanous chloride (including iron blank, temperature, and buret corrections), ml.

METHOD 602.1

SODIUM THIOSULFATE (0.2N STANDARD SOLUTION)

1. SCOPE

1.1 This method is used for the preparation of 0.2N standard solution of sodium thiosulfate.

2. APPARATUS

2.1 Iodine titration flasks, 250 ml

2.2 Solution bottle, low actinic borosilicate glass (or clear borosilicate glass painted black).

2.3 Buret, 50 ml.

3. MATERIALS

3.1 Sodium thiosulfate pentahydrate.

3.2 Sodium cabonate.

3.3 Hydrochloric acid, IN solution.

3.4 Potassium iodide, 15 percent solution (iodate free).

3.5 Potassium dichromate, National Bureau of Standards Sample No. 136, dried for 2 hours at 100°C.

3.6 Starch indicator solution as specified in Method 701.1.

4. PROCEDURE

4.1 Prepare the 0.2N solution of sodium thiosulfate as follows:

a. For each liter of solution desired, dissolve 52 g of sodium thiosulfate pentahydrate and 0.1 g of sodium carbonate in sufficient freshly boiled and cooled distilled water to make one liter.

b. Allow the solution to stand for at least 24 hours before standardization and use.

4.2 Standardize the solution as follows:

a. Dissolve 0.20 to 0.23 g of the potassium dichromate (weighed to within 0.2 mg) in 60 ml of distilled water.

b. Add 10 ml of the potassium iodide and 20 ml of the 1 N hydrochloric acid solution.

c. Stopper the flask, swirl the contents for a few seconds, and allow the flask to stand in the dark for 10 minutes.

d. Titrate the contents of the flask with the sodium thiosulfate solution (swirling continuously) until a light greenish brown color appears.

e. Add 5 ml of the starch indicator solution, and continue the titration until the deep blue starch iodide color changes to a pale bluish green.

4.3 Apply buret and temperature corrections, and calculate the normality of the sodium thiosulfate solution.

4.4 **Calculation:**

$$\text{Normality of sodium thiosulfate solution} = \frac{A}{0.04904\ B}$$

Where:

A = potassium dichromate, g.

B = Sodium thiosulfate, ml.

METHOD 603.1

FERRIC AMMONIUM SULFATE (0.15N STANDARD SOLUTION)

1. SCOPE

1.1 This method is used for the preparation of a 0.15N standard solution of ferric ammonium sulfate. (The normality of this solution remains constant indefinitely).

2. APPARATUS

2.1 Beaker, 600 ml.

2.2 Cylinder graduated, 1000 ml.

2.3 Filter paper, Whatman No. 1 or equivalent.

2.4 Titration flask (figure 1).

2.5 Buret.

2.6 Solution bottle, borosilicate (part no MS36548-3).

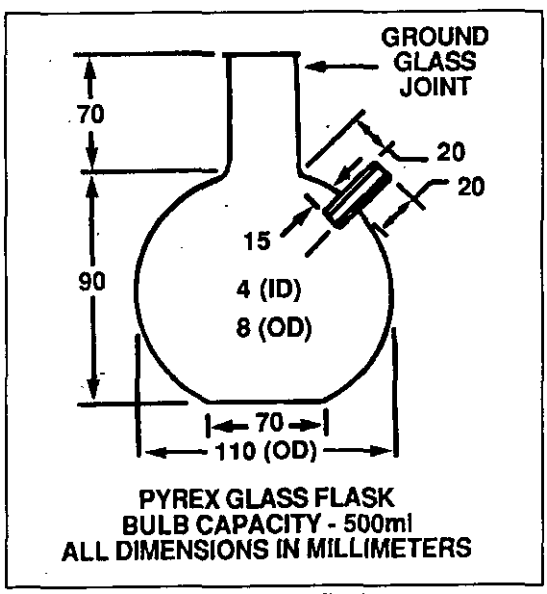


Figure 1. *Titration flask.*

3. MATERIALS

3.1 Hydrated ferric ammonium sulfate.

3.2 Sulfuric acid, 95 percent. Figure 1.

3.3 Hydrochloric acid, 15 percent.

3.4 Ammonium thiocyanate, 20 percent solution as specified in Method 706.1.

3.5 Titanous chloride, standard 0.2N solution as specified in Method 601.1, freshly standardized.

3.6 Inert gas (carbon dioxide or nitrogen), highest purity, oxygen free.

4. PROCEDURE

4.1 Prepare the solution as follows:

a. Pour 400 ml of distilled water into a 600 ml beaker, and add 75 g of hydrated ferric ammonium sulfate and 25 ml of the 95 percent sulfuric acid solution.

b. Transfer the solution to a 1000 ml graduated cylinder, and dilute to capacity with distilled water. Mix thoroughly by passing a current of air through the solution.

c. Filter the solution through the Whatman No. 1 filter paper.

4.2 Standardize the solution as follows:

a. Attach a source of inert gas to the titration flask, and allow the gas to flow gently for 5 minutes to displace the air in the flask. Continue the flow of gas through the flask throughout the titration.

b. Transfer an accurately measured portion of 40 to 45 ml of the ferric ammonium sulfate solution to the titration flask.

c. Add 15 ml of the 15 percent hydrochloric acid solution.

d. Titrate with newly standardized 0.2N titanous chloride solution until near the end point.

e. Add 5 ml of the ammonium thiocyanate solution, and continue the titration until the red color just disappears.

4.3 Apply temperature and buret corrections to the observed readings, and calculate the normality of the ferric ammonium sulfate solution.

4.4 **Calculation:**

$$\text{Normality of ferric ammonium sulfate} = \frac{AN}{B}$$

Where:

A = Titanous chloride solution, ml.

B = Ferric ammonium sulfate solution used, ml.

N = Normality of titanous chloride solution.

METHOD 604.1.1

FERROUS AMMONIUM SULFATE (0.7N SOLUTION)

1. SCOPE

1.1 This method is used for the preparation of a 0.7N solution of ferrous ammonium sulfate.

2. APPARATUS

2.1 Storage system (See figure 1, Method 601.1.1) consisting essentially of:

a. Solution bottle, clear borosolicate glass painted black.

b. Kipp generator.

c. Buret, 50 ml.

2.2 Titration flask (figure 1).

2.3 Reflux condenser.

2.4 Hotplate, three heat control

2.5 Pipette, 25 ml

3. MATERIALS

3.1 Ferrous ammonium sulfate hexahydrate.

3.2 Sulfuric acid, concentrated (1.84 specific gravity).

3.3 Inert gas (nitrogen or carbon dioxide).

3.4 Iron filings.

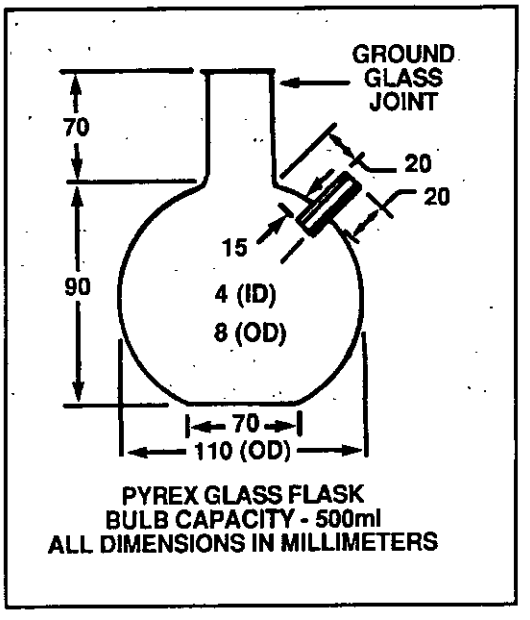


Figure 1. *Titration flask.*

3.5 Hydrochloric acid, 15 percent solution.

3.6 Glacial acetic acid.

3.7 Ammonium thiocyanate, 20 percent solution as specified in Method 706.1.

3.8 Titanous chloride, 0.2N standard solution as specified in Method 601.1

4. PROCEDURE

4.1 For each liter of solution, dissolve 275 g of ferrous ammonium sulfate hexahydrate in approximately 800 ml of distilled water, add 70 ml of the concentrated sulfuric acid and dilute to one liter with distilled water.

4.2 Mix the solution thoroughly with a current of inert gas, and store in the black coated bottle (para 2.1) under an inert gas atmosphere.

4.3 Before storing the solution (and daily thereafter) run a blank determination on 25 ml of the solution for the presence of ferric ion. If more than 0.5 ml of 0.2N standard solution of titanous chloride is necessary to reduce the ferric ion present, add iron filings and warm the solution. The blank determination is conducted as follows:

a. Attach a source of inert gas to the titration flask (figure 1) and allow the gas to flow gently for 5 minutes to displace the air in the flask. Continue the flow of gas through the flask throughout the remainder of the determination.

b. Add accurately measured portions of 25 ml of the 0.7N ferrous ammonium sulfate solution, 25 ml of the 15 percent hydrochloric acid solution, and 25 ml of glacial acetic acid.

c. Attach the flask to the reflux condenser, and boil the solution gently for 5 minutes on the hotplate. Then, without disconnecting the condenser, remove the flask from the hotplate.

d. Increase the current of inert gas (to keep air from entering the flask during cooling), and cool the solution to room temperature by immersing the flask in cold water. Then disconnect the condenser.

e. Add 5 ml of 20 percent ammonium thiocyanate solution, then titrate the contents of the flask with 0.2N titanous chloride solution until the deep red color of the ferric thiocyanate complex disappears.

NOTE: This volume of titanous chloride solution (usually 0.3 to 0.5 ml) must be subtracted from subsequent titrations involved in the standard volumetric determination of a nitrate ester.

METHOD 605.1

POTASSIUM BROMATE-BROMIDE SOLUTION

1. SCOPE

1.1 This method is used for the preparation of 0.2N and 0.5N standard solutions of potassium bromate-bromide.

NOTE: These solutions are used in the determination of such propellant constituents as ethyl centralite, diphenylamine and 2 nitrodiphenylamine by volumetric bromination. The 0.2N solution is also used for the periodic standardization of 0.1N standard solution of sodium thiosulfate.

2.0 APPARATUS

2.1 Borosilicate, glass bottle, 1 liter.

3. MATERIALS

3.1 Potassium bromate and Potassium bromide.

3.2 Sodium thiosulfate, 0.2N standard solution as specified in Method 602.1

4. PROCEDURE

4.1 Prepare a 0.2N standard solution of potassium bromate-bromide as follows:

a. Dry the potassium bromate in an oven for 2 hours at 100°C

b. Place 5.6 g of the potassium bromate in a borosilicate glass bottle.

c. Add 30 g of potassium bromide, and enough distilled water to dissolve the bromate.

d. Dilute the solution to one liter with distilled water.

e. Standardize the solution with a newly standardized 0.2N solution of sodium thiosulfate.

4.2 Prepare a 0.5N solution of potassium bromate-bromide as follows:

a. Dry the potassium bromate in an oven for 2 hours at 100°C.

b. Place 13.9 g of the potassium bromate in a borosilicate glass bottle.

c. Add 75 g of potassium bromide, and enough distilled water to dissolve the bromate.

d. Dilute the solution to one liter with distilled water.

e. Standardize the solution with a newly standardized 0.2N solution of sodium thiosulfate.

NOTE: The 0.5N standard solution of potassium bromate-bromide can be kept indefinitely.

METHOD 606.1.1

POTASSIUM PERMANGANATE (0.1N STANDARD SOLUTION)

1. SCOPE

1.1 This method is used for the preparation of a 0.1N standard solution of potassium permanganate.

2. APPARATUS

2.1 Beaker, 600 ml.

2.2 Hotplate.

2.3 Filter crucible chemical porcelain, filter disc if desired, porosity (ignited).

2.4 Buret, 50 ml.

2.5 Solution bottle, low actinic borosilicate glass (or clear borosilicate glass painted black.)

3. MATERIALS

3.1 Potassium permanganate.

3.2 Sodium oxalate, National Bureau of Standards Sample No. 40, dried for 2 hours at 105°C.

3.3 Sulfuric acid solution prepared by adding 50 ml of concentrated sulfuric acid to 950 ml of distilled water, boiling on a hot plate for 10 to 15 minutes; and cooling to room temperature.

4. PROCEDURE

4.1 Prepare the 0.1N solution of potassium permanganate as follows:

a. Dissolve 3.2 to 3.3 g of the potassium permanganate in approximately 300 ml of distilled water for each liter of solution desired.

b. Boil the olution vigorously on the hotplate for 30 minutes.

c. Filter the solution through the ignited filter crucible.

d. Dilute the filtrate to the required volume with freshly boiled distilled water.

e. Let the solution stand at room temperature for at least 12 hours before standardization and use.

4.2 Standardize the solution as follows:

NOTE: This procedure is essentially the method described by Fowler and Bright in The Journal of Research, National; Bureau of Standards, Vol. 15 (1935), page 493.

a. Place 0.3 gm of sodium oxalate in the 600 ml beaker. Add 250 ml of the sulfuric acid solution (para. 3.3) and stir until the oxalate has dissolved.

b. Add 39 to 40 ml of the 0.1N potassium permanganate solution to be standardized at a rate of 25 to 35 ml per minute, while stirring slowly.

c. Allow the solution to stand until the pink color disappears (approximately 45 seconds).

d. Heat the solution to 80 to 90°C., and complete the titration by adding potassium permanganate solution drop by drop, allowing each drop to become decolorized before adding the next. The titration may be considered complete when the faint pink coloration persists for 30 seconds.

4.3 Run a blank determination using exactly the same volume of solutions, omitting the sodium oxalate.

4.4 Calculate the normality of the potassium permanganate solution.

4.5 **Calculation:**

$$\text{Normality of potassium permanganate} = \frac{A}{0.0670\ (B - C)}$$

Where:

A = Sodium oxalate, g.

B = Potassium permanganate solution required for the determination, ml.

C = Potassium permanganate solution required for the blank, ml.

METHOD 607.1

SILVER NITRATE (STANDARD SOLUTIONS)

1. **SCOPE**

1.1 This method is used for the preparation of 0.1N and 0.05N standard solutions of silver nitrate.

2. **APPARATUS**

2.1 Volumetric flask, one-liter (painted black or covered with tape to exclude light).

3. **MATERIALS**

3.1 Silver nitrate, dried for 2 hours at 120°C.

4. **PROCEDURE**

4.1 Dissolve 16.989 g of silver nitrate in distilled water for 0.1N and use half this weight for 0.05N.

4.2 Transfer this solution quantitatively to the volumetric flask, and dilute to the required volume with freshly boiled distilled water.

METHOD 608.1

POTASSIUM THIOCYANATE (STANDARD SOLUTION)

1. SCOPE

1.1 This method is used for the preparation of 0.05 N and 0.1N standard solutions of potassium thiocyanate.

2. APPARATUS

2.1 Volumetric flask, one-liter.

3. MATERIALS

3.1 Potassium thiocyanate.

3.2 Silver nitrate, 0.05 N or 0.1N standard solution as specified in Method 607.1.

4. PROCEDURE

4.1 To prepare a 0.05N solution, dissolve 4.86 g of potassium thiocyanate in distilled water, transfer to the one liter volumetric flask, and make up to volume with distilled water. A 0.1N solution is prepared in exactly the same manner, except that 9.72 g of potassium thiocyanate is used.

4.2 Determine, by titration, the milliliters of silver nitrate solution equivalent to one milliliter of the potassium thiocyanate solution of the same normality.

METHOD 609.1

IODINE (0.02N STANDARD SOLUTION)

1. SCOPE

1.1 This method is used for the preparation of a 0.02N standard iodine solution.

2. APPARATUS

2.1 Borosilicate (or black glass bottle, 5 liter capacity minimum).

NOTE: A colorless borosilicate glass bottle painted black may be used.

3. MATERIALS

3.1 Resublimed iodine.

3.2 Potassium iodide (iodate-free).

3.3 Sodium thiosulfate, 0.2N standard solution as specified in Method 602.1.

3.4 Starch indicator.

4. PROCEDURE

4.1 Place 12.69 g of resublimed iodine in the pyrex amber glass bottle, and add a 25 ml solution consisting of 15 g of potassium iodide and distilled water.

4.2 Triturate the mixture until all the iodine has been dissolved.

4.3 Dilute the mixture to 5 liters with distilled water.

4.4 Standardize the solution with standardized 0.2N sodium thiosulfate solution using a starch indicator.

METHOD 701.1

STARCH INDICATOR SOLUTION

1. **MATERIALS**

1.1 Mercuric iodide.

1.2 Soluble starch (suitable for iodometry): 2g.

1.3 Water, freshly distilled.

2. **PROCEDURE**

2.1 Mix 2 g of the starch and several milligrams of the mercuric iodide (as a preservative) with a little distilled water. Add the mixture slowly to 500 ml of boiling distilled water. Allow the liquid to boil for 5 minutes, then cool to room temperature.

NOTE: This solution should be stable for several weeks.

METHOD 702.1

METHYL RED INDICATOR SOLUTION

1. **MATERIALS**

1.1 Methyl red, 0.1 g

1.2 Ethyl alcohol, 95 percent 100 ml.

2. **PROCEDURE**

2.1 Dissolve the methyl red in the ethyl alcohol, while stirring.

NOTE: This solution is quite stable and should be effective for several months. For the average titration involving 200 to 400 ml of solution, 3 to 4 drops of this indicator are used.

METHOD 703.1

PHENOLPHTHALEIN INDICATOR SOLUTION

1. MATERIALS

1.1 Phenolphthalein, 0.1 g.

1.2 Ethyl alcohol, 95 percent 100 ml.

1.3 Sodium hydroxide, 0.5N solution.

1.4 Hydrochloric acid, 0.5N solution.

2. PROCEDURE

2.1 Dissolve the phenolphthalein in the ethyl alcohol.

2.2 Neutralize the acidity of the alcohol by adding 0.5N solution of sodium hydroxide, drop by drop, until a faint pink color develops, then adding one drop of 0.5N hydrochloric acid solution until the color is just discharged.

METHOD 704.1

METHYL ORANGE INDICATOR SOLUTION

1. **MATERIALS**

1.1 Methyl orange 0.1 g.

1.2 Water freshly distilled: l00 ml.

2. **PROCEDURE**

2.1 Dissolve the methyl orange in the distilled water.

NOTE: This solution should be stable for several months.

METHOD 705.1

FERRIC AMMONIUM SULFATE INDICATOR SOLUTION

1. **MATERIALS**

1.1 Ferric ammonium sulfate 20 g.

1.2 Nitric acid, 70 percent 25 ml.

1.3 Water, freshly distilled 300 ml.

2. **PROCEDURE**

2.1 Dissolve the ferric ammonium sulfate in the distilled water.

2.2 Heat the solution to boiling then add the nitric acid.

2.3 Filter the solution, and store in a borosilicate glass bottle.

METHOD 705.1

FERRIC AMMONIUM SULFATE INDICATOR SOLUTION

1. MATERIALS

1.1 Ferric ammonium sulfate 20 g.

1.2 Nitric acid, 70 percent 25 ml.

1.3 Water, freshly distilled 300 ml.

2. PROCEDURE

2.1 Dissolve the ferric ammonium sulfate in the distilled water.

2.2 Heat the solution to boiling then add the nitric acid.

2.3 Filter the solution, and store in a borosilicate glass bottle.

METHOD 706.1

AMMONIUM THIOCYANATE INDICATOR SOLUTION (20-PERCENT)

1. **MATERIALS**

1.1 Ammonium thiocyanate 20 g.

1.2 Water, freshly distilled: 80 ml.

2. **PROCEDURE**

2.1 Dissolve the ammonium thiocyanate in the distilled water.

CAUTION: This solution must be colorless for use as an indicator.

METHOD 707.1

SODIUM, DIPHENYLBENZIDINE SULFONATE INDICATOR SOLUTION

1. **MATERIALS**

1.1 Sodium diphenylbenzidine sulfonate 0.5 g.

1.2 Water, freshly distilled: 100 ml.

2. **PROCEDURE**

2.1 Dissolve the sodium diphenylbenzidine sulfonate in the distilled water.

METHOD 708.1

BARIUM DIPHENYLAMINE SULFONATE INDICATOR SOLUTION

1. **MATERIALS**

1.1 Barium diphenylamine sulfonate 0.32 g.

1.2 Water, freshly distilled: 100 ml.

2. **PROCEDURE**

2.1 Dissolve the barium diphenylamine sulfonate in the distilled water.

METHOD 709.1

BROMTHYMOL BLUE INDICATOR SOLUTION 0.1 WEIGHT/PERCENT IN ETHANOL

1. **MATERIALS**

1.1 Bromthymol blue, 0.1 g.

1.2 Ethyl alcohol, 1:1, 100 ml.

2. **PROCEDURE**

2.1 Dissolve the bromthymol blue in the ethyl alcohol and filter if necessary.

METHOD 801.1.2

QUICKNESS AND FORCE MEASUREMENT OF PROPELLANT (CLOSED BOMB METHOD)

1. SCOPE

1.1 This method is used for determining the quickness and force of a test propellant, by a relative or an absolute procedure. The relative quickness (RQ) value is defined as 100 times the average of at least four ratios obtained from the rate of pressure rise of the test propellant divided by that of the reference popellant calculated at prescribed pressure points (figure 1). The relative force (RF) is 100 times the ratio of the maximum pressure developed the test and by the reference propellant. When several reference test combinations are fired, the RQ and RF mean, and range are reported.

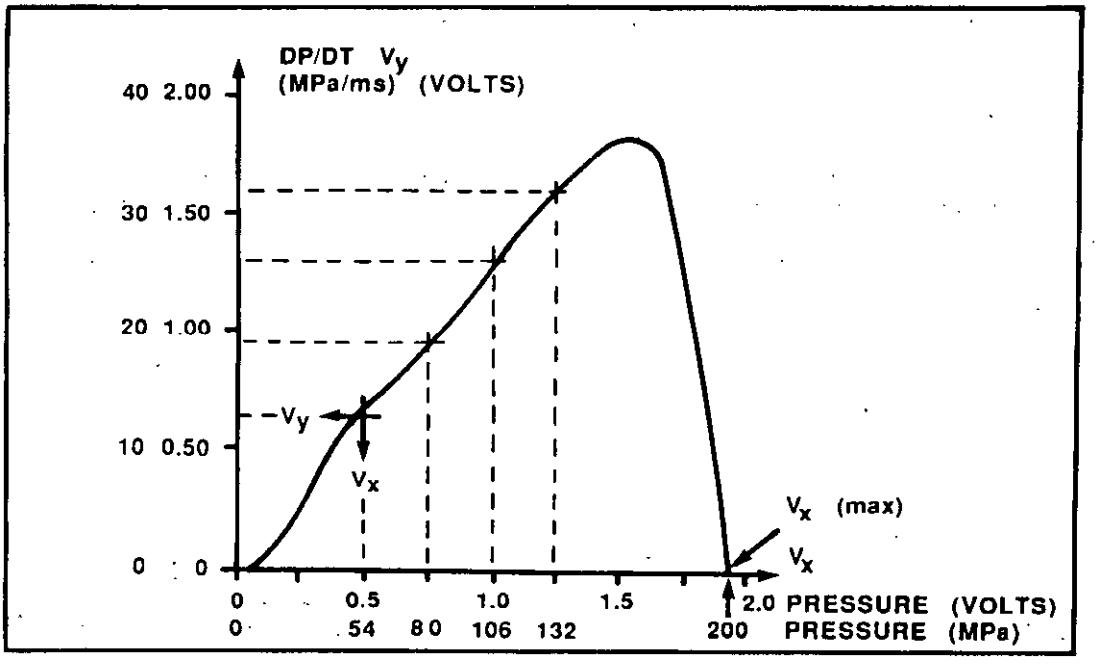


Figure 1. *Rate of Pressure Rise (dp/dt) vs Pressure (p).*

1.2 Absolute quickness (AQ) and absolute force (AF) do not involve a reference propellant and pressure is read in engineering units. AQ is expressed in MPa /millisecond, and is the area under the closed bomb, dp/dt vs p curve. AF is expressed in MPa and is the maximum pressure attained. For several firings, the AQ and AF mean, and range are reported.

2. SPECIMEN

2.1 Peak pressure developed by a test specimen in the closed bomb depends on the loading density, defined as the weight of the sample divided by the volume of the closed bomb. This pressure generally correponds to peak pressures in actual gun systems. The following values are to be used as a guide for propellant. All propellant sample weights shall be accurate within ± 0.05 gram.

Loading Density (grams per cubic centimeter, g/cm3)	Peak Pressure (megapascals, MPa)
0.1	100 – 140
0.2	200 – 275

(One megapascal equals 145.037 pounds per square inch)

3. APPARATUS

3.1 Closed Bomb. Standard bombs are constant volume, thick-walled cylindrical vessels (capable of withstanding gun pressures) with inside diameter from 4.4 to 5.1 cm for the 200 and the 700 cm^3 bombs, and from 7.6 to 8.9 cm for the 2400 cm^3 bomb. The bombs shall be equipped with firing electrodes to effect ignition, a pressure transducer, a gas release valve, and a thermocouple. The bombs shall be surrounded by a temperature controlled water jacket to maintain the required test temperature.

3.2 Data Acquisition system.

3.2.1 The data acquisition system shall consist of a calibrated pressure transducer, an analog to digital converter, and a digital processor. Analog and digital filters wherever employed shall not distort the pressure trace or its derivative. Further extension of the system can include a differentiating circuit, an oscilloscope, and equipment for photographing the dp/dt vs pressure trace. (figure 2.)

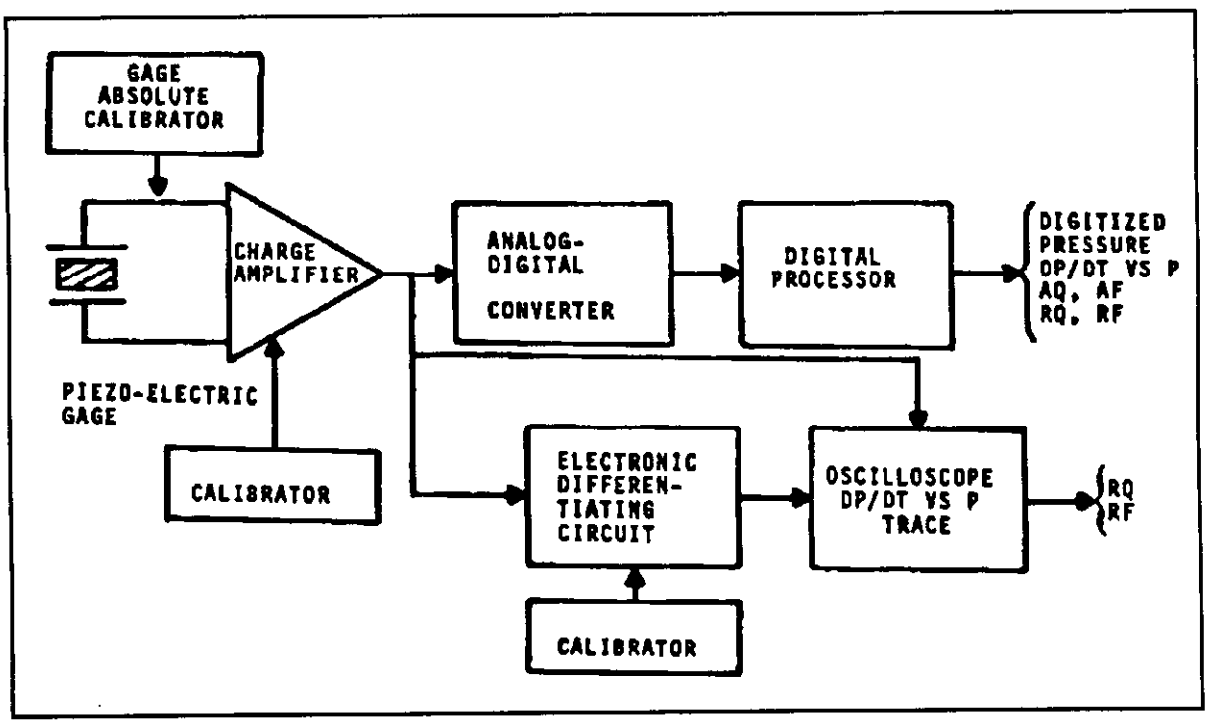


Figure 2. *Closed Bomb Data Acquisition.*

3.2.2 The constant time sampling interval for the pressure signal shall be chosen such that the pressure rise between any two successive samples shall not exceed 10.0 MPa (for 0.2g/cm3 loading density). Numerical method shall be used to both smooth and differentiate the pressure data. The resulting pressure and dp/dt data shall be equivalent to the input to the oscilloscope, thus providing backup in case of equipment failure.

3.3 Pressure transducer.

3.3.1 The pressure transducer shall be piezo-electric type with a frequency response of at least 25 kilohertz and a response to applied pressure which is linear over the test range (0-275 MPa). The transducer shall be calibrated periodically (at least once a month) with a dead weight tester and readout device with an accuracy of 0.1%. If significant changes in gage sensitivity are noted, its use should be discontinued.

3.4 Ignition system.

3.4.1 For the 200 cm^3 bomb, the samples shall be ignited with an electric squib and 0.5 - 1.0 gram of black powder, or a fuze wire with guncotton and one gram of CBI. Heavier charges are used in the larger bombs. A variant ignition system may be substituted subject to the approval of the government.

4. PROCEDURE

4.1 The volume of the closed bomb shall be determined periodically or whenever any component parts are changed. This can be accomplished by filling with water and measuring the volume of the water.

4.2 The bomb and the propellant to be tested shall be conditioned to 21 ± 1°C or to a variant temperature subject to the approval of the government.

4.3 The loading density shall be selected to produce peak pressure in the closed bomb comparable to that obtained in actual gun systems. All propellant sample weights shall be accurate to within ± 0.05 gram. (paragraph 2.1).

4.4 A warm-up shot shall be made prior to the start of the firing series. At least three firings of both the reference and the test samples shall be used for computations. The closed bomb shall be swabbed after each shot.

5. CALCULATIONS

5.1 RQ and RF values by an analog oscilloscope trace shall be obtained by choosing the sensitivity settings of the recording instruments so that the maximum pressure value (Vx max) lies between 1.75 and 2.00 volts. The Vx max (maximum pressure) is the maximum voltage attained along the abscissa. The Vy measurements shall be made at Vx values of 0.50, 0.75, 1.00, and 1.25 volts. Vy is the voltage ordinate reading on a dp/dt vs pressure trace (figure 1). When the traces of the reference and the test propellant are similar in shape, the RQ can be calculated directly from the ratio of the Vy values, and the RF from the ratio of the maximum abscissa voltages.

A sample calculation is shown for 3 reference and 3 test firings:

$$RQ = \frac{1}{m} \sum_{i=1}^{m} \left(\frac{100}{n} \sum_{j=1}^{n} \frac{T_{ij}}{R_{ij}} \right)$$

$$RF = \frac{100}{m} \sum_{i=1}^{m} \left(\frac{T_{pmax\,i}}{R_{pmax\,i}} \right)$$

Where:

m = number of reference or test firings.

n = number of data points per firings = at least 4.

T_{ij} = dp/dt test propellant value of ith firing and jth data point.

R_{ij} = dp/dt reference propellant value of ith firing and jth data point.

$T_{pmax\,i}$ = test propellant maximum pressure for ith firing.

$R_{pmax\,i}$ = reference propellant maximum pressure for ith firing.

$$\text{RQ for lst firing} = \frac{100}{4} \left(\frac{15.065}{14.955} + \frac{21.264}{21.167} + \frac{28.717}{28.110} + \frac{35.694}{35.088} \right) = 101.270$$

$$\text{RQ for 2nd firings} = \frac{100}{4} \left(\frac{15.382}{14.845} + \frac{21.381}{21.174} + \frac{28.841}{27.896} + \frac{35.763}{35.370} \right) = 102.273$$

$$\text{RQ for 3rd firings} = \frac{100}{4} \left(\frac{14.872}{14.803} + \frac{20.988}{20.871} + \frac{28.544}{27.600} + \frac{35.639}{35.177} \right) = 101.440$$

The above values are averaged to obtain the mean relative quickness, RQ = 1001.66. The RQ range is 1.00.

$$\text{RF for 1st firings} = 100 \left(\frac{202.680}{196.798} \right) = 102.989$$

$$\text{RF for 2nd firings} = 100 \left(\frac{204.520}{196.789} \right) = 102.583$$

$$\text{RF for 3rd firings} = 100 \left(\frac{205.624}{200.494} \right) = 102.559$$

The mean relative force becomes, RF = 102.71. The RF range is 0.43.

5.2 RQ and RF values by the direct digital process shall be obtained by the formulas of 5.1, with the four pressure or voltage points chosen to correspond with those used for the oscilloscope. These shall be at approximately 27, 40, 53, and 66% of the peak pressure or peak voltage measured for the reference propellant. Data is smoothed and differentiated as in 3.2.2.

5.3 For analytical investigation of burning properties of propellant lots, an optional reporting method consists of listing the rate of pressure rise in engineering units (MPa/ms) at the following five discrete pressures:

MPa: 7, 14, 21, 28, 35

For the higher pressure range, the average pressure time derivative is given over each of the following 35 MPa intervals:

35 – 70	175 – 210
70 – 105	210 – 245
105 – 140	245 – 280
140 – 175	---------

METHOD 802.1

HEAT OF EXPLOSION (COMBUSTION) (ADIABATIC CALORIMETER METHOD)

1. SCOPE

1.1 The quantity directly measured in this bomb calorimeter procedure is the total or gross heat of explosion or combustion of solid propellants.

1.2 The method can be used to determine the calorific value of the following types of exothermic reactions:

1.2.1 Explosion of self-oxidizing solid propellant formulations in a nitrogen atmosphere.

1.2.2 Combustion of solid or liquid substances requiring an oxygen atmosphere.

1.3 The method involves the burning of a weighed sample in a nitrogen or oxygen filled bomb submerged in a measured quantity of water, all held within an adiabatic chamber.

1.4 The quantity of heat emitted from the burning of the sample is measured by recording the temperature of the water at the beginning and end of the experiment. By accurately measuring the temperature rise in the water, and knowing the water equivalent of the calorimeter, the number of heat units liberated can be calculated. The individual measurements are reproducible to within ± 6.9 calories per gram at 95 present confidence limits.

2. SPECIMEN

2.1 Select a sample weight to give a 1 to 3°C rise in temperature. Weigh the sample to the nearest 0.2 mg into a tared combustion cup. Recommended quantities are, 5.4 grams for double base propellants and a 3 gram load for high energy composites.

3. APPARATUS

Equipment	Description
3.1 Calorimeter Adiabatic Oxygen bomb-type and related equipment or equivalent	Series 1200 or 1241, Parr Instrument Co., Moline, Illinois, or equivalent
3.2 Calorimeter, master controller	Series 2900 or 1680, Parr Instrument Co., Moline, Illinois, or equivalent.
3.3 Calorimeter, bucket filling system	Accuracy ± 0.2 ml with temperature control of ± 0.5°C, Parr No. 1561 or equivalent.

3.4 Thermometer, differential or electronic	
Differential	5°C range, 0.01°C graduation, Beckman Instrument Co., or equivalent.
Electronic	10°C range, 0.001°C resolution, Parr Instrument Co., Moline, Illinois or equivalent.
3.5 Balance torsion	0.2g sensitivity, 5 kg capacity
3.6 Screens Sieves	No. 20 and 50, USA Standard

4. MATERIAL

4.1 Nitrogen	Purified, maximum 0.01 percent oxygen
4.2 Oxygen	Pure
4.3 Benzoic acid pellets	Calorific Standard Quality 1.0 or 0.2 gram size pellets; Parr No. 3413 or 3414, or equivalent.

5. CALIBRATION

5.1 The energy or water equivalent of the bomb calorimeter system is determined by measuring the temperature rise produced in the system by the combustion of a known quantity of standard benzoic acid.

5.2 Accurately weigh to 0.1 mg a specimen of benzoic acid in a tared combustion cup. Place the cup in its holder on the bomb head and bring the fuse wire in contact with the specimen using the procedure described in the manufacturer's manual. Place the assembled bomb head, along with one ml of distilled water in the bomb and screws on the retaining cap.

5.3 Volumetrically fill or tare the calorimeter bucket and fill with 2000 ± 0.2 g of distilled water. Pressurize the bomb with 25-30 atmospheres of oxygen and then submerge it in the calorimeter bucket and attach the ignition wire to the firing terminal of the bomb. Observe the submerged bomb for gas leakage as evidenced by bubbles. Do not fire the bomb if it is leaking.

5.4 Place the calorimeter bucket inside the calorimeter jacket, close the cover and lower the thermometers in position. Turn on the automatic teperature controller and allow ten minutes to establish temperature equilibrium between the bomb bucket and the calorimeter jacket. Record the initial temperature. Fire the charge.

5.5 Allow the temperature in the calorimeter to equilibrate with the temperature in the bomb bucket. (Adiabatic conditions may also be maintained by manual manipulation of the hot and cold water supplies). Record the final maximum temperature when three identical readings have been made at one minute intervals.

5.6 Measure the unburned fuse wire so that the measured heat of combustion may be corrected for the heat contributed by fuse wire. Calculate the water equivalent using the equation given below. Calibrate each calorimeter system monthly.

$$E = \frac{(6318)\ (m) + (C) + (e_1)}{\Delta T}$$

Where:

E = water equivalent of calorimeter in calories per degree centrigrade.

6318 = heat of combustion of standard benzoic acid in calories per gram.

m = weight of standard benzoic acid sample in grams.

C = correction for combustion of fuse wire in calories.

T = temperature rise, in degrees centrigrade, corrected for thermometer error and emergent stem correction.

e_1 = correction for the heat of formation of nitric acid in calories.

5.7 Alternate Method. Activate Parr Master Control Systems for high precision reference method as specified in ANSI/ASTM standard method D2015 with the following steps:

5.7.1 After the operator pushes the start button and enters the three pieces of data needed to start the run, the Master Control shifts to the Pre-period mode and holds in this mode for 5 minutes to obtain a stable temperature in the calorimeter.

5.7.2 At the end of the 5 minutes pre-period the Master Control starts to take and compare temperature readings at 30 second intervals.

5.7.3 When it finds that the temperature has remained constant within 0.001°C for two minutes (5 consecutive readings) it fires the bomb and records the average of these five readings as the initial temperature.

5.7.4 It then checks the temperature 50 seconds after firing. If it observes a temperature rise of at least 0.05° during this period, it assumes that ignition was obtained, and the system then shifts into the Post period mode.

5.7.5 The Master Control now looks for a new equilibrium temperature, again taking the comparing readings at 30 second intervals.

5.7.6 When the temperature has remained constant within 0.001°C for two minutes (5 consecutive readings) it averages these five readings and records the average as the final temperature. This completes the test.

6. PROCEDURE

6.1 Cut high energy cast propellant and high energy propellant into 1/8 inch cubes. (Casting powder will not be ground for this test). Prepare double base propellants in accordance with Method 509.3

6.2 Attach a 10 centimeter length of fuse wire to the elecrodes in accordance with the manufacturer's instructions.

6.3 Select a sample weight to give a 1 to 3°C rise in temperature.

6.4 Weigh the sample to the nearest 0.1 milligram into a tared combustion cup.

6.5 Place the combustion cup in the holder beneath the bomb head and bring the fuse wire in contact with the sample.

6.6 Place the bomb head in the bomb cylinder and screw on the retaining cap.

6.7 Tare the bomb bucket and fill with 2000 ± 0.2 grams of distilled water. Assemble the bomb which has been twice purged with nitrogen and then pressurized with 25 atmospheres of nitrogen.

6.8 Insert the bomb bucket into the calorimeter jacket and submerge the bomb in the bomb bucket and attach the ignition wire to the bomb.

6.9 Observe the submerged bomb to determine if gas leakage is occurring as evidenced by bubbles.

CAUTION: DO NOT FIRE BOMB IF IT IS LEAKING.

6.10 Close the cover and if using a differential thermometer, lower the thermometers into position.

6.11 Turn on the automatic temperature controller and allow ten minutes to establish temperature equilibrium between the bomb bucket and the calorimeter jacket. (Adiabatic conditions may be established and maintained by manual manipulation of the hot and cold water supplies.)

6.12 Record the initial temperature. Fire the charge.

6.13 Allow the automatic temperature controller to equilibrate the bomb and jacket temperatures after firing.

6.14 Record the final maximum temperature when three identical readings have been made at one minute intervals.

6.15 Alternate method. Activate Parr Master Control Systems for high precision reference method as specifed in ANSI/ASTM Standard Method D2015 with the following steps.

6.15.1 After the operator pushes the Start button and enters the three pieces of data needed to start the run, the Master Control shifts to the Pre-period mode and holds in this mode for 5 minutes to obtain a stable temperature in the calorimeter.

6.15.2 At the end of the 5 minute pre-period the Master Control starts to take and compare temperature readings at 30 second intervals.

6.15.3 When it finds that the temperature has remained constant within 0.001°C for two minutes (5 consecutive readings) it fires the bomb and records the average of these five readings as the initial temperature.

6.15.4 It then checks the temperature 50 seconds after firing. If it observes a temperature rise of at least 0.05°C during this period, it assumes that ignition was obtained, and the system then shifts into the Post Period mode.

6.15.5 The Master Control now looks for a new equilibrium temperature, again taking and comparing readings at 30 second intervals.

6.15.6 When the temperature has remained constant within 0.001°C for two minutes (5 consecutive readings) it averages these five readings and records the average as the final temperature. This completes the test.

6.16 Remove the bomb from the calorimeter, release the pressure into a hood, disassemble and clean. Calculate the heat of explosion.

6.17 **Calculation:**

$$\text{Heat of Explosion } (Q) = \frac{(E)(\Delta T)}{m}$$

Where:

Q = heat of explosion in calories per gram.

E = water equivalent in calories per degree centigrade.

ΔT = Temperature rise in degrees centigrade corrected for thermometer error and emergent stem correction.

m = weight of sample in grams.

METHOD 803.1.1

LINEAR BURNING RATE OF PROPELLANTS (STRAND BURNER METHOD)

1. SCOPE

1.1 This method is used to determine the linear burning rate of propellants by the strand burner technique. The data is obtained as designated pressures and temperatures. It is used to determine whether specific lots of rocket propellants fulfill the rate and performance requirements. This method is difficult to use when the burning rate exceeds 3 inches per second. (All test temperatures will be considered in degrees Fahrenheit (°F) and the pressures in pounds per square inch (psi).

2. SPECIMEN

2.1 The specimen under test is characterized by the rates obtained at the various pressures and temperatures. Specimens that are cylindrical in shape, 6" to 7" long, with a diameter of 1/8" to 3/8" are preferred, but need not necessarily be round or symetrical. The length requirements is not absolute, but should be a minimum of three inches. For the best results, the burning rate should be obtained over a length of 5 inches and must be made to burn vertically.

2.2 Specimens should be fired at 200 psi intervals (or less), at a minimum of three points above and below the required pressure range. Firings should be made at low, intermedial, and high temperatures or as specified in the applicable propellant specification.

2.3 At each pressure level single tests are conducted, unless otherwise requested, or the operator on observing his pressure vs. burning rate plot, detects a questionable rate. Single tests are usually adequate; in critical regions of pressure and temperature duplicate result may be advisable.

3. APPARATUS

3.1 Bomb (Test cell and holder). The bomb is a Crawford type Strand Burning Rate Bomb. It is made of type 303 stainless steel, and has a volume of approximately 60 cubic inches. It has an O-Ring closure, and a 5000 psi working pressure. Each unit must be hydro-statically tested for 30 minutes at 10,000 psi pressure. The bomb shall be equipped with electrical wiring, contacts for ignition and timing, and an opening for pressurizing and exhausting gass.

3.2 Temperature conditioning bath. Three conditioning chambers with the following ranges and capacities as necessary.

3.2.1 Hot: Range from 130 to 210°F controllable to ± 1°F.

3.2.2 Ambient: Range from 50 to 105°F controllable to ± 2°F.

3.2.3 Cold: Range from -85 to +30°F controllable to ± 2°F.

Each conditioning chamber should contain one burning rate bomb and one conditioning chamber. The low temperature bath is cooled by mechanical refrigeration. The ambient temperature bath has both mechanical refrigeration and electrical heating. The high temperature bath has electrical heaters.

3.3 *Electrical system. The electrical system consists of the following:*

3.3.1 Ignition, timing and control unit containing timing clock, relay circuits, ignition transformer, and electrical continuity check.

3.3.2 *Temperature control unit for obtaining the required test temperature.*

3.3.3 Pressure control unit set to regulate compressor at preset pressures.

3.4 Gas storage system and compressor. The gas storage system shall consist of a storage tank of approximately one half cubic foot. The gas compressor shall have a capacity of 14 scfm at 2200 psi suction nitrogen, and 1 scfm at 300 psi suction nitrogen . Minimum discharge pressure 5000 psi All connections, fittings, and tubing shall have a minimum rated capacity of 10,000 psi and made of type 304 stainless steel. The tanks shall be rated at 7,500 psi operating pressure and be hydrostatically tested to 10,000 psi. The system shall have all necessary controls and instruments to automatically maintain a constant supply of nitrogen gas of 500 psi.

NOTE: 1 psi = 6.9 kPa

3.5 *In addition a bank of nitrogen cylinders shall be available and connected in a suitable* manner to supply sufficient gas directly to the test chambers and to the compressor.

3.6 All fittings and connectors from test chambers, control board, compressor storage system and nitrogen cylinder bank shall be rated at the 10,000 psi working level.

3.7 Gages. Pressure gages necessary for this operation are as follows:

3.7.1 A calibrated gage of 5000 psi capacity graduated in 10 psi. This gage is used to observe and control the pressure at which the strands are burned.

3.7.2 One surge tank and one storage tank gage, each of 6000 psi capacity, graduated in 50 psi. These are used to indicate the amount of nitrogen gas in these tanks.

3.7.3 One manifold tank gage of 3000 psi graduated in 50 psi. This gage indicates the pressure in the nitrogen cylinder, which feeds gas directly to the test chambers and also to the compressor.

4. MATERIALS

4.1 *Nitrogen gas of 99.9% purity.*

4.2 Compound bituminous, solvent type, black, (see 5.1.1). Polyvinyl alcohol solution and polyvinyl chloride may be used as an alternate coating inhibitor.

4.3 *Nichrome wire No. 26 gage.*

4.4 Fuse wire 0.50 ampere.

4.5 Fuse wire 0.25 ampere.

4.6 Fuse wire 1.0 ampere.

5. PROCEDURE

5.1 Preparation of strands:

5.1.1 Strands shall be approximately seven inches long and 1/8" diameter. The strands are clamped at the top by clips an into a bath of the Bituminous Compound (4.2), which is maintained at 75°F. They are then suspended in racks and air dried. This operation is repeated three times or until an adequate inhibiting coat is obtained. The Bituminous Compound (4.2) may be thinned with gasoline if required. The compound dries in about three hours. A good coating is needed to assure vertical burning. Any other inhibitor may be used provided that it does not react or dissolve the propellant or interfere in any way with propellant burning.

5.1.2 The inhibited strand is placed in a jig which has three holes. One is 1/4" from the top of the strand and 1/4" above a second hole. A third hole is drilled exactly 5" below the second hole. All holes are drilled with a No. 80 drill bit. Four inches of nichrome wire (4.3) is threaded through the top for ignition, and four inches of fuze wire (4.4 or 4.5) depending on the flame temperature and the burning rate of the propellant, is threaded through the two holes which are exactly 5" apart. These fuse wires are the timing wires. They start and stop the timing circuit as the strand burns. The jig holds the strand firmly and assures the accurate and reproducible drilling of each hole. See figure 1 for alternate test specimen setup.

5.2 Test method. The required number of strands shall be prepared. The conditioning baths shall be checked for temperature and temperature control.

5.2.1 The bomb head shall be then placed into the body and screwed into position.

5.2.3 The connector from the timing and control unit shall be attached to the bomb and each bomb shall be tested to assure the proper electrical continuity.

5.2.4 The bombs in each of the three conditioning baths, which are in series with each other, and the surge tank shall be pressurized to the required level and the strands shall be conditioned to the bath temperature. (This takes approximately 10 minutes). The three bombs and the surge tank shall be isolated from the rest of the system by closing the proper valves.

5.2.5 The clock shall be reset to zero and the firing switch to one of the bombs shall be closed. As the strand burns, gas is exhausted in order to maintain the original pressure (± 10 psi). (The surge tank acts, therefore, as a ballast). The times of burning (between the two fuse wires) shall be recorded, converted to a burning rate, and plotted as a function of pressure. The

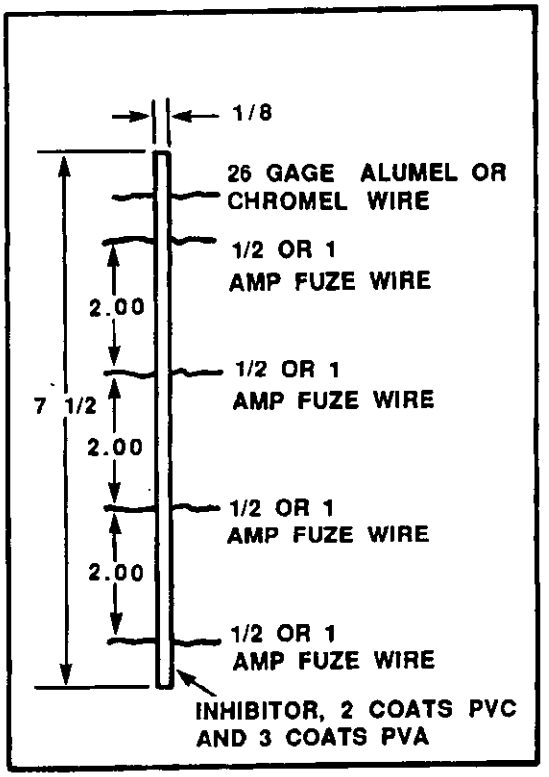


Figure 1. *Typical inhibited burning-rate strand.*

calculation shall be made as soon as possible in order to determine whether a rerun is necessary.

5.2.6 After all three bombs have been fired, they are isolated from the rest of the system as the gases are exhausted. The heads shall be then cleaned and new strands shall be mounted in position.

6. CALIBRATION

6.1 Gages. The surge tank, manifold, and storage tank gages shall be calibrated at least twice a year. The precision gage used to measure and monitor the exact pressure in the bomb shall be calibrated at least once every three months.

6.2 Thermometers. All thermometers used shall be checked once a year.

7. CALCULATIONS

7.1 The conversion of time of burning to the burning rate is obtained by the direct division of the length of strand burned (usually 5 inches) by the time of burning in seconds.

NOTE: When utilizing alternate test specimen setup, the three incremental burning times shall be averaged prior to conversion.

7.2 The rate of burning at a given temperature is then plotted against the pressure in psi on log-log paper. All three temperature curves are usually plotted on the same graph.

7.3 A nomograph can also be used. The time in seconds is etched on the straight edge, and corresponds to the burning rate when properly alligned on the log-log paper.

7.4 The average burning rate, ro, of each measured length of strand between fuse wires is determined for each strand to the nearest 0.001 in/sec and the results averaged. Provided that three clocks and three equal increments of strand length are used in the testing of each strand, the following procedure may be used for accepting or rejecting data and providing a basis for partial retesting if such appears desirable. The burning rates for each of the three increments of length are recorded for each strand. The burning rate for the slowest burning increment of each strand is subtracted from the burning rate for the fastest burning increment of the same strand. Wherever this difference exceeds a value, ro, defined in the applicable specification, the reported value of average burning rate, ro may be determined by averaging the burning rate . However, if no two burning rates of the three increments of a strand agree to within a specified value, ro, of one another, a second strand may be burned to replace the unsatisfactory data. If failure of one of the three clocks should occur during burning of a strand, the average burning rate may be determined from the rates calculated from the other two clock readings provided that these two burning rates do not differ by more than ro. If failure of more than one clock should occur, another strand shall be burned to replace the unsatisfactory data. The strands required for any desired replacement of unsatisfactory data shall be taken frcm extra strand provided for in the original test sample.

7.5 Detailed computation procedures for each type of rocket propellant powder are included in the applicable specification.

METHOD 804.1

QUICKNESS AND FORCE MEASUREMENT OF PROPELLANT (ALTERNATE CLOSED BOMB METHOD)

1. SCOPE

1.1 This test method is used to obtain data for determining the relative quickness (rate of pressure rise) and relative force (maximum pressure) of test propellant under varying conditions of pressure, loading density and temperature.

1.2 Relative quickness (RQ) is defined as the ratio of dp/dt in psi/sec of the test propellant to the dp/dt of the standard propellant taken at the same pressure, initial temperature and loading density in the same closed bomb. (figure 1.)

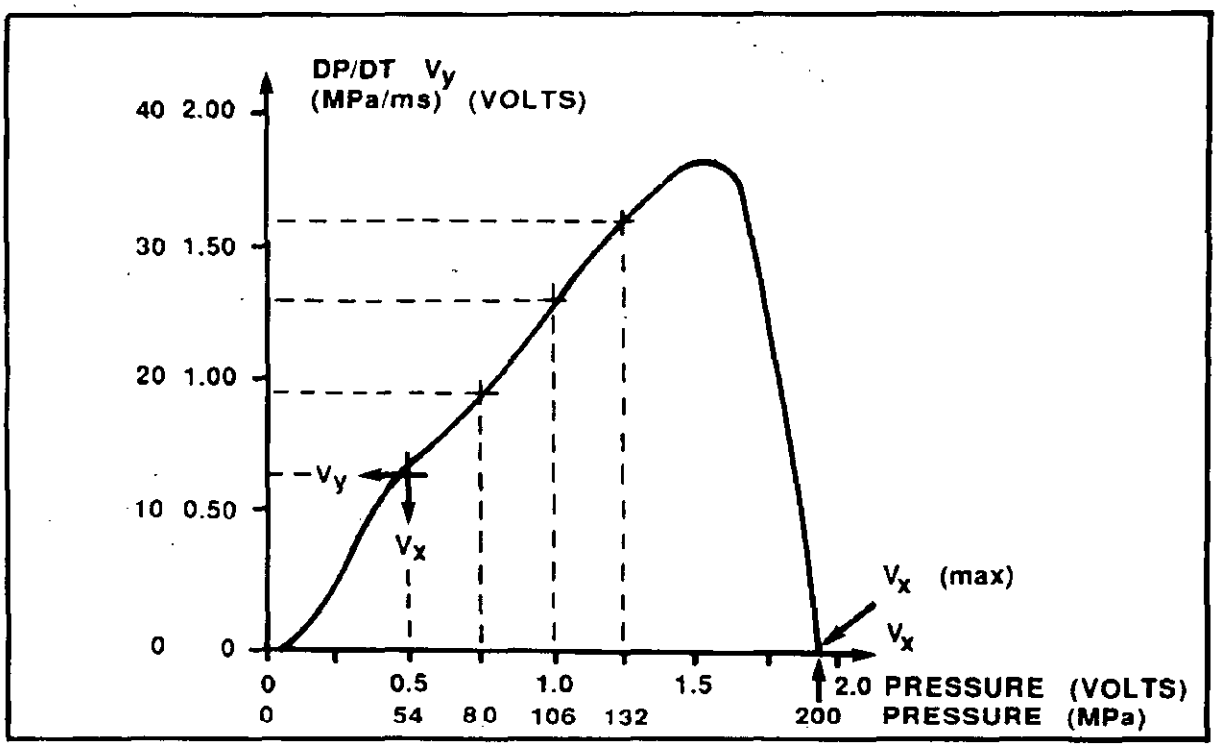


Figure 1. *Rate of Pressure Rise (dp/dt) vs Pressure (P).*

1.3 Relative force (RF) is defined as the ratio of the maximum pressures developed between the test propellant and standard propellant when tested in the same closed bomb, at the same loading density and same initial temperature.

2. SPECIMEN

2.1 The peak pressure developed by a test propellant in the closed bomb is dependent on its loading density g/cm^3, defined as the weight of the sample divided by the volume of the closed bomb. This pressure generally corresponds to peak pressure in actual gun systems. The following loading

density values are to be used as a guide for propellant testing. Propellant sample weight shall be accurate within 0.05 g.

Loading density (grams per cubic centimeter, gm/cm3)	Peak pressure (megapascals, mPa)
0.1	100 – 140
0.2	200 – 275

(One megapascal equals 145.037 pounds per square inch)

3. APPARATUS

3.1 Closed bomb

3.1.1 Standard bombs are constant volume, thick-walled cylindrical vessels (capable of withstanding gun pressures) with inside diameter from 4.4 to 5.1 cm for the 200 and the 700 cm^3 bombs, and from 7.6 to 8.9 cm for the 2400 cm^3 bomb. The bombs shall be equipped with firing electrodes to effect ignition, a pressure transducer, a gas release valve, and a thermocouple, The bombs shall be surrounded by a temperature controlled water jacket to maintain the required test temperature.

3.2 Data acquisition system.

3.2.1 The data acquisition system shall consist of a pressure transducer, a calibrated electronic circuit for pressure, an analog to digital converter of at least twelve bits, and a digital processor. Analog filters employed shall not degrade the pressure trace. Further extension of the system may include a calibrated electronic circuit for dp/dt, a cathode ray oscilloscope, and equipment for photographing the dp/dt vs pressure trace.

3.2.2 The constant time sampling interval for the pressure signal shall be chosen such that the pressure rise between any two successive samples shall not exceed 10 MPa (for 0.2 g/cm^3 loading density). Numerical methods shall be used for both smoothing and differentiating the pressure data. The resulting pressure and dp/dt data shall be equivalent to the input to the oscilloscope, thus providing backup in case of equipment failure.

3.3 Pressure transducer

3.3.1 The pressure transducer shall be piezo-electric type with a frequency response of at least 25 kilohertz and a response to applied pressure which is linear over the test range (0-275 MPa). The transducer shall be calibrated periodically (at least once per month) with a dead weight tested and readout device with an accuracy of 0.1%. If significant changes in gage sensitivity are noted, its use should be discontinued.

3.4 Ignition System.

3.4.1 For the 200 cm^3 bomb, the samples shall be ignited with an electric squib and 0.5 - 1.0 gram of black powder, or a fuze wire with guncotton and one gram of CBI. Heavier charges are used in the larger bombs. A variant ignition system may be substituted subject to the approval of the government.

4. PROCEDURE

4.1 The volume of the closed bomb shall be determined periodically or whenever any component parts are changed. This can be accomplished by filling with water and measuring the volume of the water.

4.2 The bomb and the propellant to be tested shall be conditioned to $32.2 \pm 2^{\circ}C$ or to a variant temperature subject to the approval of the government.

4.3 The loading density shall be selected to produce peak pressure in the closed bomb comparable to that obtained in actual gun system. All propellant sample weights shall be accurate to within $\pm$ 0.05 gram. (para 2.1).

4.4 A warm-up shot shall be made prior to the start of testing. Firings of reference and test propellants shall be made and records of the results for RQ and RF shall be retained; at least 3 firings of both the reference and the test samples shall be used for computations. The closed bomb shall be swabbed after each shot.

5. CALCULATIONS

5.1 **Calculations** (A typical sample calculation is show for 3 reference and 3 test firings):

$$RQ = \frac{1}{m} \sum_{i=1}^{m} \left(\frac{100}{n} \sum_{j=1}^{n} \frac{T_{ij}}{R_{ij}} \right)$$

$$RF = \frac{100}{m} \sum_{i=1}^{m} \left(\frac{T_{pmax\ i}}{R_{pmax\ i}} \right)$$

Where:

m = number of reference or test firings.

n = number of data points per firings = at least 4.

T_{ij} = dp/dt test propellant value of ith firing and jth data point.

R_{ij} = dp/dt reference propellant value of ith firing and jth data point.

$T_{pmax\ i}$ = test propellant maximum pressure for ith firing.

$R_{pmax\ i}$ = reference propellant maximum pressure for ith firing.

RQ for lst firings = $\frac{100}{4}\left(\frac{17.26}{16.76} + \frac{23.76}{23.26} + \frac{29.76}{29.26} + \frac{35.76}{35.50}\right) = 101.89$

RQ for 2nd firings = $\frac{100}{4}\left(\frac{17.00}{16.76} + \frac{23.76}{23.26} + \frac{29.76}{29.00} + \frac{36.00}{35.26}\right) = 102.07$

RQ for 3rd firings = $\frac{100}{4}\left(\frac{17.26}{16.76} + \frac{23.76}{23.50} + \frac{29.76}{29.26} + \frac{36.36}{35.26}\right) = 102.16$

The above values are averaged to obtain the mean relative quickness.

RQ = 102.04

The RQ range is 0.27

RF for lst firings = $100\ (\frac{1.838}{1.838}) = 100.00$

RF for 2nd firings = $100\ (\frac{1.838}{1.813}) = 101.38$

RF for 3rd firings = $100\ (\frac{1.850}{1.838}) = 100.65$

The mean relative force becomes RF = 100.68. The RF range is 1.38.

An alternate method may be used by averaging the individual voltage steps from a minimum of 3 standards and computing as follows:

RQ for lst firings = $\frac{100}{4}(\frac{17.26}{16.76} + \frac{23.76}{23.34} + \frac{29.76}{29.17} + \frac{35.76}{35.34}) = 102.00$

RQ for 2nd firings = $\frac{100}{4}(\frac{17.00}{16.76} + \frac{23.76}{23.34} + \frac{29.76}{29.17} + \frac{36.00}{35.34}) = 101.78$

RQ for 3rd firings = $\frac{100}{4}(\frac{17.26}{16.76} + \frac{23.76}{23.34} + \frac{29.76}{29.17} + \frac{36.26}{35.34}) = 102.35$

The above values are averaged to obtain the mean relative quickness.

RQ = 102.04

The RQ range is 0.57

RF for lst firings = $100\ (\frac{1.838}{1.830}) = 100.44$

RF for 2nd firings = $100\ (\frac{1.828}{1.830}) = 100.44$

RF for 3rd firings = $100\ (\frac{1.850}{1.830}) = 101.09$

The mean relative force becomes RF = 100.66. The RF range is 0.65

5.2 RQ and RF values by the direct digital process shall be obtained by the formulas of 5.1 with the four pressure or voltage point chosen to correspond with those used for the oscilloscope. These shall be at approximately 27, 40, 53 and 66% of the peak pressure or voltage measured for the reference propellant firings. Data is smoothed and differentiated as in 3.2.2.

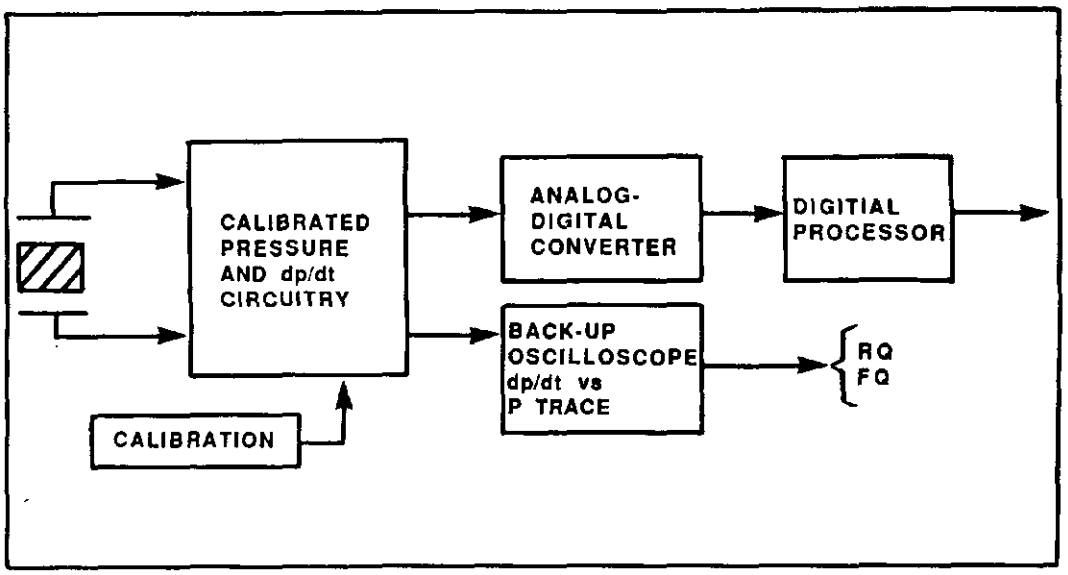


Figure 2. *Closed Bomb Data Acquisition.*

*U.S. GOVERNMENT PRINTING OFFICE: 1991--604-034/50368

CONCLUDING MATERIAL

Custodians:

Army-AR
Navy-OS

Preparing Activity

Army-AR

Project Number:

1376-0377

STANDARDIZATION DOCUMENT IMPROVEMENT PROPOSAL

INSTRUCTIONS

1. The preparing activity must complete blocks 1, 2, 3, and 8. In block 1, both the document number and revision letter should be given.
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I RECOMMEND A CHANGE:	1. DOCUMENT NUMBER	2. DOCUMENT DATE (YYMMDD)
	MIL-STD-286C	28 AUGUST 1991

3. DOCUMENT TITLE
PROPELLANTS, SOLID: SAMPLING, EXAMINATION AND TESTING

4. NATURE OF CHANGE *(Identify paragraph number and include proposed rewrite, if possible. Attach extra sheets if needed.)*

5. REASON FOR RECOMMENDATION

6. SUBMITTER

a. NAME (Last, First, Middle Initial)	b. ORGANIZATION	
c. ADDRESS (Include Zip Code)	d. TELEPHONE (Include Area Code) (1) Commercial (2) AUTOVON (If applicable)	7. DATE SUBMITTED (YYMMDD)

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a. NAME	b. TELEPHONE (Include Area Code)	
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