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EXHIBIT 150
PART 9

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Document Name: ASTM D3454: Standard Test Method for Radium-226 in Water

CFR Section(s): 40 CFR 136.3(a) Table IE

Standards Body: American Society for Testing and Materials

APPROVED

Official Incorporator:
THE EXECUTIVE DIRECTOR
OFFICE OF THE FEDERAL REGISTER
WASHINGTON, D.C.

Designation: D 3454 – 97

Standard Test Method for Radium-226 in Water [1]

This standard is issued under the fixed designation D 3454; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the measurement of soluble, suspended, and total radium-226 in water in concentrations above 3.7×10^{-3} Bq/L. This test method is not applicable to the measurement of other radium isotopes.

1.2 This test method may be used for quantitative measurements by calibrating with a radium-226 standard, or for relative measurements by comparing the measurements made with each other.

1.3 This test method does not meet the current requirements of Practice D 2777.

1.4 The values stated in SI units are to be regarded as the standard. The inch-pound units given in parentheses are for information only.

1.5 Hydrofluoric acid (HF) is very hazardous and should be used in a well-ventilated hood. Wear rubber gloves, safety glasses or goggles, and a laboratory coat. Avoid breathing any HF fumes. Clean up all spills promptly and wash thoroughly after using HF.

1.6 *This standard does not purport to address all of the other safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1129 Terminology Relating to Water[2]

D 1193 Specification for Reagent Water[2]

D 2777 Practice for Determination of Precision and Bias Applicable Methods of Committee D-19 on Water[2]

D 3370 Practices for Sampling Water from Closed Conduits[2]

D 3649 Practice for High-Resolution Gamma-Ray Spectrometry of Water[3]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D 1129, and to other published glossaries.[4]

4. Summary of Test Method

4.1 This test method[5] is based on the emanation and scintillation counting of radon-222, a gaseous daughter product of radium-226, from a solution.

4.2 Radium-226 is collected from water by coprecipitation on a relatively large amount of barium sulfate. The barium-radium sulfate is decomposed by fuming with phosphoric acid, and the resulting glassy melt is dissolved by evaporation with dilute hydrochloric acid to form soluble barium-radium phosphates and chlorides. These salts are dissolved and the solution is stored for ingrowth of radon-222. After a suitable ingrowth period, the radon gas is removed from the solution by purging with gas and transferred to a scintillation counting chamber. About 4 h after radon-222 collection, the scintillation chamber is counted for alpha activity. The radium-226 concentration is calculated from the alpha count rate of radon-222 and its immediate daughters. The radioactive decay characteristics of radium-226 and its immediate decay progeny are listed in Table 1.

5. Significance and Use

5.1 The most prevalent of the five radium isotopes in ground water, having a half life greater than one day, are radium-226 and radium-228. These two isotopes also present the greatest health risk compared to the other naturally occurring nuclides of equal concentrations if ingested via the water pathway.

5.2 Although primarily utilized on a water medium, this technique may be applicable for the measurement of the radium-226 content of any media once the medium has been completely decomposed and put into an aqueous solution.

5.3 The general methodology and basis of this technique are

[1] This test method is under the jurisdiction of ASTM Committee D 19 on Water and is the direct responsibility of Subcommittee D19.04 on Methods of Radiochemical Analysis.

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[2] *Annual Book of ASTM Standards,* Vol 11.01.

[3] *Annual Book of ASTM Standards,* Vol 11.02.

[4] American National Standard Glossary of Terms in Nuclear Science and Technology, N1.1-1967.

[5] This test method is based on a previously published method by Rushing, D.E., Garcia, W.J., and Clark, D.A. "The Analysis of Effluents and Environmental Samples from Uranium Mills and of Biological Samples for Radium, Polonium and Uranium," Radiological Health and Safety in Mining and Milling of Nuclear Materials, Vol. II, IAEA, Vienna, Austria, 1964), p. 187.

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TABLE 1 Radioactive Decay Characteristics of Radium-226 and Its Daughters

Radionuclide	Half-life	Mode of Decay
Radium-226	1602 years	α
Radon-222	3.82 days	α
Polonium-218	3.05 min	α
Lead-214	26.8 min	β, γ
Bismuth-214	19.7 min	β, γ
Polonium-214	164 μ s	α
Lead-210	22.3 years	β, γ

similar to the methodology "Radium-226 in Drinking Water (Radon Emanation Technique)" as described in the document *EPA-600//4-80-032*.[6]

6. Interferences

6.1 Only the gaseous alpha-emitting radionuclides interfere, namely, radon-219 and radon-220. Their half lives are 3.9 and 54.5 s respectively; their presence indicates the presence of their parents, radium-223 and radium-224. These short-lived radon isotopes decay before the radon-222 is counted; it is their alpha-emitting decay products that would interfere. These interferences are very rare in water samples but are frequently observed in certain uranium mill effluents.

7. Apparatus

7.1 *Radon Bubbler*[7] (Fig. 1).

7.2 *Radon Scintillation Chamber*[8] (also known as Lucas Cell) (Fig. 2).

7.3 *Manometer*, open-end capillary tube or vacuum gage having a volume which is small compared to the volume of the scintillation chamber, 0, ± 760 mm Hg (Fig. 3).

7.4 *Gas Purification Tube*, 7 to 8 mm outside diameter standard wall glass tubing, 100 mm long, constricted at lower end to hold a glass wool plug (Fig. 3). The upper half of the tube is filled with magnesium perchlorate and the lower half with a sodium hydrate-asbestos absorbent.

7.5 *Scintillation Counter Assembly*, consisting of a 50 mm (2 in.) or more in diameter photomultiplier tube mounted in a light-tight housing and coupled to the appropriate preamplifier, high-voltage supply, and scaler. A high-voltage safety switch should open automatically when the light cover is removed to avoid damage to the photomultiplier tube. The preamplifier should incorporate a variable gain adjustment. The counter should be equipped with a flexible ground wire which is attached to the chassis photomultiplier tube by means of an alligator clip or similar device. The operating voltage is ascertained by determining a plateau using radon-222 in the scintillation chamber as the alpha source. The slope of the plateau should not exceed 2 %/100 V. The counter and the scintillation chamber should be calibrated and used as a unit when more than one counter is available. The background counting rate for the counter assembly without the scintillation chamber should range from 0.00 to 0.03 cpm.

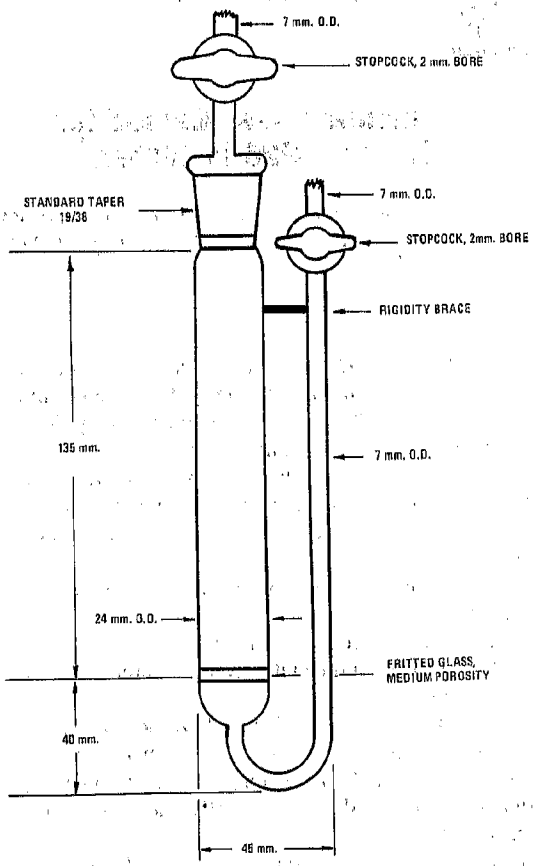


FIG. 1 Radon Bubbler

7.6 *Membrane Filters*, 0.45-μm pore size.[9]

7.7 *Silicone Grease*, high-vacuum, for bubbler stopcocks.

7.8 *Platinum Ware*, crucibles, 20 to 30 mL, and one 500-mL capacity dish. Platinum ware is cleaned by immersing and rotating in a molten bath of potassium pyrosulfate, removing, cooling, and rinsing in hot tap water, digesting in hot HCl (1+1), rinsing in water, and finally flaming over a burner.

7.9 *Laboratory Glassware*—Glassware may be decontaminated before and between uses by heating for 1 h in EDTA-Na_2CO_3 decontaminating solution at 90 to 100°C, then rinsing in water, in (1+11) HCl and again in water.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be

[6] "Radium-226 in Drinking Water (Radon Emanation Technique)," *Prescribed Procedures for Measurement of Radioactivity in Drinking Water*, August 1980.

[7] Available from Corning Glass Works, Special Sales Section, Corning, N.Y. 11830.

[8] Available from W. H. Johnston Laboratories, 3617 Woodland Ave., Baltimore, MD 21215, and Rocky Mountain Scientific Glass Blowing Co., 4990 E. Asbury Ave. Denver, CO 80222.

[9] Type HAWP (Millipore filter Corp., Bedford, MA) has been found satisfactory. An equivalent may be used.

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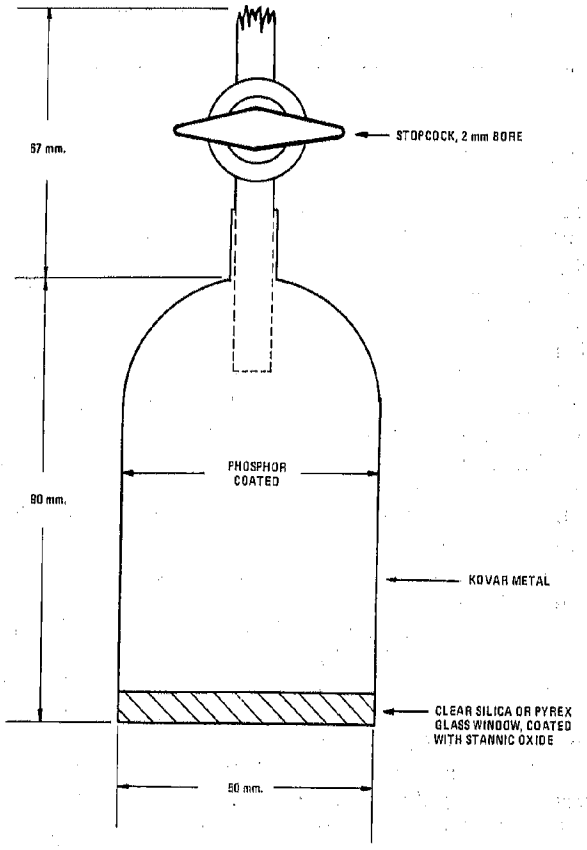


FIG. 2 Radon Scintillation Chamber

used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society.[10] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean conforming to Specification D 1193, Type III.

8.3 *Radioactive Purity of Reagents*—Radioactive purity shall be such that the measured results of blank samples do not exceed the calculated probable error of the measurement or are within the desired precision.

8.4 *Ammonium Sulfate Solution* (100 g/L)—Dissolve 10 g of ammonium sulfate ($(NH_4)_2SO_4$) in water and dilute to 100 mL.

8.5 *Barium Chloride Carrier Solution Stock,* (17.8 g/L)—Dissolve 17.8 g of barium chloride ($BaCl_2 \cdot 2H_2O$) in water and dilute to 1 L. This solution will contain 10 mg Ba^{++}/mL.

8.6 *Barium-133 Tracer Solution*—(approximately 2.74 × 10^3 Bq/mL).

[10] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on testing of reagents not listed by the American Chemical Society, see "Analar Standards for Laboratory Chemicals," BDH Ltd., Poole, Dorset, U.K., and the "United States Pharmacopeia," and National Formulary, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

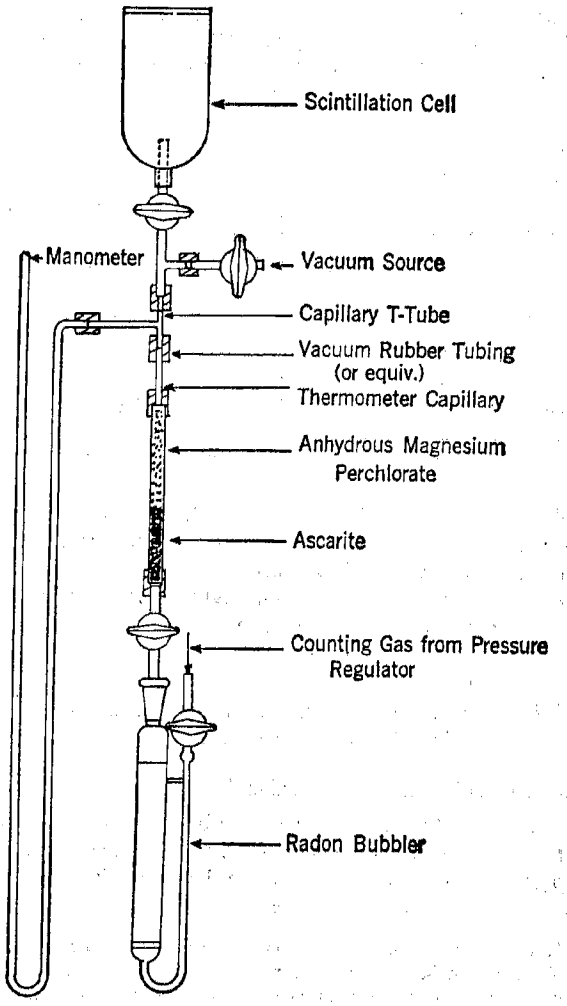


FIG. 3 De-emanation Assembly

8.7 *Barium Chloride Carrier Solution, Working*—Add 100 mL of barium chloride carrier stock solution and 10 mL of barium-133 tracer solution to 890 mL of water and mix thoroughly. This solution will contain approximately 1 g of Ba^{++}/L. Allow to stand for 24 h and filter through a membrane filter.

8.8 *EDTA-Sodium Carbonate Decontaminating Solution*—Dissolve 10 g of disodium ethylenediaminetetraacetate and 10 g of sodium carbonate (Na_2CO_3) in water and dilute to 1 L.

8.9 *Flux*—To a large platinum dish (about 500-mL capacity) add 30 mg of $BaSO_4$, 65.8 g of K_2CO_3, 50.5 g of Na_2CO_3, and 33.7 g of $Na_2B_4O_7 \cdot 10\ H_2O$. Mix well and heat cautiously until the water is expelled; fuse and mix thoroughly by swirling. Cool flux, grind it in a porcelain mortar to pass a U. S. Standard No. 10 (2.00-mm) (or finer) sieve. Store in an airtight bottle. (Flux can be prepared in smaller batches.)

8.10 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl).

8.11 *Hydrochloric Acid Solution* (1 + 1)—Mix 1 volume of concentrated HCl (sp gr 1.19) with 1 volume of water.

8.12 *Hydrochloric Acid Solution* (1 + 11)—Mix 1 volume

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of concentrated HCl (sp gr 1.19) with 11 volumes of water.

8.13 *Hydrochloric Acid Solution* (1 + 49)—Mix 1 volume of concentrated HCl (sp gr 1.19) with 49 volumes of water.

8.14 *Hydrochloric Acid Solution* (1 + 119)—Mix 1 volume of concentrated HCl (sp gr 1.19) with 119 volumes of water.

8.15 *Hydrofluoric Acid* (sp gr 1.15)—Concentrated hydrofluoric acid (HF). Use extreme caution.

8.16 *Hydrogen Peroxide* (1 + 9)—Mix 1 volume of H_2O_2 (30 %) with 9 volumes of water.

8.17 *Magnesium Perchlorate*—Anhydrous magnesium perchlorate $Mg(ClO_4)_2$.

8.18 *Phosphoric Acid* (sp gr 1.69)—Concentrated phosphoric acid (H_3PO_4).

8.19 *Radium Standard Solution* (0.37 Bq/mL).[11]

8.20 *Sodium Hydroxide-Coated Silicate Absorbent, Proprietary*, [12] 8 to 20 mesh.

8.21 *Sulfuric Acid* (sp gr 1.84)—Concentrated sulfuric acid (H_2SO_4).

8.22 *Sulfuric Acid Solution* (1 + 359)—Mix 1 volume of concentrated H_2SO_4(sp gr 1.84) with 359 volumes of water. This solution is 0.1 *N*. Slowly add acid to water.

8.23 *Helium*, in a high-pressure cylinder with a two-stage pressure regulator and needle valve.

9. Sampling

9.1 Collect the sample in accordance with the applicable standards as described in Practices D 3370.

10. Calibration and Standardization

10.1 Close the inlet stopcock of a bubbler, (Note 1) add 5 mL of $BaCl_2 \cdot 2H_2O$ carrier solution, 1 mL of concentrated HCl (sp gr 1.19), 3 mL (1.1 Bq) of standard radium solution and fill the bubbler ⅔ to ¾ full with water.

NOTE 1—Before using, test bubblers by placing about 10 mL of water in them and passing air through them at the rate of 3 to 5 mL/min. This should form many fine bubbles rather than a few large ones. Do not use bubblers requiring excessive pressure to initiate bubbling. Reject unsatisfactory bubblers. Corning's" medium-porosity" fitted glass disks are usually satisfactory.

10.2 Insert the outlet stopcock into the bubbler with the stopcock open. Adjust the helium regulator (diaphragm) valve so that a very slow stream of gas will flow with the needle valve open. Attach the helium supply to the inlet of bubbler and adjust the inlet pressure to produce a froth a few millimetres thick. Establish a zero ingrowth time by purging the liquid with helium for 15 to 20 min.

10.3 In rapid succession, close the inlet stopcock, remove the gas connection, and the close outlet stopcock. Record the date and time and store the bubbler preferably for 2 to 3 weeks before collecting and counting the radon-222.

10.4 Attach a scintillation chamber as shown in Fig. 3; *substitute a glass tube with a stopcock for the bubbler* so that the helium gas can be turned on and off conveniently. Open the stopcock on the scintillation chamber; close the stopcock to the gas and gradually open the stopcock to vacuum source to evacuate the cell. Close the stopcock to the vacuum source and check the manometer reading for 2 min to test the system, especially the scintillation chamber for leaks. If leaks are detected they should be identified and sealed.

10.5 Open the stopcock to the helium gas and allow the gas to enter the chamber slowly until atmospheric pressure is reached. Close all the stopcocks.

10.6 Place the scintillation chamber on the photomultiplier tube (in a light-tight housing), wait 10 min, and obtain a background count rate (preferably over a period of at least 100 min). Phototube must not be exposed to external light with the high voltage applied.

10.7 With the scintillation chamber and bubbler in positions indicated in Fig. 3 and all stopcocks closed, open the stopcock to vacuum and then to the scintillation chamber. Evacuate the scintillation cell and the gas purification system. Close the stopcock to vacuum and check for leaks as in 10.4.

10.8 Adjust the helium regulator (diaphragm) valve so that a very slow stream of gas will flow with the needle valve open. Attach the helium supply to the inlet of the bubbler.

10.9 Very cautiously open the bubbler outlet stopcock to equalize pressure and transfer all or most of the fluid in the inlet side arm to the bubbler chamber.

10.10 Close the outlet stopcock and very cautiously open the inlet stopcock to flush remaining fluid from the side arm and fritted disk. Close the inlet stopcock.

10.11 Repeat steps 10.9 and 10.10 several times to obtain more nearly equal pressure on the two sides of the bubbler.

10.12 With the outlet stopcock fully open, cautiously open the inlet stopcock so that the flow of gas produces a froth a few millimetres thick at the surface of bubbler solution. Maintain the flow rate by adjusting the pressure with the regulator valve and continue de-emanation until the pressure in the scintillation chamber reaches the atmospheric pressure. The total elapsed time for de-emanation should be 15 to 20 min.

10.13 In rapid succession, close the stopcock to the scintillation chamber, close the bubbler inlet and the outlet stopcocks, shut off and disconnect the gas supply. Record the date and time, which is the end of ingrowth and the beginning of decay.

10.14 Store the bubbler for another radon-222 ingrowth in the event a subsequent de-emanation is desired. The standard bubbler containing the standard may be kept and reused indefinitely.

10.15 Four hours after de-emanation, place the scintillation chamber on the photomultiplier tube, wait 10 min, and count with desired statistical accuracy is achieved. Record the date and time the counting was started and finished.

10.16 Calculate the calibration constant E, for the scintillation chamber as follows:

$$E = c/A(1 - e^{-\lambda t_1})(e^{-\lambda t_2})$$

where:

c = net count rate, cpm (cpm standard – cpm background),
A = activity of radium-226 in the bubbler, dpm,
t_1 = ingrowth time of radon-222, h,
t_2 = decay time of radon-222 occurring between de-emanation and counting, h, and

[11] Standard radium solutions are available from the National Institute of Standards and Technology.

[12] Ascarite II has been found to be suitable and is available from VWR Scientific.

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λ = decay constant of radon-222 (0.00755 h^{-1}).

10.17 Carry out the background measurements and calibrations with each scintillation chamber used, and repeat frequently as the calibration constant can change with time.

10.18 To remove radon-222 and prepare the scintillation chamber for reuse, evacuate and cautiously refill with helium. Repeat this evacuation and refilling twice. For chambers containing high activities of radon-222 repeat the procedure more often.

11. Procedure

11.1 *Soluble Radium-226*:

11.1.1 Filter the sample through a membrane filter. Take a 1-L aliquot, or a smaller volume so as not to exceed 1.1 Bq of radium-226, and transfer to a 1500-mL beaker. Acidify with 20 mL of concentrated HCl (sp gr 1.19) per litre of filtrate, heat, and add with vigorous stirring 50 mL of $BaCl_2$ working carrier solution. For sample volumes less than a litre, dilute to 1 L with HCl (1 + 49) prior to the addition of carrier.

11.1.2 Cautiously and with vigorous stirring, add 20 mL of H_2SO_4 (sp gr 1.84). Cover the beaker and allow to stand overnight.

11.1.3 Filter the supernate through a membrane filter, using H_2SO_4 (1 + 359) to transfer the Ba-Ra precipitate to the filter. Wash the precipitate twice with H_2SO_4 (1 + 359).

11.1.4 Place the filter in a platinum crucible, add 0.5 mL of concentrated HF (sp gr 1.15) and 3 drops (0.15 mL) of $(NH_4)_2SO_4$ solution, and evaporate to dryness.

11.1.5 Carefully ignite the filter and residue over a small flame until the carbon is burned off (after charring of filter, a Meeker burner may be used).

11.1.6 Cool, add 1 mL of concentrated H_3PO_4 (sp gr 1.69), and heat on a hot plate to about 200°C. Gradually raise temperature to about 300 to 400°C for 30 min.

11.1.7 Swirl the crucible over a low bunsen flame, adjusted to avoid spattering. Swirl so that the crucible walls are covered with hot concentrated H_3PO_4 (sp gr 1.69). Continue to heat until the $BaSO_4$ dissolves to give a clear melt (just below redness), and then heat for 1 min more to ensure removal of SO_3.

11.1.8 Cool, fill the crucible one-half full with HCl (1 + 1), heat on a steam bath, then gradually add the water to within 2 mm of the top of the crucible.

11.1.9 Evaporate on the steam bath until there are no more vapors of HCl.

11.1.10 Add 6 mL of HCl (1 + 11), swirl, and warm to dissolve the $BaCl_2$ crystals.

11.1.11 Close the inlet stopcock of a greased and tested radon bubbler. Add a drop of water to the fritted disk and transfer the sample from the platinum crucible to the bubbler using a medicine dropper. Rinse the crucible with at least three 2-mL portions of water. Add water until the bubbler is ⅔ to ¾ full.

11.1.12 De-emanate the solution in accordance with 10.2 and 10.3.

11.1.13 After 3 weeks of radon-222 ingrowth, de-emanate and count as described in 10.7 through 10.15.

11.1.14 Transfer the solution in the bubbler to a gamma-counting container. Wash the bubbler thoroughly with HCl (1 + 11) and combine with the sample in a container. Measure the barium-133 gamma activity in a gamma counter. For a discussion of gamma ray counting refer to Practice D 3649. Calculate the sample yield, Y, by dividing the barium-133 activity of the sample by the barium-133 activity of a 50-mL aliquot of $BaCl_2$ carrier working solution counted under identical conditions of volume and geometry as the sample.

11.1.15 The sample may be stored for a second ingrowth or discarded and the bubbler cleaned for reuse. A thorough rinsing with HCl (1 + 49) is a satisfactory cleaning procedure. If however, the radium-226 in a bubbler exceeded 10 pCi, a more rigorous cleaning may be necessary. Remove the stopcock grease, using a cloth and solvent, and then immerse for 1 h in hot (90 to 100°C) EDTA – Na_2CO_3 solution. Heat the bubblers gradually to avoid thermal shock to the fritted glass disks. Remove, cool at room temperature, and rinse with distilled water. Immerse in HCl (1 + 11) and warm for about 30 min. Remove, cool, and rinse with distilled water. Dry and regrease the stopcocks.

11.1.16 Remove radon-222 from the scintillation chamber as described in 10.18.

11.2 *Suspended Radium-226*:

11.2.1 Filter a volume of sample containing up to 30 pCi of radium-226 and 1.0 g of inorganic suspended matter through a membrane filter. If desired the filter and suspended matter from step 10.1.1 may be used.

11.2.2 Place the membrane filter and suspended material into a weighed 30-mL platinum crucible. Carefully ignite over a small flame until the carbon is burned off (after charring of the filter, a Meeker burner may be used).

11.2.3 Cool and weigh the crucible to estimate the residue.

11.2.4 Add 8 g of flux for each gram of residue, but not less than 2 g of flux, and mix with a glass stirring rod.

11.2.5 Heat over a Meeker burner until melting begins, then more carefully to avoid spattering. Continue heating for 20 min after bubbling stops with occasional swirling of the crucible to mix the contents and achieve a uniform melt. A clear melt is usually obtained only when the suspended solids are present in small amounts or have a high silica content.

11.2.6 Remove the crucible from the burner and rotate it as the melt cools to distribute it in a thin layer on the crucible walls.

11.2.7 To a 500 mL beaker containing 120 mL H_2O, slowly add, with stirring, 20 mL of concentrated H_2SO_4 (sp gr 1.84) and 5 mL of H_2O_2(1+9) for each 8 g of flux used.

11.2.8 Place the crucible in a beaker, cover, and swirl the beaker to dissolve the melt.

11.2.9 When the melt is dissolved, lift the crucible with platinum-tipped tongs, and rinse with water, allowing rinse water to go into the beaker.

11.2.10 When the melt is dissolved, rinse and remove the crucible from the beaker and save for reuse in step 11.2.13.

11.2.11 Heat the solution and slowly add 50 mL of $BaCl_2$ working solution with vigorous stirring. Cover the beaker and allow to stand overnight for precipitation.

11.2.12 Add 1 mL of H_2O_2 (1+9) and if the yellow color (from titanium) deepens, add additional H_2O_2 until there is no further color change.

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11.2.13 Continue as described in steps 11.1.3 to 11.1.16.

11.3 *Soluble and Suspended Radium–226:*

11.3.1 Take a 1-L aliquot of the thoroughly mixed sample, or a smaller volume so as not to exceed (1.1 Bq) of radium-226 and transfer to a 1500-mL beaker. Acidify with 20 mL of concentrated HCl (sp gr 1.19) per litre of sample, heat, and add with vigorous stirring 50 mL of $BaCl_2$ working carrier solution. For sample volumes less than a litre, dilute to 1 L with HCl (1 + 49) prior to the addition of carrier.

11.3.2 Cautiously and with vigorous stirring add 20 mL of concentrated H_2SO_4 (sp gr 1.84). Cover the beaker and allow to stand overnight.

11.3.3 Filter the supernate through a membrane filter, using H_2SO_4(1 + 359) to transfer the solids to the filter. Wash the solids twice with H_2SO_4 (1 + 359).

11.3.4 Continue as described in steps 11.2.2 to 11.2.10.

11.3.5 Digest the sample for 1 h on a steam bath and add 1 mL of H_2O_2 (1 + 9). If the yellow color (from titanium) deepens, add additional H_2O_2 until there is no further color change.

11.3.6 Continue as described in steps 11.1.3 to 11.1.16.

12. Calculation

12.1 Calculate the concentration of radium-226 in becquerels per litre as follows:

$$D = \frac{c}{EVR} \times \frac{1}{1 - e^{-\lambda t_1}} \times \frac{1}{e^{-\lambda t_2}}$$

where:

D = concentration of Radium-226, Bq/L,
c = calibration constant for the scintillation cell, cpm/disintegrations per minute,
v = volume of sample used, L,
R = recovery factor,
t_1 = elapsed time between the first and second de-emanations; λ is the decay constant of radon-222 (0.181 d^{-1}), days,
t_2 = time interval between the second de-emanation and time of mid count, h; λ is the decay constant of radon-222 (0.00755 h^{-1}),
c = net count rate (sample-background), cps

12.2 The total propagated uncertainty (1 s) for the concentration of Radium-226 is calculated as follows:

$$S_D(\text{Bq/L}) = D(\text{Bq/L})*[(S_C/C)^2 + (S_E/E)^2 + (S_V/V)^2 + (S_R/R)^2]^{1/2} \quad (1)$$

where:

S_C = one sigma uncertainty of the net sample counting rate,
S_E = one sigma uncertainty of the detection efficiency of the scintillation cell,
S_V = one sigma uncertainty of the sample volume, and
S_R = one sigma uncertainty in the fractional radium recovery.

The one sigma uncertainty (S_C) in the net sample counting rate is calculated from the following:

$$S_C = (G/t_G^2 + B/t_B^2)^{1/2} \quad (2)$$

where:

G = sample gross counting rate, s^{-1},
B = background counting rate, s^{-1},
t_G = sample counting time, s, and
t_B = background counting time, s.

12.3 The *a priori* minimum detectable concentration (*MDC*) is calculated as follows:

$$MDC(\text{Bq/L}) = \frac{2.71 + 4.65*(t_B*B)^{1/2}}{t_G*E*R*V*F} \quad (3)$$

where:

F = product of the ingrowth and two decay factors,
E = detection efficiency,
R = fractional recovery, and
V = sample volume.

13. Precision and Bias [13]

13.1 The available data do not permit a precision and bias statement to be made in accordance with Practice D 2777.

13.2 A limited collaborative study of this test method was conducted. Seven labs participated by processing one sample at four levels. These collaborative data were obtained on distilled water with reagent grade chemicals added to vary the hardness. The resultant hardness was 125 mg/L for levels A and B and 610 mg/L for levels C and D.

13.3 *Precision*—The overall precision of this test method within its designated range varies with the quantity being tested according to Fig. 4. The relative precision for this test method is approximately 5 %.

13.4 *Bias*—A limited collaborative study of this test method indicated that a negative bias of approximately 3 % was present, based on the average recovery of the known amount of radium-226 added. Recoveries were as follows:

Level	pci/L	Added, Bq/L	Found, Bq/L	Bias, %
A	12.12	0.448	0.4351	−2.9
B	8.96	0.331	0.3221	−2.7
C	25.53	0.944	0.9214	−2.4
D	18.84	0.697	0.6831	−2.0

14. Quality Control

14.1 Whenever possible, the project leader, as part of the external quality control program, should submit quality control samples to the analyst along with routine samples in such a way that the analyst does not know which of the samples are the quality control samples. These external quality control samples which usually include duplicate and blank samples, should test sample collection and preparation as well as sample analysis whenever this is possible. In addition, analysts are expected to run internal quality control samples that will indicate to them whether the analytical procedures are in control. Both the external and internal quality control samples should be prepared in such a way as to duplicate the chemical matrix of the routine samples, insofar as this is practical. The quality control samples that are routinely used consist of five basic types: blank samples, replicate samples, reference materials, control samples, and spiked samples.

15. Keywords

15.1 coprecipitation; emanation; radioactivity; radium-226;

[13] Supporting data for this test method have been filed at ASTM Headquarters. Request RR:D-19-1130.

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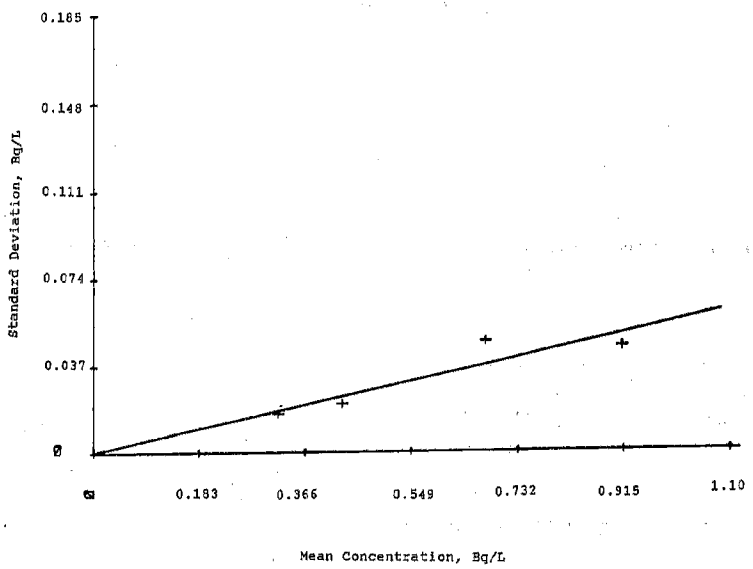


FIG. 4 Overall Standard Deviation versus Mean Concentration

radon-222; water

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Document Name: ASTM D3588: Standard Practice for Calculating Heat Value, Compressibility Factor, and Relative Density (Specific Gravity) of Gaseous Fuels

CFR Section(s): 40 CFR 75, Appendix F

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APPROVED

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Standard Practice for Calculating Heat Value, Compressibility Factor, and Relative Density of Gaseous Fuels[1]

This standard is issued under the fixed designation D 3588; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice covers procedures for calculating heating value, relative density, and compressibility factor at base conditions (14.696 psia and 60°F (15.6°C)) for natural gas mixtures from compositional analysis.[2] It applies to all common types of utility gaseous fuels, for example, dry natural gas, reformed gas, oil gas (both high and low Btu), propane-air, carbureted water gas, coke oven gas, and retort coal gas, for which suitable methods of analysis as described in Section 6 are available. Calculation procedures for other base conditions are given.

1.2 The values stated in inch-pound units are to be regarded as the standard. The SI units given in parentheses are for information only.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1717 Methods for Analysis of Commercial Butane-Butene Mixtures and Isobutylene by Gas Chromatography[3]

D 1945 Test Method for Analysis of Natural Gas by Gas Chromatography[4]

D 1946 Practice for Analysis of Reformed Gas by Gas Chromatography[4]

D 2163 Test Method for Analysis of Liquefied Petroleum (LP) Gases and Propane Concentrates by Gas Chromatography[5]

D 2650 Test Method for Chemical Composition of Gases by Mass Spectrometry[6]

2.2 *GPA Standards:*

GPA 2145 Physical Constants for the Paraffin Hydrocarbons and Other Components in Natural Gas[7]

GPA Standard 2166 Methods of Obtaining Natural Gas Samples for Analysis by Gas Chromatography[7]

GPA 2172 Calculation of Gross Heating Value, Relative Density, and Compressibility Factor for Natural Gas Mixtures from Compositional Analysis[7,8]

GPA Standard 2261 Method of Analysis for Natural Gas and Similar Gaseous Mixtures by Gas Chromatography[7]

GPA Technical Publication TP-17 Table of Physical Properties of Hydrocarbons for Extended Analysis of Natural Gases[7]

GPSA Data Book, Fig. 23-2, Physical Constants[7]

2.3 *TRC Document:*

TRC Thermodynamic Tables—Hydrocarbons[9]

2.4 *ANSI Standard:*

ANSI Z 132.1-1969: Base Conditions of Pressure and Temperature for the Volumetric Measurement of Natural Gas[10,11]

3. Terminology

3.1 *Definitions:*

3.1.1 *British thermal unit*—the defined International Tables British thermal unit (Btu).

3.1.1.1 *Discussion*—The defining relationships are:

$$1\ \text{Btu}\cdot\text{lb}^{-1} = 2.326\ \text{J}\cdot\text{g}^{-1}\ \text{(exact)}$$

$$1\ \text{lb} = 453.592\ 37\ \text{g (exact)}$$

By these relationships, 1 Btu = 1 055.055 852 62 J (exact). For most purposes, the value (rounded) 1 Btu = 1055.056 J is adequate.

3.1.2 *compressibility factor (z)*—the ratio of the actual

[1] This practice is under the jurisdiction of ASTM Committee D-3 on Gaseous Fuels and is the direct responsibility of Subcommittee D03.03 on Determination of Heating Value and Relative Density of Gaseous Fuels.

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[2] A more rigorous calculation of *Z(T,P)* at both base conditions and higher pressures can be made using the calculation procedures in "Compressibility and Super Compressibility for Natural Gas and Other Hydrocarbon Gases," American Gas Association Transmission Measurement Committee Report 8, AGA Cat. No. XQ1285, 1985, AGA, 1515 Wilson Blvd., Arlington, VA 22209.

[3] Discontinued, see *1983 Annual Book of ASTM Standards*, Vol 05.01.

[4] *Annual Book of ASTM Standards*, Vol 05.05.

[5] *Annual Book of ASTM Standards*, Vol 05.01.

[6] *Annual Book of ASTM Standards*, Vol 05.02.

[7] Available from Gas Processors Association, 6526 E. 60th, Tulsa, OK 74145.

[8] A program in either BASIC or FORTRAN suitable for running on computers, available from the Gas Processors Association, has been found satisfactory for this purpose.

[9] Available from Thermodynamics Research Center, The Texas A&M University, College Station, TX 77843-3111.

[10] Available from the American National Standards Institute, 11 W. 42nd St., 13th Floor, New York, NY 10036.

[11] Supporting data are available from ASTM Headquarters. Request RR:D03-1007.

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volume of a given mass of gas at a specified temperature and pressure to its volume calculated from the ideal gas law under the same conditions.

3.1.3 *gross heating value*—the amount of energy transferred as heat from the complete, ideal combustion of the gas with air, at standard temperature, in which all the water formed by the reaction condenses to liquid. The values for the pure gases appear in GPA Standard 2145, which is revised annually. If the gross heating value has a volumetric rather than a mass or molar basis, a base pressure must also be specified.

3.1.4 *net heating value*—the amount of energy transferred as heat from the total, ideal combustion of the gas at standard temperature in which all the water formed by the reaction remains in the vapor state. Condensation of any "spectator" water does not contribute to the net heating value. If the net heating value has a volumetric rather than a mass or molar basis, a base pressure must also be specified.

3.1.5 *relative density*—the ratio of the density of the gaseous fuel, under observed conditions of temperature and pressure, to the density of dry air (of normal carbon dioxide content) at the same temperature and pressure.

3.1.6 *standard cubic foot of gas*—the amount of gas that occupies 1 ft^3 (0.028 m^3) at a temperature of 60°F (15.6°C) under a given base pressure and either saturated with water vapor (wet) or free of water vapor (dry) as specified (see ANSI Z 132.1). In this practice, calculations have been made at 14.696 psia and 60°F (15.6°C), because the yearly update of GPA 2145 by the Thermodynamics Research Center, on which these calculations are based, are given for this base pressure. Conversions to other base conditions should be made at the end of the calculation to reduce roundoff errors.

3.1.7 *standard temperature (USA)*—60°F (15.6°C).

3.2 *Symbols*:

3.2.1 *Nomenclature*:

3.2.1.1 B—second virial coefficient for gas mixture

3.2.1.2 $\sqrt{\beta_{ij}}$—summation factor for calculating real gas correction (alternate method)

3.2.1.3 (cor)—corrected for water content

3.2.1.4 (dry)—value on water-free basis

3.2.1.5 d—density for gas relative to the density of air.

3.2.1.6 d^{id}—ideal relative density or relative molar mass, that is, molar mass of gas relative to molar mass of air

3.2.1.7 G^{id}—molar mass ratio

3.2.1.8 H_m^{id}—gross heating value per unit mass

3.2.1.9 H_v^{id}—gross heating value per unit volume

3.2.1.10 H_n^{id}—gross heating value per unit mole

3.2.1.11 h_m^{id}—net heating value per unit mass

3.2.1.12 h_v^{id}—net heating value per unit volume

3.2.1.13 h_n^{id}—net heating value per unit mole

3.2.1.14 a, b, c—in Eq 1, integers required to balance the equation: C, carbon; H, hydrogen; S, sulfur; O, oxygen

3.2.1.15 *(id)*—ideal gas state

3.2.1.16 *(l)*—liquid phase

3.2.1.17 M—molar mass

3.2.1.18 m—mass flow rate

3.2.1.19 n—number of components

3.2.1.20 P—pressure in absolute units (psia)

3.2.1.21 Q^{id}—ideal energy per unit time released as heat upon combustion

3.2.1.22 R—gas constant, 10.7316 psia.ft^3/(lb mol•R) in this practice (based upon R = 8.314 48 J/(mol•K))

3.2.1.23 (sat)—denotes saturation value

3.2.1.24 T—absolute temperature, °R = °F + 459.67 or K = °C + 273.15

3.2.1.25 *(T, P)*—value dependent upon temperature and pressure

3.2.1.26 V—gas volumetric flow rate

3.2.1.27 x—mole fraction

3.2.1.28 Z—gas compressibility factor repeatability of property

3.2.1.29 δ—repeatability of property

3.2.1.30 ρ—density in mass per unit volume

3.2.1.31 $\sum_{j=1}^{n}$—property summed for Components 1 through n, where n represents the total number of components in the mixture

3.2.2 *Superscripts*:

3.2.2.1 *id*—ideal gas value

3.2.2.2 *l*—liquid

3.2.2.3 σ—value at saturation (vapor pressure)

3.2.2.4 ′—reproducibility

3.2.3 *Subscripts*:

3.2.3.1 *a*—value for air

3.2.3.2 *a*—relative number of atoms of carbon in Eq 1

3.2.3.3 *b*—relative number of atoms of hydrogen in Eq 1

3.2.3.4 *c*—relative number of atoms of sulfur in Eq 1

3.2.3.5 *j*—property for component *j*

3.2.3.6 *ii*—non-ideal gas property for component *i*

3.2.3.7 *ij*—non-ideal gas property for mixture of *i* and *j*

3.2.3.8 *jj*—non-ideal gas property for component *j*

3.2.3.9 *w*—value for water

3.2.3.10 1—property for Component 1

3.2.3.11 2—property for Component 2

4. Summary of Practice

4.1 The ideal gas heating value and ideal gas relative density at base conditions (14.696 psia and 60°F (5.6°C)) are calculated from the molar composition and the respective ideal gas values for the components; these values are then adjusted by means of a calculated compressibility factor.

5. Significance and Use

5.1 The heating value is a measure of the suitability of a pure gas or a gas mixture for use as a fuel; it indicates the amount of energy that can be obtained as heat by burning a unit of gas. For use as heating agents, the relative merits of gases from different sources and having different compositions can be compared readily on the basis of their heating values. Therefore, the heating value is used as a parameter for determining the price of gas in custody transfer. It is also an essential factor in calculating the efficiencies of energy conversion devices such as gas-fired turbines. The heating values of a gas depend not only upon the temperature and pressure, but also upon the degree of saturation with water vapor. However, some calorimetric methods for measuring heating values are based upon the gas being saturated with water at the specified conditions.

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5.2 The relative density (specific gravity) of a gas quantifies the density of the gas as compared with that of air under the same conditions.

6. Methods of Analysis

6.1 Determine the molar composition of the gas in accordance with any ASTM or GPA method that yields the complete composition, exclusive of water, but including all other components present in amounts of 0.1 % or more, in terms of components or groups of components listed in Table 1. At least 98 % of the sample must be reported as individual components (that is, not more than a total of 2 % reported as groups of components such as butanes, pentanes, hexanes, butenes, and so forth). Any group used must be one of those listed in Table 1 for which average values appear. The following test methods are applicable to this practice when appropriate for the sample under test: Test Methods D 1717, D 1945, D 2163, and D 2650.

7. Calculation—Ideal Gas Values; Ideal Heating Value

7.1 An ideal combustion reaction in general terms for fuel and air in the ideal gas state is:

$$C_aH_bS_c(id) + (a + b/4 + c)O_2(id) = aCO_2(id) + (h/2)H_2O\,(id \text{ or } l) + cSO_2(id) \quad (1)$$

where *id* denotes the ideal gas state and *l* denotes liquid phase. The ideal net heating value results when all the water remains in the ideal gas state. The ideal gross heating value results when all the water formed by the reaction condenses to liquid. For water, the reduction from $H_2O(id)$ to $H_2O(l)$ is $H_w^{id} - H_w^l$, the ideal enthalpy of vaporization, which is somewhat larger than the enthalpy of vaporization $H_w^v - H_w^l$.

7.1.1 Because the gross heating value results from an ideal combustion reaction, ideal gas relationships apply. The ideal gross heating value per unit mass for a mixture, H_m^{id}, is:

TABLE 1 Properties of Natural Gas Components at 60°F and 14.696 psia[A]

Compound	Formula	Molar Mass, lb·lbmol^{-1}[B]	Molar Mass Ratio, G^{id}[C]	Ideal Gross Heating Value[D]			Ideal Net Heating Value			Summation Factor, b_s, psia^{-1}
				H_n^{id}, kJ · mol^{-1}	H_m^{id}, Btu · lbm^{-1}	H_v^{id}, Btu · ft^{-3}	h_n^{id}, kJ · mol^{-1}	h_m^{id}, Btu · lbm^{-1}	h_v^{id}, Btu · ft^{-3}	
Hydrogen	H_2	2.0159	0.069 60	286.20	6 1022	324.2	241.79	51 566	273.93	0
Helium	He	4.0026	0.138 20	0	0	0	0	0	0	0
Water	H_2O	18.0153	0.622 02	44.409	1059.8	50.312	0	0	0	0.0623
Carbon monoxide	CO	28.010	0.967 11	282.9	4342	320.5	282.9	4 342	320.5	0.0053
Nitrogen	N_2	28.0134	0.967 23	0	0	0	0	0	0	0.0044
Oxygen	O_2	31.9988	1.104 8	0	0	0	0	0	0	0.0073
Hydrogen sulfide	H_2S	34.08	1.176 7	562.4	7 094.2	637.1	517.99	6 534	586.8	0.0253
Argon	Ar	39.948	1.379 3	0	0	0	0	0	0	0.0071
Carbon dioxide	CO_2	44.010	1.519 6	0	0	0	0	0	0	0.0197
Air	[E]	28.9625	1.000 0	0	0	0	0	0	0	0.0050
Methane	CH_4	16.043	0.553 92	891.63	23 891	1010.0	802.71	21 511	909.4	0.0116
Ethane	C_2H_6	30.070	1.038 2	1562.06	22 333	1769.7	1428.83	20 429	1618.7	0.0239
Propane	C_3H_8	44.097	1.522 6	2220.99	21 653	2516.1	2043.3	19 922	2314.9	0.0344
i-Butane	C_4H_{10}	58.123	2.006 8	2870.45	21 232	3251.9	2648.4	19 590	3000.4	0.0458
n-Butane	C_4H_{10}	58.123	2.006 8	2879.63	21 300	3262.3	2657.6	19 658	3010.8	0.0478
i-Pentane	C_5H_{12}	72.150	2.491 2	3531.5	21 043	4000.9	3265.0	19 456	3699.0	0.0581
n-Pentane	C_5H_{12}	72.150	2.491 2	3535.8	21 085	4008.9	3269.3	19 481	3703.9	0.0631
n-Hexane	C_6H_{14}	86.177	2.975 5	4198.1	20 943	4755.9	3887.2	19 393	4403.9	0.0802
n-Heptane	C_7H_{16}	100.204	3.459 8	4857.2	20 839	5502.5	4501.9	19 315	5100.3	0.0944
n-Octane	C_8H_{18}	114.231	3.944 1	5515.9	20 759	6248.9	5116.2	19 256	5796.2	0.1137
n-Nonane	C_9H_{20}	128.258	4.428 4	6175.9	20 701	6996.5	5731.8	19 213	6493.6	0.1331
n-Decane	$C_{10}H_{22}$	142.285	4.912 7	6834.9	20 651	7742.9	6346.4	19 176	7189.9	0.1538
Neopentane	C_5H_{12}	72.015	2.491 2	3517.27	20 958	3985	3250.8	19 371	3683	
2-Methylpentane	C_6H_{14}	86.177	2.975 5	4190.43	20 905	4747	3879.6	19 355	4395	0.080
3-Methylpentane	C_6H_{14}	86.177	2.975 5	4193.03	20 918	4750	3882.2	19 367	4398	0.080
2,2-Dimethylbutane	C_6H_{14}	86.177	2.975 5	4180.63	20 856	4736	3869.8	19 306	4384	0.080
2,3-Dimethylbutane	C_6H_{14}	86.177	2.975 5	4188.41	20 895	4745	3877.5	19 344	4393	0.080
Cyclopropane	C_3H_6	42.081	1.452 9	2092.78	21 381	2371	1959.6	20 020	2220	...
Cyclobutane	C_4H_8	56.108	1.937 3	2747.08	21 049	2747	2569.4	19 688	2911	...
Cyclopentane	C_5H_{10}	70.134	2.421 5	3322.04	20 364	3764	3100.0	19 003	3512	...
Cyclohexane	C_6H_{12}	84.161	2.905 9	3955.84	20 208	4482	3689.4	18 847	4180	...
Ethyne (acetylene)	C_2H_2	26.038	0.899 0	1301.32	21 487	1474	1256.9	20 753	1424	0.021
Ethene (ethylene)	C_2H_4	28.054	0.968 6	1412.06	21 640	1600	1323.2	20 278	1499	0.020
Propene (propylene)	C_3H_6	42.081	1.452 9	2059.35	21 039	2333	1926.1	19 678	2182	0.033
Benzene	C_6H_6	78.114	2.697 1	3202.74	18 177	3742	3169.5	17 444	3591	0.069
Butanes (ave)	C_4H_{10}	58.123	2.006 8	2875	21 266	3257	2653	19 623	3006	0.046
Pentanes (ave)	C_5H_{12}	72.150	2.491 2	3534	21 056	4003	3267	19 469	3702	0.062
Hexanes (ave)	C_6H_{14}	86.177	2.975 5	4190	20 904	4747	3879	19 353	4395	0.080
Butenes (ave)	C_4H_8	56.108	1.937 2	2716	20 811	3077	2538	19 450	2876	0.046
Pentenes (ave)	C_5H_{10}	70.134	2.421 5	3375	20 691	3824	3153	19 328	3572	0.060

[A] This table is consistent with GPA 2145-89, but it is necessary to use the values from the most recent edition of GPA 2145 for custody transfer calculations.
[B] 1984 Atomic Weights: C = 12.011, H = 1.00794, O = 15.9994, N = 14.0067, S = 32.06.
[C] Molar mass ratio is the ratio of the molar mass of the gas to that of air.
[D] Based upon ideal reaction; the entry for water represents the total enthalpy of vaporization.
[E] Composition from: F. E. Jones, *J. Res. Nat. Bur. Stand.*, Vol. 83, 419, 1978.

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$$H_m^{id} = \sum_{j=1}^{n} x_j M_j H_{m,j}^{id} / \sum_{j=1}^{n} x_j M_j \quad (2)$$

where: x_j is the mole fraction of Component j, M_j is the molar mass of Component j from Table 1, and n is the total number of components.

7.1.2 $H_{m,j}^{id}$ is the pure component, ideal gross heating value per unit mass for Component j (at 60°F (15.6°C) in Table 1). Values of H_m^{id} are independent of pressure, but they vary with temperature.

7.2 *Ideal Gas Density*

7.2.1 The ideal gas density, ρ^{id}, is:

$$\rho^{id} = (P/RT) \sum_{j=1}^{n} x_j M_j = MP/RT \quad (3)$$

where: M is the molar mass of the mixture,

$$M = \sum_{j=1}^{n} x_j M_j \quad (4)$$

P is the base pressure in absolute units (psia), R is the gas constant, 10.7316 psia.ft^3/(lb mol•°R) in this practice, based upon R = 8.314 48 J/(mol•K), T is the base temperature in absolute units (°R = °F + 459.67). Values of the ideal gas density at 60°F (15.6°C) and 14.696 psia are in GPA Standard 2145.

7.3 *Ideal Relative Density*:

7.3.1 The ideal relative density d^{id} is:

$$d^{id} = \sum_{j=1}^{n} x_j d_j = \Sigma\, x_j M_j / M_a = M/M_a \quad (5)$$

where: M_a is the molar mass of air. The ideal relative density is the molar mass ratio.

7.4 *Gross Heating Value per Unit Volume*:

7.4.1 Multiplication of the gross heating value per unit mass by the ideal gas density provides the gross heating value per unit volume, H_v^{id}:

$$H_v^{id} = \rho^{id} H_m^{id} = \sum_{j=1}^{n} x_j H_{vj}^{id} \quad (6)$$

$H_{v,j}^{id}$ is the pure component gross heating value per unit volume for Component j at specified temperature and pressure (60°F (15.6°C) and 14.696 psia in Table 1, ideal gas values).

7.4.2 Conversion of values in Table 1 to different pressure bases results from multiplying by the pressure ratio:

$$H_v^{id}(P) = H_v^{id}(P = 14.696) \times P/14.696 \quad (7)$$

7.5 *Real Gas Values—Compressibility Factor*:

7.5.1 The compressibility factor is:

$$Z(T,P) = \rho^{id}/\rho = (MP/RT)/\rho \quad (8)$$

where ρ is the real gas density in mass per unit volume. At conditions near ambient, the truncated virial equation of state satisfactorily represents the volumetric behavior of natural gas:

$$Z(T,P) = 1 + BP/RT \quad (9)$$

where B is the second virial coefficient for the gas mixture. The second virial coefficient for a mixture is:

$$B = x_1^2 B_{11} + x_2^2 B_{22} + \cdots + x_n^2 B_{nn} + 2x_1 x_2 B_{12} + \cdots + 2x_{n-1} x_n B_{n-1,n} = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j B_{ij} \quad (10)$$

where B_{jj} is the second virial coefficient for Component j and B_{ij} is the second cross virial coefficient for Components i and j. The second virial coefficients are functions of temperature. Eq 9 can be used with Eq 10 for calculation of the compressibility factor for the various pressure bases, but it is not accurate at pressures greater than two atmospheres. Special treatment is not required for H_2 and He at mole fractions up to 0.01. Calculations can be made with $B_{jj} = 0$ for hydrogen and helium.

7.5.2 Eq 9 and Eq 10 for calculation of $Z(T,P)$ for a gas mixture are rigorous but require considerable calculations and information that is not always available. An alternative, approximate expression for $Z(T,P)$ that is more convenient for hand calculations is:

$$Z(T,P) = 1 - P[\sum_{j=1}^{n} x_j \sqrt{\beta_{jj}}]^2 \quad (11)$$

where $\beta_{jj} = B_{jj}/RT$ and $\sqrt{\beta_{jj}}$ is the summation factor for Component j. Values of $\sqrt{\beta_{jj}}$ at 60°F (15.6°C) appear in Table 2. The method based upon Eq 11 has been adopted for this practice.

7.6 *Real Gas Density*:

7.6.1 The real gas density ρ at a specific temperature and pressure is:

$$\rho = \rho^{id}/Z \quad (12)$$

where: ρ^{id} and Z are evaluated at the same temperature and pressure.

7.7 *Real Relative Density*:

7.7.1 The real relative density, d is:

$$d = \rho/\rho_a = MZ_a/M_a Z \quad (13)$$

7.8 *Real Heating Value*—The real heating value is not given by division of the ideal heating value by the compressibility factor. Real gas heating values differ from the ideal gas values by less than one part in 10^4 at 14.696 psia, which is of the order of the accuracy of the heating values.

7.9 *Gross Heating Value of Water Wet Gas*:

7.9.1 If the gas contains water as a component but the compositional analysis is on a dry basis, it is necessary to adjust the mole fractions to reflect the presence of water. The corrected mole fractions are:

$$x_j(\text{cor}) = x_j(1 - x_w) \quad (14)$$

The mole fraction of water can range from zero up to the saturated value. The saturated value for x_w is, assuming Raoult's Law:

$$x_w(\text{sat}) = P_w^\sigma/P \quad (15)$$

where: P_w^σ is the vapor pressure of water (0.256 36 psia at 60°F (15.6°C)).

7.9.2 Technically, water has a gross heating value, the ideal enthalpy of condensation. If only the water that is formed during the combustion condenses, then the heat released upon combustion of a wet gas with dry air becomes:

$$H_v^{id}(\text{wet gas}) = (1 - x_w) H_v^{id}(\text{dry gas}) \quad (16)$$

For water-saturated gas, x_w at 60°F (15.6° C) is $0.256\,36/P_b$ where P_b is the base pressure. Eq 16 is adequate for custody transfer applications as a matter of definition. However, this

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TABLE 2 Example Calculations of Gas Properties at 60°F and 14.696 psia (Gas Analysis on Dry Basis)[A]

NOTE 1—Division of Hv^{id} by Z does not give a real gas heating value but rather an ideal gas heating value per real cubic feet. Any digits carried beyond 1 part in 1000 are not significant but only allieviate roundoff error. Although CO_2 has a carbon atom, its $\alpha = 0$ because it is not part of the fuel formula $C_\alpha H_\beta S_\gamma$.

Compound	x_i	α_i	β_i	γ_i	Hv_i^{id}	G_i^{id}	b_i	$x_i\alpha_i$	$x_i\beta_i$	$x_i\gamma_i$	$x_i\,Hv_i^{id}$	$x_i\,G_i^{id}$	$x_i b_i$
Methane	0.8302	1	4	0	1010.0	0.553 92	0.0116	0.8302	3.3208	0	838.5	0.4599	0.009 63
Ethane	0.0745	2	6	0	1769.7	1.038 20	0.0239	0.1490	0.4470	0	131.8	0.0773	0.001 78
Propane	0.0439	3	8	0	2516.1	1.522 60	0.0344	0.1317	0.3512	0	110.5	0.0668	0.001 51
i-Butane	0.0083	4	10	0	3251.9	2.006 80	0.0458	0.0332	0.0830	0	27.0	0.0167	0.000 38
n-Butane	0.0108	4	10	0	3262.3	2.006 80	0.0478	0.0432	0.1080	0	35.2	0.0217	0.000 52
i-Pentane	0.0031	5	12	0	4000.9	2.491 20	0.0581	0.0155	0.0372	0	12.4	0.0077	0.000 18
n-Pentane	0.0025	5	12	0	4008.9	2.491 20	0.0631	0.0125	0.03	0	10.0	0.0062	0.000 16
Hexane	0.0030	6	14	0	4755.9	2.975 50	0.0802	0.0180	0.0420	0	14.3	0.0089	0.000 24
Helium	0.0003	0	0	0	0	0.138 20	0	0	0	0	0	0.0000	0.000 00
Nitrogen	0.0032	0	0	0	0	0.967 23	0.0044	0	0	0	0	0.0031	0.000 01
Carbon dioxide	0.0202	0	0	0	0	1.519 60	0.0197	0	0	0	0	0.0307	0.000 40
Summation	1.0000	...	...	...	...	...	...	1.2333	4.4192	0	1179.7	0.6991	0.014 81

[A] x_w = (0.256 36)/14.696 = 0.0174
G^{id} (dry gas) = 0.6991
Z (dry gas) = 1 − [0.014 81]²(14.696) = 0.9968
Z (dry air) = 1 − [0.0050]²(14.696) = 0.9996
G (dry gas, dry air) = 0.6991(0.9996)/0.9968 = 0.7011
G (dry gas, sat air) = 0.6991(0.9995)/0.9968 = 0.7010
Hv^{id} (dry gas, dry air) = 1179.7 Btu·ft^{-3}
Hv^{id} (sat gas, dry air) = 1179.7(0.9826) = 1159.1 Btu·ft^{-3}
$1 - x_w$ = 0.9826
G^{id} (sat gas) = 0.6991(0.9826) + 0.0174(0.622 02) = 0.6978
Z (sat gas) = 1 − [0.9826(0.014 81) + 0.0174(0.0623)]²(14.696) = 0.9964
Z (sat air) = 1 − [0.9826(0.0050) + 0.0174(0.0623)]²(14.696) = 0.9995
G (sat gas, dry air) = 0.6978(0.9996)/0.9964 = 0.7001
G (sat gas, sat air) = 0.6978(0.9995)/0.9964 = 0.7000
$\{Hv^{id}/Z\}$(dry gas, dry air) = 1179.7/0.9968 = 1183.5 Btu·ft^{-3}
$\{Hv^{id}/Z\}$ (sat gas, dry air) = 1159.1/(0.9964) = 1163.3 Btu·ft^{-3}

equation does not accurately describe the effect of water upon the heating value. Appendix X1 contains a rigorous examination of the effect of water.

7.10 *Calculation of the Ideal Energy Released as Heat:*

7.10.1 When multiplied by the gas flow rate, the ideal gross heating value provides the ideal energy released as heat upon combustion, $\dot{Q}^{id}$, an ideal gas property:

$$\dot{Q}^{id} = \dot{m}H_m^{id} \tag{17}$$

where m is the mass flow rate. For an ideal gas, the mass flow rate is related to the volumetric flow rate, V^{id}, by:

$$\dot{m} = \dot{V}^{id}\,\rho^{id} \tag{18}$$

and

$$\dot{Q}^{id} = \dot{V}^{id}H_v^{id} \tag{19}$$

7.10.2 The ideal gas flow rate is related to the real gas flow rate by:

$$\dot{V}^{id} = \dot{V}/Z \tag{20}$$

where V is the real gas volumetric flow rate and $Z(T,P)$ is the real gas compressibility factor at the same T and P. Hence, combining Eq 19 and Eq 20 gives:

$$\dot{Q}^{id} = H_v^{id}\,\dot{V}/Z\,(T,P) \tag{21}$$

NOTE 1—The ideal energy released per unit time as heat upon combustion, $\dot{Q}^{id}$, can be calculated using the mass flow rate (Eq 17), the ideal gas flow rate (Eq 19), or the real gas flow rate (Eq 21), but is always an ideal gas property. Division of H_v^{id} by the gas compressibility factor $Z(T,P)$ does not produce a real gas heating value but only allows calculation of $\dot{Q}^{id}$ using the real gas flow rate rather than the ideal gas flow rate.

8. Precision

8.1 The properties reported in this practice derive from experimental enthalpy of combustion measurements which, in general, are accurate to 1 part in 1000. The extra digits that appear in the accompanying tables alleviate problems associated with roundoff errors and internal consistency, but they are not significant.

8.2 The values of properties in this practice are those that appear in GPA Standard 2172-97, Fig. 23-2 of the GPSA Engineering Data Book, GPA TP-17, and the TRC Thermodynamic Tables—Hydrocarbons. GPA Standard 2145 is updated annually and the values in that standard should be used in all calculations.

NOTE 2—Three sources of error must be considered: errors in heating values of the components, errors in the calculated compressibility factor, and errors in the composition. The uncertainty (twice the standard deviation) of the ideal gas heating values for components should be 0.03 %. Such errors affect the bias and the agreement between calculated and measured heating values, but they do not affect the precision. Error in the calculated compressibility factor varies with the composition of the gas, but for natural gas, this error should be less than 0.03 % and negligible compared to errors arising from uncertainty in composition. In this practice, the errors in the heating values of the components and the calculated compressibility factor, Z, are neglected. The precision of the method is related to the repeatability and reproducibility of the analysis. An example appears in Table 3.

NOTE 3—It is essential to include all components in the gas sample that appear with mole fractions greater than or equal to 0.001 in the analysis. Some routine analyses do not determine compounds such as He and H_2S, but these compounds are important to the calculations.

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TABLE 3 Example Calculations of Gas Properties at 60°F and 14.696 psia (Gas Analysis on Wet Basis)[A]

NOTE 1—Division of Hv^{id} by Z does not give a real gas heating value but rather an ideal gas heating value per real cubic feet. Any digits carried beyond 1 part in 1000 are not significant but only allieviate roundoff error. Although CO_2 has a carbon atom, its $\alpha = 0$ because it is not part of the fuel formula $C_\alpha H_\beta S_\gamma$.

Compound	x_i	α_i	β_i	γ_i	Hv_i^{id}	G_i^{id}	b_i	$x_i\alpha_i$	$x_i\beta_i$	$x_i\gamma_i$	$x_i\,Hv_i^{id}$	$x_i\,G_i^{id}$	$x_i b_i$
Methane	0.8157	1	4	0	1010.0	0.553 92	0.0116	0.8157	3.2629	0	823.9	0.4518	0.009 46
Ethane	0.0732	2	6	0	1769.7	1.038 20	0.0239	0.1464	0.4392	0	129.5	0.0760	0.001 75
Propane	0.0431	3	8	0	2516.1	1.522 60	0.0344	0.1294	0.3451	0	108.5	0.0657	0.001 48
i-Butane	0.0082	4	10	0	3251.9	2.006 80	0.0458	0.0326	0.0816	0	26.5	0.0164	0.000 37
n-Butane	0.0106	4	10	0	3262.3	2.006 80	0.0478	0.0424	0.1061	0	34.6	0.0213	0.000 51
i-Pentane	0.0030	5	12	0	4000.9	2.491 20	0.0581	0.0152	0.0366	0	12.2	0.0076	0.000 18
n-Pentane	0.0025	5	12	0	4008.9	2.491 20	0.0631	0.0123	0.0295	0	9.8	0.0061	0.000 15
Hexane	0.0029	6	14	0	4755.9	2.975 50	0.0802	0.0177	0.0413	0	14.0	0.0088	0.000 24
Helium	0.0003	0	0	0	0	0.138 20	0	0	0	0	0	0	0
Nitrogen	0.0031	0	0	0	0	0.967 23	0.0044	0	0	0	0	0.0030	0
Carbon dioxide	0.0198	0	0	0	0	1.519 60	0.0197	0	0	0	0	0.0302	0.000 39
Water	0.0174	0	0	0	50.3	0.622 02	0.0623	0	0	0	0.9	0.0108	0.001 09
Summation	1.0000	...	...	...	...	...	...	1.2118	4.3421	0	1160.0	0.6977	0.015 64

[A] G_i^{id} (sat gas) = 0.6977
Z (sat gas) = 1 − [0.015 64]²(14.696) = 0.9964
Z (dry air) = 1 − [0.0050]²(14.696) = 0.9996
G (sat gas, dry air) = 0.6977(0.9996)/0.9964 = 0.6999
Hv^{id} (sat gas, dry air) = 1160.0 − 0.9 = 1159.1 Btu·ft^{-3}
Z (sat air) = 1 − [0.9826(0.050) + 0.0174(0.0623)]²(14.696) = 0.9995
G (sat gas, sat air) = 0.6977(0.9995)/0.9964 = 0.6999
$\{Hv^{id}/Z\}$(sat gas, dry air) = 1159.1/(0.9964) = 1163.3 Btu·ft^{-3}

8.3 *Repeatability*:

8.3.1 If all the components are analyzed and the results are normalized, then the repeatability of the heating value, δH is:

$$\frac{\delta H}{H^{id}} = \sqrt{\frac{1}{(H^{id})^2}\sum_{j=1}^{n}[(H^{id} - H_j^{id})\delta x_j]^2} \qquad (22)$$

8.3.2 If the results of the analysis are made to sum to 1.0 by calculating the methane mole fraction as the difference between 1.0 and the sum of the mole fractions of the other components, then

$$\frac{\delta H}{H^{id}} = \sqrt{\frac{1}{(H^{id})^2}\sum_{j=1}^{n}[H_j^{id}\delta x_j]^2} \qquad (23)$$

where δx_j is the repeatability of the method of analysis for Component j. The differences between heating values calculated from successive pairs of analysis performed by the same operator using the same sample of gas and the same instrument should exceed $2\delta H$ in only 5 % of the tests when δH is taken as one standard deviation.

8.4 *Reproducibility*—The reproducibility $\delta H'$ is calculated from Eq 22 and Eq 23 using $\delta x'_j$, the reproducibility of the method of analysis for Compound j. The difference between heating values calculated from analysis obtained in different laboratories is expected to exceed $\delta H'$ for only 5 % of the analyses.

APPENDIXES

(Nonmandatory Information)

X1. EFFECT OF WATER UPON THE HEATING VALUE

X1.1 Custody transfer of natural gas uses a simple pricing equation that states that the cost of gas is the rate of energy released upon combustion multiplied by the price of gas per energy unit multiplied by the time or accounting period. The rate of energy released upon combustion is the product of the heating value of the gas and the flow rate of the gas. The flow rate of the gas requires knowledge of the compressibility factor and the relative density of the gas. All three custody transfer properties (heating value, compressibility factor, and relative density) can be calculated from the composition given pure component property tables. The equations for calculating the properties of dry natural gas are well known, but this appendix also presents an account of the effects of water contained in the gas and in the air used to burn the gas.

X1.2 The heating value of a natural gas is the absolute value of its enthalpy of combustion in an ideal combustion reaction. The heating value is, therefore, an ideal gas property that can be calculated unambiguously from tables of pure component values and it has no pressure dependence.

X1.3 An ideal combustion reaction with fuel and air in the ideal gas state and the possibility of water in the fuel and air is:

$$C_\alpha H_\beta S_\gamma(id) + (\alpha + \beta/4 + \gamma)(1 + \epsilon)O_2(id) + 0.043\,83(\alpha + \beta/4 + \gamma)(1 + \epsilon)\mathrm{Ar}(id) + [0.001\,62(\alpha + \beta/4 + \gamma)(1 + \epsilon) + x_e/(1 - x_N - x_C)]\mathrm{CO}_2(id) \qquad (X1.1)$$

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TABLE X1.1 Example Calculation of Precision

Compound	Composition, x_j	$H_v^{id} - H_{vl}^{id}$ Btu·ft^{-3}	Repeatability		Reproducibility	
			δx_j	$[(H_v^{id} - H_{vl}^{id})\delta x_j]^2$ (Btu·ft^{-3})^2	$\delta x'_j$	$[(H_v^{id} - H_{vl}^{id})\delta x'_j]^2$ (Btu·ft^{-3})^2
Methane	0.8302	169.7	0.0010	0.029	0.0020	0.115
Ethane	0.0745	−590.0	0.0002	0.014	0.0004	0.056
Propane	0.0439	−1336.4	0.0002	0.071	0.0004	0.286
Isobutane	0.0083	−2072.2	0.0001	0.043	0.0002	0.171
Butane	0.0108	−2082.6	0.0002	0.173	0.0004	0.694
Isopentane	0.0031	−2821.2	0.0001	0.080	0.0002	0.318
Pentane	0.0025	−2829.2	0.0001	0.080	0.0002	0.320
Hexane	0.0030	−3576.2	0.0001	0.128	0.0002	0.512
Helium	0.0003	1179.7	0.0001	0.014	0.0002	0.056
Nitrogen	0.0032	1179.7	0.0001	0.014	0.0002	0.056
Carbon dioxide	0.0202	1179.7	0.0002	0.056	0.0004	0.223
Total	1.0000			0.702		2.807

$$+ [3.728\,73(\alpha + \beta/4 + \gamma)(1 + \epsilon) + x_N / (1 - x_N - x_C)]N_2(id) + (n_w^g + n_w^a)H_2O\,(id)$$

$$= [\alpha + 0.001\,62(\alpha + \beta/4 + \gamma)(1 + \epsilon) + x_C/(1 - x_N - x_C)]CO_2(id) + n_w^v H_2O\,(id) + n_w^l H_2O\,(l) + \gamma SO_2(id) + [3.728\,73(\alpha + \beta/4 + \gamma)(1 + \epsilon) + x_N/(1 - x_N - x_C)]N_2(id)$$

$$+ 0.043\,83(\alpha + \beta/4 + \gamma)(1 + \epsilon)Ar\,(id) + (\alpha + \beta/4 + \gamma)\epsilon O_2(id)$$

where: α, β, and γ are stoichiometric coefficients, ϵ is the fraction excess air, the composition of air is assumed to be that of Table X1.1, n_w^g and the moles of water contained in the gas, n_w^a are the moles of water contained in the air, n_w^v are the moles of water contained in the product gas mixture, n_w^l are the moles of gas that actually condense, X_c is the mole fraction of CO_2 in the gas, and x_N is the mole fraction of N_2 in the gas. If air has been injected into the gas, it is assumed that the effect is accounted for in the excess fraction ϵ. Fuel gas mixtures would have non-integer values of α, β and γ.

X1.4 It is customary to define hypothetical reference states for the water formed by the reaction denoted by Eq 1 (as opposed to "spectator" water that enters the reaction carried by the gas or air). If we assume that the water formed in the reaction remains in the ideal gas state, the heating value is termed "net." If we assume that the water formed in the reaction condenses totally to the liquid state, the heating value is termed "gross." The gross heating value is greater than the net heating value by the ideal enthalpy of vaporization for water:

$$\text{heating value (gross)} - \text{heating value (net)} = H_w(id) - H_w(l) \quad \text{(X1.2)}$$

where:
H = enthalpy,
l = liquid state, and
w = water.

The quantity $H_w\,(id) - H_w(l)$ is the ideal enthalpy of vaporization for water.

X1.5 It is possible to calculate a real gas heating value rather than using a hypothetical state, but the calculations are tedious, the numerical values are negligibly different, and the mathematical simplicity of the defining equation is lost. It is customary in the gas industry to use gross heating value for most calculations, so for the remainder of this appendix, the term "heating value" refers to the gross value.

X1.6 Eq 7 in Section 7 provides the recipe to convert the heating value from one base pressure to another. Note that when using Eq 7, H_v^{id} should be calculated using the values from Table 1 before converting the pressure; the individual values in Table 1 should not be converted. Conversion to another temperature is more complicated. Heating value data exist at 25°C based upon the reaction:

$$C_\alpha H_\beta S_\gamma(id) + (\alpha + \beta/4 + \gamma)O_2(id) = \alpha CO_2(id) + (\beta/2)H_2O\,(l) + \gamma SO_2(id) \quad \text{(X1.3)}$$

X1.7 The experiments use pure oxygen and are corrected to stoichiometric proportions. It is necessary to correct the sensible heat effects to arrive at a different temperature:

$$Hn^{id}(T) = Hn^{id}(25) + \int_{25}^{T}[\sum_{r'} C_p^{id} - \sum_{r} C_p^{id}]dT \quad \text{(X1.4)}$$

where:

$$\sum_{r'} C_p^{id} = \alpha C_{p,CO_2}^{id} + (\beta/2)C_{p,H_2O}^{id} + \gamma C_{p,SO_2}^{id} \quad \text{(X1.5)}$$

$$\sum_{r} C_p^{id} = C_{p,C_\alpha H_\beta S_\gamma}^{id} + (\alpha + \beta/4 + \gamma)C_{p,O_2}^{id} \quad \text{(X1.6)}$$

and: C_p^{id} is the ideal specific heat at constant pressure, r denotes reactants and r' denotes products.

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X2. ACCOUNTING FOR WATER

X2.1 If the gas contains water (or must be assumed to be saturated) but the compositional analysis is on a dry basis, it is necessary to adjust the mole fractions to account for the fact that water has displaced some gas, thus lowering the heating value. The mole fraction of water in the gas results from the definition of relative humidity:

$$x_w = h^g P_w^\sigma / P = n_w /(1 + n_w) \quad \text{(X2.1)}$$

(Based upon one mole of the fuel $C_\alpha H_\beta S_\gamma$) where h^g is the relative humidity of the gas, P_w^σ is the vapor pressure of water, and n_w denotes moles of water. For saturated gas h^g is unity. Rearranging Eq X2.1 gives the moles of water:

$$n_w = x_w/(1 - x_w) \quad \text{(X2.2)}$$

The corrected mole fractions then become:

$$x_i(\text{cor}) = x_i\left[\frac{1}{1 + n_w}\right] = x_i\left[\frac{1}{1 + x_w/(1-x_w)}\right] = (1 - x_w)x_i \quad \text{(X2.3)}$$

and the heating value becomes:

$$Hv^{id} = (1 - x_w)\sum_{i=1}^{N} x_i^{dry} Hv_i^{id} \quad \text{(X2.4)}$$

where water is not included in the N components of the summation. If the compositional analysis determines x_w, and water is included in the N components of the summation:

$$Hv^{id} = \sum_{i=1}^{N} x_i^{wet} Hv_i^{id} - x_w Hv_w^{id} \quad \text{(X2.5)}$$

X2.2 It is necessary to remove the effect of water because, although water has a heating value, it is only a condensation effect. Water carried by wet gas (spectator water) does not actually condense, and only water formed in the reaction contributes to heating value.

X2.3 Accounting for water in the above manner is sufficient for defined custody transfer conditions, but when trying to model actual situations, the question becomes much more complicated. It is obvious that all of the reaction water actually cannot condense because in a situation in which both gas and air are dry some of the reaction water saturates the product gases and the remainder condenses. It is possible to account for these effects in a general manner. To do so, it is necessary to calculate n_w^g, n_w^a, n_w^v, and n_w^l.

$$n_w^g/[1 + (x_N + x_C)/(1 - x_N - x_C) + n_w^g] = h^g P_w^\sigma/P \quad \text{(X2.6)}$$

$$n_w^g = (h^g P_w^\sigma/P)/[(1 - x_N - x_C)(1 - h^g P_w^\sigma/P)$$

$$n_w^a/[4.774\,18(\alpha + \beta/4 + \gamma)(1 + \epsilon) + n_w^a] = h^a P_w^\sigma/P \quad \text{(X2.7)}$$

$$n_w^a = 4.774\,18(\alpha + \beta/4 + \gamma)(1 + \epsilon)(h^a P_w^\sigma/P)/(1 - h^a P_w^\sigma/P)$$

$$n_w^v/\{\alpha + \gamma + (x_N + x_C)/(1 - x_N - x_C) + (\alpha + \beta/4 + \gamma)[0.001\,62(1 + \epsilon) \quad \text{(X2.8)}$$

$$+3.728\,73(1 + \epsilon) + 0.043\,83(1 + \epsilon) + \epsilon] + n_w^v\} = P_w^\sigma/P$$

$$n_w^v = \{\alpha + \gamma + (x_N + x_C)/(1 - x_N - x_C) + (\alpha + \beta/4 + \gamma)[0.001\,62(1 + \epsilon)$$

$$+3.728\,73(1 + \epsilon) + 0.043\,83(1 + \epsilon) + \epsilon]\}(P_w^\sigma/P)/(1 - P_w^\sigma/P)$$

$$n_w^l = \beta/2 + n_w^g + n_w^a - n_w^v \quad \text{(X2.9)}$$

where: h_a is the relative humidity of the air. Eq X2.6 and Eq X2.7 are reformulations of Eq X2.1 to reflect inlet conditions. Eq X2.8 reflects Eq X2.1 for the saturated product gas (it must be saturated before any water can condense). Eq X2.9 is a water balance: $\beta/2$ are the moles of water formed by the reaction, $n_w^g + n_w^a$ are the moles of water that enter with the gas and air, n_w^v are the moles of water that saturate the product gas, and n_w^l are the moles of water that condense. Therefore, the complete correction for the effect of water on heating value is:

$$H_v^{id} = H_v^{id}(\text{Eq X2.4 or Eq X2.5}) + (h^g P_w^\sigma/P)/(1 - x_n - x_c)(1 - h^g P_w^\sigma/P) \quad \text{(X2.10)}$$

$$+ 4.774\,18(\alpha + \beta/4 + \gamma)(1 + \epsilon)(h^a P_w^\sigma/P)/(1 - h^a P_w^\sigma/P) - [\alpha + \gamma + (x_n - x_c)$$

$$(1 - x_n - x_c) + (\alpha + \beta/4 + \gamma)(3.774\,18 + 4.774\,18\,\epsilon)] \times (P_w^\sigma/P)/(1 - P_w^\sigma)\}H_w^{id}]$$

X2.4 Depending upon the relative humidities of the gas and air, the observed heating value can be greater or smaller than that calculated using Eq X2.4 or Eq X2.5. A humidity of air exists for each gas above which Hv^{id} is greater than that calculated by Eq X2.4 or Eq X2.5. That critical value depends upon the gas composition, the humidity of the gas, and the amount of excess air. For pure, dry methane with no excess air, $h_a = 0.793\,45$.

X3. REAL GAS PROPERTIES

X3.1 In principal, we have enough information to convert the heating value to a real gas property (it is not necessary to do so for relative density because the molar mass ratio, G^{id}, is the desired property). This is simply a matter of evaluating the integral:

$$Hn - Hn^{id} = \int_0^P \left\{\left[\left(\frac{\partial H}{\partial P}\right)_T\right]_r - \left[\left(\frac{\partial H}{\partial P}\right)_T\right]_r\right\} dP \quad \text{(X3.1)}$$

where:

$$\left(\frac{\partial H}{\partial V}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P = B - T\frac{dB}{dT} = 2RT^2 b\frac{dB}{dT} \quad \text{(X3.2)}$$

where V is the molar volume. The temperature dependence of b must be defined, but in the custody transfer region it is easy to do so. The products and reactants again correspond to Eq X1.3.

X3.2 While it is obviously possible to make the required calculations to convert the heating value into a real gas

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property, it serves no custody transfer purpose to do so. As we have seen, the cost equation is unchanged; the calculations while obvious are tedious. Hv is slightly different from Hv^{id} because the base pressure is low; the likelihood of having all the information required to use Eq X3.1 is remote. The heating value is defined in a hypothetical state. It is not possible, at base conditions, to have all the water formed in the reaction be either all gas or all liquid; some of the water formed is in each state. Thus, if the definition is of a hypothetical state, using a hypothetical real gas rather than an ideal gas state adds nothing but complexity.

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This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 100 Barr Harbor Drive, West Conshohocken, PA 19428.

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CERTIFICATE

By Authority Of
THE UNITED STATES OF AMERICA
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By the Authority Vested By Part 5 of the United States Code § 552(a) and Part 1 of the Code of Regulations § 51 the attached document has been duly INCORPORATED BY REFERENCE and shall be considered legally binding upon all citizens and residents of the United States of America. *HEED THIS NOTICE*: Criminal penalties may apply for noncompliance.

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CFR Section(s):

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Official Incorporator:
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OFFICE OF THE FEDERAL REGISTER
WASHINGTON, D.C.

Designation: D 3697 – 92 (Reapproved 1996)

Standard Test Method for Antimony in Water[1]

This standard is issued under the fixed designation D 3697; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method[2] covers the determination of dissolved and total recoverable antimony in water by atomic absorption spectroscopy.

1.2 This test method is applicable in the range from 1 to 15 µg/L of antimony. The range may be extended by less scale expansion or by dilution of the sample.

1.3 The precision and bias data were obtained on reagent water, tap water, salt water, and two untreated wastewaters. The information on precision and bias may not apply to other waters.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific precautionary statements, see 5.1 and 8.12.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1129 Terminology Relating to Water[3]

D 1193 Specification for Reagent Water[3]

D 2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D-19 on Water[3]

D 3370 Practices for Sampling Water from Closed Conduits[3]

D 4691 Practice for Measuring Elements in Water by Flame Atomic Absorption Spectrophotometry[3]

D 4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents[3]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D 1129.

3.2 *Definition of Term Specific to This Standard:*

3.2.1 *total recoverable antimony*— an arbitrary analytical term relating to forms of antimony that are determinable by the digestion method which is included in the procedure. Some organic compounds may not be completely recovered.

4. Summary of Test Method

4.1 Organic antimony-containing compounds are decomposed by adding sulfuric and nitric acids and repeatedly evaporating the sample to fumes of sulfur trioxide. The antimony so produced, together with inorganic antimony originally present, is subsequently reacted with potassium iodide and stannous chloride, and finally with sodium borohydride to form stibine. The stibine is removed from solution by aeration and swept by a flow of nitrogen into a hydrogen flame where it is determined by atomic absorption at 217.6 nm.

5. Significance and Use

5.1 Because of the association with lead and arsenic in industry, it is often difficult to assess the toxicity of antimony and its compounds. In humans, complaints referable to the nervous system have been reported. In assessing human cases, however, the possibility of lead or arsenic poisoning must always be borne in mind. Locally, antimony compounds are irritating to the skin and mucous membranes.

6. Interference

6.1 Since the stibine is freed from the original sample matrix, interferences in the flame are minimized.

6.2 Selenium and arsenic, which also form hydrides, do not interfere at concentrations of 100 µg/L. Higher concentrations were not tested.

7. Apparatus

7.1 *Atomic Absorption Spectrophotometer,* for use at 217.6 nm with a scale expansion of approximately 3. A general guide for the use of flame atomic absorption applications is given in Practice D 4691.

NOTE 1—The manufacturer's instructions should be followed for all instrumental parameters.

7.1.1 *Antimony Electrodeless Discharge Lamp.*

7.2 *Recorder or Digital Readout*—Any multirange variable speed recorder or digital readout accessory, or both, that is compatible with the atomic absorption spectrophotometer is suitable.

7.3 *Stibine Vapor Analyzer,* assembled as shown in Fig. 1.

NOTE 2—A static system, such as one using a balloon, has been found to be satisfactory. See McFarren, E. F., "New, Simplified Method for Metal Analysis," *Journal of American Water Works Assoc.,* JAWWA, Vol 64, 1972, p. 28.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications for the Committee on Analytical Reagents of the American Chem-

[1] This test method is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

Current edition approved June 15, 1992. Published October 1992. Originally published as D 3697 – 78. Last previous edition D 3697 – 86.

[2] Platte, J. A., and Marcy, V. M., "A New Tool for the Water Chemist," *Industrial Water Engineering,* IWEGA, May 1965.

[3] *Annual Book of ASTM Standards,* Vol 11.01.

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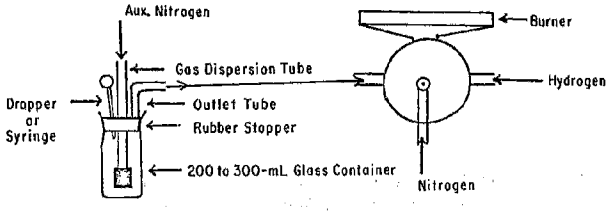


FIG. 1 Stibine Vapor Analyzer

ical Society, where such specifications are available.[4] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193, Type I, II, or III water. Type I is preferred and more commonly used. Type II water was specified at the time of round robin testing of these test methods.

NOTE 3—The user must ensure the type of reagent water chosen is sufficiently free of interferences. The water should be analyzed using the test method.

8.3 *Antimony Solution, Stock* (1.00 mL = 100 μg Sb)—Dissolve 274.3 mg of antimony potassium tartrate, $KSbOC_4H_4O_6 \cdot 1/2H_2O$, in water and dilute to 1000 mL with water.

8.4 *Antimony Solution, Intermediate* (1.00 mL = 10 μg Sb)—Dilute 50.0 mL of antimony stock solution to 500.0 mL with water.

8.5 *Antimony Solution, Standard* (1.0 mL = 0.10 μg Sb)—Dilute 5.0 mL of antimony intermediate solution to 500.0 mL with water. Prepare fresh before each use. This standard is used to prepare working standards at the time of analysis.

8.6 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl).

8.7 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO_3).

8.8 *Nitric Acid* (1+1)—Add 250 mL of concentrated nitric acid (sp gr 1.42) to 250 mL of water.

8.9 *Potassium Iodide Solution* (15 g/100 mL)—Dissolve 15 g of potassium iodide (KI) in 100 mL of water. This solution is stable when stored in an amber bottle or in the dark.

8.10 *Sodium Borohydride Solution* (4 g/100 mL)—Dissolve 4 g of sodium borohydride ($NaBH_4$) and 2 g of sodium hydroxide (NaOH) in 100 mL water. Prepare weekly.

8.11 *Stannous Chloride Solution* (4.6 g/100 mL of concentrated HCl)—Dissolve 5 g of stannous chloride ($SnCl_2 \cdot H_2O$) in 100 mL of concentrated HCl (sp gr 1.19). This solution is stable if a few small pieces of mossy tin are added to prevent oxidation.

8.12 *Sulfuric Acid* (1+1) **Cautiously,** and with constant stirring and cooling, add 250 mL of concentrated sulfuric acid (H_2SO_4, sp gr 1.84) to 250 mL of water.

8.13 *Hydrogen,* commercially available. Set pressure on burner control box to 8 psig (55 KPa) and adjust flowmeter to approximately 6 L/min.

8.14 *Nitrogen,* commercially available. Set pressure on burner control box to 30 psig (206.8 KPa) and adjust flowmeter for maximum sensitivity by volatilizing standards. A flow of approximately 9 L/min has been found satisfactory. This will vary depending on the burner used.

9. Sampling

9.1 Collect the sample in accordance with Practices D 3370. The holding time for the samples may be calculated in accordance with Practice D 4841.

9.2 Immediately preserve samples with HNO_3 (sp gr 1.42) to a pH of 2 or less at the time of collection; normally about 2 mL/L is required. If only dissolved antimony is to be determined, filter the sample through a (No. 325) 0.45-μm membrane filter before acidification.

10. Standardization

10.1 Clean all glassware before use by rinsing first with HNO_3 (1+1) and then with water.

10.2 Prepare, in 200 to 300-mL wide-mouth glass containers, a blank and sufficient standards that contain from 0.0 to 1.5 μg of antimony by diluting 0.0 to 15.0-mL portions of the antimony standard solution to 100 mL with water.

10.3 Proceed as directed in 11.3 to 11.8.

10.4 Prepare an analytical curve by plotting recorder scale readings versus micrograms of antimony on linear graph paper or calculate a standard curve. Alternatively, read directly in concentration if a concentration readout is provided with the instrument.

11. Procedure

11.1 Clean all glassware before use by rinsing first with HNO_3 (1+1) and then with water.

11.2 Pipet a volume of well-mixed acidified sample containing less than 1.5 μg of antimony (100-mL max) into a 200 to 300-mL wide-mouth glass container, and dilute to 100 mL with water (see Fig. 1).

NOTE 4—If only dissolved antimony is to be determined, use a filtered and acidified sample (9.2).

11.3 To each container, add 7 mL of H_2SO_4 (1+1) and 5 mL of concentrated HNO_3. Add a small boiling chip and carefully evaporate to fumes of SO_3. Maintain an excess of HNO_3 until all organic matter is destroyed. This prevents darkening of the solution and possible reduction and loss of antimony. Cool, add 25 mL of water, and again evaporate to fumes of SO_3 to expel oxides to nitrogen.

11.4 Cool, and adjust the volume of each container to approximately 100 mL with water.

11.5 To each container, add successively, with thorough mixing after each addition, 8 mL of concentrated HCl, 1 mL of KI solution, and 0.5 mL of $SnCl_2$ solution. Allow about 15 min for reaction.

[4] *Reagent Chemicals, American Chemical Society Specifications,* American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

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TABLE 1 Recovery and Precision Data

Method	Test Solution	Number of Labs	True Value, µg/L	Mean Value, µg/L	S_T, µg/L	S_o, µg/L	Bias, %	Stated Range, µg/L	R^2	Precision Regression Equations
Hydride/ Flame AAS	RGW	4	3.0	3.15	0.92	0.70	+5.0	1–15	0.80	$S_T = 0.451 + 0.104\,\bar{x}$
			7.0	6.42	0.88	0.78	−8.3[y]		0.89	$S_o = 0.255 + 0.109\,\bar{x}$
			12.0	11.16	1.71	1.54	−7.0			
	WOC	4	3.0	2.74	0.66	0.66	−8.7		0.98	$S_T = 0.346 + 0.132\,\bar{x}$
			7.0	6.00	1.22	0.95	−14.3[y]		1.00	$S_o = 0.386 + 0.0967\,\bar{x}$
			12.0	10.73	1.73	1.43	−10.6[y]			

11.6 Attach one container at a time to the rubber stopper containing the gas dispersion tube.

11.7 Fill the medicine dropper or syringe with 1 mL of $NaBH_4$ solution and insert into the hole in the rubber stopper.

11.8 Add the $NaBH_4$ solution to the sample solution. After the recorder reading (scale reading) has reached a maximum and has returned to the baseline, remove the container. Rinse the gas dispersion tube in water before proceeding to the next sample. Treat each succeeding sample, blank, and standard in a like manner.

12. Calculation

12.1 Determine the weight or concentration of antimony in each sample by referring to 10.4. If the weight is determined from the analytical curve, calculate the concentration of antimony in the sample in micrograms per litre, as follows:

$$\text{Antimony, } \mu g/L = 1000 \times W/V$$

where:

V = volume of sample, mL, and

W = weight of antimony in sample, µg.

13. Precision and Bias

13.1 The single operator and overall precision of this test method for four laboratories, which included a total of six operators analyzing each sample on three different days, within its designated range varies with the quantity being tested.

13.2 Recoveries of known amounts of antimony (from antimony potassium tartrate) in a series of prepared standard for the same laboratories and operators are given in Table 1.

13.3 The precision and bias data were obtained on reagent water, tap water, salt water, and two untreated wastewaters. The information on precision and bias may not apply to other waters.

13.4 This precision and bias statement conforms to the edition of Practice D 2777 that was in place at the time of round-robin testing. It does not meet the requirements of the current edition of Practice D 2777.

14. Keywords

14.1 antimony; atomic absorption; vapor hydride generation; water

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CERTIFICATE

By Authority Of
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By the Authority Vested By Part 5 of the United States Code § 552(a) and Part 1 of the Code of Regulations § 51 the attached document has been duly INCORPORATED BY REFERENCE and shall be considered legally binding upon all citizens and residents of the United States of America. *HEED THIS NOTICE*: Criminal penalties may apply for noncompliance.

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THE EXECUTIVE DIRECTOR
OFFICE OF THE FEDERAL REGISTER
WASHINGTON, D.C.

Designation: D 396 – 98

An American National Standard

Standard Specification for Fuel Oils[1]

This standard is issued under the fixed designation D 396; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 This specification (Note 1) covers grades of fuel oil intended for use in various types of fuel-oil-burning equipment under various climatic and operating conditions. These grades are described as follows:

1.1.1 Grades 1 and 2 are distillate fuels for use in domestic and small industrial burners. Grade 1 is particularly adapted to vaporizing type burners or where storage conditions require low pour point fuel.

1.1.2 Grades 4 (Light) and 4 are heavy distillate fuels or distillate/residual fuel blends used in commercial/industrial burners equipped for this viscosity range.

1.1.3 Grades 5 (Light), 5 (Heavy), and 6 are residual fuels of increasing viscosity and boiling range, used in industrial burners. Preheating is usually required for handling and proper atomization.

NOTE 1—For information on the significance of the terminology and test methods used in this specification, see Appendix X1.

NOTE 2—A more detailed description of the grades of fuel oils is given in X1.3.

1.2 This specification is for the use of purchasing agencies in formulating specifications to be included in contracts for purchases of fuel oils and for the guidance of consumers of fuel oils in the selection of the grades most suitable for their needs.

1.3 Nothing in this specification shall preclude observance of federal, state, or local regulations which can be more restrictive.

1.4 All values are stated in SI units and are regarded as standard.

NOTE 3—The generation and dissipation of static electricity can create problems in the handling of distillate burner fuel oils. For more information on the subject, see Guide D 4865.

2. Referenced Documents

2.1 *ASTM Standards:*

D 56 Test Method for Flash Point by Tag Closed Tester[2]

D 86 Test Method for Distillation of Petroleum Products[2]

D 93 Test Methods for Flash Point by Pensky-Martens Closed Cup Tester[2]

D 95 Test Method for Water in Petroleum Products and Bituminous Materials by Distillation[2]

D 97 Test Method for Pour Point of Petroleum Oils[2]

D 129 Test Method for Sulfur in Petroleum Products (General Bomb Method)[2]

D 130 Test Method for Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test[2]

D 445 Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity)[2]

D 473 Test Method for Sediment in Crude Oils and Fuel Oils by the Extraction Method[2]

D 482 Test Method for Ash from Petroleum Products[2]

D 524 Test Method for Ramsbottom Carbon Residue of Petroleum Products[2]

D 1266 Test Method for Sulfur in Petroleum Products (Lamp Method)[2]

D 1298 Practice for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method[2]

D 1552 Test Method for Sulfur in Petroleum Products (High-Temperature Method)[2]

D 2622 Test Method for Sulfur in Petroleum Products by X-Ray Spectrometry[3]

D 2709 Test Method for Water and Sediment in Distillate Fuels by Centrifuge[3]

D 3245 Test Method for Pumpability of Industrial Fuel Oils[3]

D 3828 Test Methods for Flash Point by Small Scale Closed Tester[3]

D 4052 Test Method for Density and Relative Density of Liquids by Digital Density Meter[3]

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products[3]

D 4294 Test Method for Sulfur in Petroleum Products by Energy-Dispersive X-Ray Fluorescence Spectrometry[3]

D 4865 Guide for Generation and Dissipation of Static Electricity in Petroleum Fuel Systems[4]

D 5949 Test Method for Pour Point of Petroleum Products

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[1] This specification is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.E on Burner, Diesel, Non-aviation Gas Turbine, and Marine Fuels .

Current edition approved Apr. 10, 1998. Published September 1998. Originally published as D 396 – 34 T. Last previous edition D 396 – 96.

[2] *Annual Book of ASTM Standards*, Vol 05.01.

[3] *Annual Book of ASTM Standards*, Vol 05.02.

[4] *Annual Book of ASTM Standards*, Vol 05.03.

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(Automatic Pressure Pulsing Method)[4]
D 5950 Test Method for Pour Point of Petroleum Products (Automatic Tilt Method)[4]
D 5985 Test Method for Pour Point of Petroleum Products (Rotational Method)[4]
2.2 *Other Documents:*[5]
26 CFR Part 48 Diesel Fuel Excise Tax; Dye Color and Concentration
40 Part 80 Regulation of Fuel and Fuel Additives

3. General Requirements

3.1 The grades of fuel oil specified herein shall be homogeneous hydrocarbon oils, free from inorganic acid, and free from excessive amounts of solid or fibrous foreign matter.

3.2 All grades containing residual components shall remain uniform in normal storage and not separate by gravity into light and heavy oil components outside the viscosity limits for the grade.

4. Detailed Requirements

4.1 The various grades of fuel oil shall conform to the limiting requirements shown in Table 1. A representative sample shall be taken for testing in accordance with Practice D 4057.

4.2 Modifications of limiting requirements to meet special operating conditions agreed upon between the purchaser, the seller, and the supplier shall fall within limits specified for each grade, except as stated in supplementary footnotes for Table 1.

5. Test Methods

5.1 The requirements enumerated in this specification shall be determined in accordance with the following ASTM test methods,[6] except as may be required under 5.1.1.

5.1.1 *Flash Point*—Test Method D 93, except where other methods are prescribed by law. For all grades, Test Method D 3828 may be used as an alternate with the same limits. For Grades No. 1 and No. 2, Test Method D 56 may be used as an alternate with the same limits, provided the flash point is below

[5] Available from Superintendent of Documents, U. S. Government Printing Office, Washington, DC 20402.

[6] For information on the precision of the ASTM test methods for fuel oils refer to "An Evaluation of Methods for Determination of Sulfur in Fuel Oils" by A. R. Crawford, Esso Mathematics & Systems Inc. and G. V. Dyroff, Esso Research and Engineering Co., 1969. This document is available from the Publications Section, API Library American Petroleum Institute, 1220 L St., N.W., Washington, DC 20005.

TABLE 1 Detailed Requirements for Fuel Oils[A]

Property	ASTM Test Method[B]	No. 1[C]	No. 2[C]	Grade No. 4 (Light)[C]	No. 4	No. 5 (Light)	No. 5 (Heavy)	No. 6
Flash Point °C, min	D 93	38	38	38	55	55	55	60
Water and sediment, % vol, max	D 2709	0.05	0.05	...	...	...	...	...
	D 95 + D 473	...	...	(0.50)[D]	(0.50)[D]	(1.00)[D]	(1.00)[D]	(2.00)[D]
Distillation temperature °C	D 86							
10 % volume recovered, max		215	...	...	...	...	...	...
90 % volume recovered, min		...	282	...	...	...	...	...
max		288	338	...	...	...	...	...
Kinematic viscosity at 40°C, mm^2/s	D 445							
min		1.3	1.9	1.9	>5.5	...	...	...
max		2.1	3.4	5.5	24.0[E]			
Kinematic viscosity at 100°C, mm^2/s	D 445							
min		...	...	...	...	5.0	9.0	15.0
max		...	...	...	...	8.9[E]	14.9[E]	50.0[E]
Ramsbottom carbon residue on 10 % distillation residue % mass, max	D 524	0.15	0.35	...	...	...	...	...
Ash, % mass, max	D 482	...	...	0.05	0.10	0.15	0.15	...
Sulfur, % mass max[F]	D 129	0.50	0.50	...	...	...	...	...
Copper strip corrosion rating, max, 3 h at 50°C	D 130	No. 3	No. 3	...	...	...	...	...
Density at 15°C, kg/m^3	D 1298							
min		...	...	>876[G]	...	...	...	...
max		850	876	...	...	...	...	...
Pour Point °C, max[H]	D 97	−18	−6	−6	−6	...	...	[I]

[A] It is the intent of these classifications that failure to meet any requirement of a given grade does not automatically place an oil in the next lower grade unless in fact it meets all requirements of the lower grade. However, to meet special operating conditions modifications of individual limiting requirements may be agreed upon among the purchaser, seller and manufacturer.

[B] The test methods indicated are the approved referee methods. Other acceptable methods are indicated in Section 2 and 5.1.

[C] Under United States regulations, Grades No. 1, No. 2, and No.4 (Light) are required by 40 CFR Part 80 to contain a sufficient amount of the dye Solvent Red 164 so its presence is visually apparent. At or beyond terminal storage tanks, they are required by 26 CFR Part 48 to contain the dye Solvent Red 164 at a concentration spectrally equivalent to 3.9 lbs per thousand barrels of the solid dye standard SolventRed 26.

[D] The amount of water by distillation by Test Method D 95 plus the sediment by extraction by Test Method D 473 shall not exceed the value shown in the table. For Grade No. 6 fuel oil, the amount of sediment by extraction shall not exceed 0.50 mass %, and a deduction in quantity shall be made for all water and sediment in excess of 1.0 mass %.

[E] Where low sulfur fuel oil is required, fuel oil falling in the viscosity range of a lower numbered grade down to and including No. 4 can be supplied by agreement between the purchaser and supplier. The viscosity range of the initial shipment shall be identified and advance notice shall be required when changing from one viscosity range to another. This notice shall be in sufficient time to permit the user to make the necessary adjustments.

[F] Other sulfur limits may apply in selected areas in the United States and in other countries.

[G] This limit assures a minimum heating value and also prevents misrepresentation and misapplication of this product as Grade No. 2.

[H] Lower or higher pour points can be specified whenever required by conditions of storage or use. When a pour point less than − 18°C is specified, the minimum viscosity at 40°C for grade No. 2 shall be 1.7 mm^2/s and the minimum 90 % recovered temperature shall be waived.

[I] Where low sulfur fuel oil is required, Grade No. 6 fuel oil will be classified as Low Pour (+ 15°C max) or High Pour (no max). Low Pour fuel oil should be used unless tanks and lines are heated.

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93°C and the viscosity is below 5.5 mm^2/s at 40°C. This test method will give slightly lower values. In cases of dispute, Test Method D 93 shall be used as the referee method.

5.1.2 *Pour Point*—Test Method D 97. For all grades, the automatic Test Methods D 5949, D 5950, and D 5985 can be used as alternates with the same limits. In case of dispute, Test Method 97 shall be used as the referee method. Alternative test methods that indicate flow point properties can be used for low sulfur residual fuels by agreement between purchaser and supplier.

5.1.3 *Water and Sediment*—The water and sediment in Grade Nos. 1 and 2 shall be determined in accordance with Test Method D 2709 and in Grade Nos. 4, 5, and 6 by Test Method D 95 and Test Method D 473. A density of 1.0 kg/L shall be used for the Test Method D 95 water.

5.1.4 *Carbon Residue*—Test Method D 524.

5.1.5 *Ash*—Test Method D 482.

5.1.6 *Distillation*—Distillation of Grade No. 1 and No. 2 oils shall be determined in accordance with Test Method D 86.

5.1.7 *Viscosity*—Viscosity shall be determined in accordance with Test Method D 445.

5.1.8 *Density*—Practice D 1298. Test Method D 4052 can be used as an alternate with the same limits. In case of dispute, Practice D 1298 shall be used as the referee method.

5.1.9 *Corrosion*—Test Method D 130, 3 h test at 50°C.

5.1.10 *Sulfur*—Test Method D 129. Test Methods D 1552, D 2622, and D 4294 can also be used for all grades. In addition, Test Method D 1266 can be used for Grade 1, but only with samples having sulfur contents of 0.4 mass per cent and less (down to 0.01 %). In case of dispute, Test Method D 129 is the referee test method for this specification.

6. Keywords

6.1 burner fuels; fuel oils; furnace oils; petroleum and petroleum products; specifications

APPENDIX

(Nonmandatory Information)

X1. SIGNIFICANCE OF ASTM SPECIFICATION FOR FUEL OILS

X1.1 Scope

X1.1.1 This specification divides fuel oils into grades based upon the types of burners for which they are suitable. It places limiting values on several of the properties of the oils in each grade. The properties selected for limitation are those that are believed to be of the greatest significance in determining the performance characteristics of the oils in the types of burners in which they are most commonly used.

X1.2 Classes

X1.2.1 Because of the methods employed in their production, fuel oils fall into two broad classifications: distillates and residuals. The distillates consist of overhead or distilled fractions. The residuals are bottoms remaining from the distillation, or blends of these bottoms with distillates. In this specification, Grades No. 1 and No. 2 are distillates and the grades from No. 4 to No. 6 are usually residual, although some heavy distillates can be sold as Grade No. 4.

X1.3 Grades

X1.3.1 *Grade No. 1* is a light distillate intended for use in burners of the vaporizing type in which the oil is converted to a vapor by contact with a heated surface or by radiation. High volatility is necessary to ensure that evaporation proceeds with a minimum of residue.

X1.3.2 *Grade No. 2* is a heavier distillate than grade No. 1. It is intended for use in atomizing type burners which spray the oil into a combustion chamber where the tiny droplets burn while in suspension. This grade of oil is used in most domestic burners and in many medium capacity commercial-industrial burners where its ease of handling and ready availability sometimes justify its higher cost over the residual fuels.

X1.3.3 *Grade No. 4 (Light)* is a heavy distillate fuel or distillate/residual fuel blend meeting the specification viscosity range. It is intended for use both in pressure-atomizing commercial-industrial burners not requiring higher cost distillates and in burners equipped to atomize oils of higher viscosity. Its permissible viscosity range allows it to be pumped and atomized at relatively low-storage temperatures.

X1.3.4 *Grade No. 4* is usually a heavy distillate/residual fuel blend but can be a heavy distillate fuel meeting the specification viscosity range. It is intended for use in burners equipped with devices that atomize oils of higher viscosity than domestic burners can handle. Its permissible viscosity range allows it to be pumped and atomized at relatively low storage temperatures. Thus, in all but extremely cold weather it requires no preheating for handling.

X1.3.5 *Grade No. 5 (Light)* is residual fuel of intermediate viscosity for burners capable of handling fuel more viscous than grade No. 4 without preheating. Preheating may be necessary in some types of equipment for burning and in colder climates for handling.

X1.3.6 *Grade No. 5 (Heavy)* is a residual fuel more viscous than Grade No. 5 (Light) and is intended for use in similar service. Preheating may be necessary in some types of equipment for burning and in colder climates for handling.

X1.3.7 *Grade No. 6*, sometimes referred to as Bunker C, is a high-viscosity oil used mostly in commercial and industrial heating. It requires preheating in the storage tank to permit pumping, and additional preheating at the burner to permit atomizing. The extra equipment and maintenance required to handle this fuel usually preclude its use in small installations.

X1.3.8 Residual fuel oil supplied to meet regulations requiring low sulfur content can differ from the grade previously

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supplied. It may be lower in viscosity (and fall into a different grade number). If it must be fluid at a given temperature, Test Method D 97 need not accurately reflect the pour point which can be expected after a period of storage. It is suggested that the purchaser and supplier discuss the proper handling and operating techniques for a given low-sulfur residual fuel oil in the installation where it is to be used.

X1.4 Significance of Test Methods

X1.4.1 The significance of the properties of fuel oil on which limitations are placed by the specification is as follows:

X1.4.1.1 *Flash Point*—The flash point of a fuel oil is an indication of the maximum temperature at which it can be stored and handled without serious fire hazard. The minimum permissible flash point is usually regulated by federal, state, or municipal laws and is based on accepted practice in handling and use.

X1.4.1.2 *Pour Point*—The pour point is an indication of the lowest temperature at which a fuel oil can be stored and still be capable of flowing under very low forces. The pour point is prescribed in accordance with the conditions of storage and use. Higher pour point fuels are permissible where heated storage and adequate piping facilities are provided. An increase in pour point can occur when residual fuel oils are subjected to cyclic temperature variations that can occur in the course of storage or when the fuel is preheated and returned to storage tanks. To predict these properties, Test Method D 3245 may be required.

X1.4.1.3 *Water and Sediment*—Appreciable amounts of water and sediment in a fuel oil tend to cause fouling of facilities for handling it, and to give trouble in burner mechanisms. Sediment may accumulate in storage tanks and on filter screens or burner parts, resulting in obstruction to flow of oil from the tank to the burner. Water in distillate fuels can cause corrosion of tanks and equipment and it can cause emulsions in residual fuels.

X1.4.1.4 *Carbon Residue*—The carbon residue of a fuel is a measure of the carbonaceous material left after all the volatile components are vaporized in the absence of air. It is a rough approximation of the tendency of a fuel to form deposits in vaporizing burners, such as pot-type and sleeve-type burners, where the fuel is vaporized in an air-deficient atmosphere.

X1.4.1.4.1 To obtain measurable values of carbon residue in the lighter distillate fuel oils, it is necessary to distill the oil to remove 90 % of it in accordance with Section 9 of Test Method D 524, and then determine the carbon residue concentrated in the remaining 10 % bottoms.

X1.4.1.5 *Ash*—The amount of ash is the quantity of noncombustible material in an oil. Excessive amounts can indicate the presence of materials that cause high wear of burner pumps and valves, and contribute to deposits on boiler heating surfaces.

X1.4.1.6 *Distillation*—The distillation test shows the volatility of a fuel and the ease with which it can be vaporized. The test is of greater significance for oils that are to be burned in vaporizing type burners than for the atomizing type. For example, the maximum 10 % and 90 % distilled temperatures are specified for grade No. 1 fuel. The limiting 10 % value assures easy starting in vaporizing type burners and the 90 % limit excludes heavier fractions that would be difficult to vaporize.

X1.4.1.6.1 The limits specified for grade No. 2 heating oil define a product that is acceptable for burners of the atomizing type in household heating installations. Distillation limits are not specified for fuel oils of grades Nos. 4, 5, and 6.

X1.4.1.7 *Viscosity Limits for Grades Nos. 1 and 2*—The viscosity of an oil is a measure of its resistance to flow. In fuel oil it is highly significant since it indicates both the relative ease with which the oil will flow or can be pumped, and the ease of atomization.

X1.4.1.7.1 Viscosity limits for No. 1 and No. 2 grades are specified to help maintain uniform fuel flow in appliances with gravity flow, and to provide satisfactory atomization and constant flow rate through the small nozzles of household burners. For the heavier grades of industrial and bunker fuel oils, viscosity is of major importance, so that adequate preheating facilities can be provided to permit them to be pumped to the burner and to provide good atomization. However, it is equally important that the maximum viscosity under the existing conditions be such that the oil can be pumped satisfactorily from the storage tank to the preheater.

X1.4.1.8 *Density*—Density alone is of little significance as an indication of the burning characteristics of fuel oil. However, when used in conjunction with other properties, it is of value in mass-volume relationships and in calculating the specific energy (heating value) of an oil.

X1.4.1.9 *Corrosion*—The corrosion test serves to indicate the presence or absence of materials that could corrode copper, brass, and bronze components of the fuel system. This property is specified only for Nos. 1 and 2 distillate fuel oils.

X1.4.1.10 Limited sulfur content of fuel oil can be required for special uses in connection with heat treatment, nonferrous metal, glass, and ceramic furnaces or to meet federal, state, or local legislation or regulations.

X1.4.1.11 *Nitrogen*—Nitrogen oxide emission regulations have been imposed on certain combustion facilities as a function of fuel nitrogen content. For purposes of these regulations, distillate fuels, low nitrogen residual fuels, and high nitrogen residual fuels have been defined by their nitrogen content. Installations are required to meet different emission standards according to the classification of the fuel being used. When regulations require such a distinction to be made, fuel nitrogen specifications can be needed in the contractual agreement between the purchaser and the supplier.

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Designation: MPMS Chapter 8.2

Standard Practice for Automatic Sampling of Petroleum and Petroleum Products[1]

This standard is issued under the fixed designation D 4177; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense. Consult the DoD Index of Specifications and Standards for the specific year of issue which has been adopted by the Department of Defense.

This practice has been approved by the sponsoring committees and accepted by the cooperating organizations in accordance with established procedures.

1. Scope

1.1 This practice covers information for the design, installation, testing, and operation of automated equipment for the extraction of representative samples of petroleum and petroleum products from a flowing stream and storing them in a sample receiver. If sampling is for the precise determination of volatility, use Practice D 5842 in conjunction with this practice. For sample mixing, refer to Practice D 5854. Petroleum products covered in this practice are considered to be a single phase and exhibit Newtonian characteristics at the point of sampling.

1.2 *Applicable Fluids*—This practice is applicable to petroleum and petroleum products with vapor pressures at sampling and storage temperatures less than or equal to 101 kPa (14.7 psi). Refer to D 5842 when sampling for Reid vapor pressure (RVP) determination.

1.3 *Non-applicable Fluids*—Petroleum products whose vapor pressure at sampling and sample storage conditions are above 101 kPa (14.7 psi) and liquified gases (that is, LNG, LPG etc.) are not covered by this practice.

1.3.1 While the procedures covered by this practice will produce a representative sample of the flowing liquid into the sample receiver, specialized sample handling may be necessary to maintain sample integrity of more volatile materials at high temperatures or extended residence time in the receiver. Such handling requirements are not within the scope of this practice. Procedures for sampling these fluids are described in Practice D 1265, Test Method D 1145, and GPA 2166.

1.4 Annex A2 contains theoretical calculations for selecting the sampler location. Annex A3 lists acceptance methodologies for sampling systems and components. Annex A4 gives performance criteria for permanent installations, while Annex A5 has the criteria for portable sampling units. Appendix X1 is a design data sheet for automatic sampling systems; Appendix X2 compares the percent sediment and water to unloading time period.

1.5 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

2. Referenced Documents

2.1 *ASTM Standards:*

D 923 Test Method for Sampling Electrical Insulating Liquids[2]

D 1145 Test Method for Sampling Natural Gas[3]

D 1265 Practice for Sampling Liquified Petroleum (LP) Gases—Manual Method[4]

D 4057 Manual Sampling of Petroleum and Petroleum Products[5]

D 4928 Test Method for Water in Crude Oils by Coulometric Karl Fischer Titration[6]

D 5842 Practice for Sampling and Handling of Fuels for Volatility Measurements[6]

D 5854 Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products[6]

2.2 *API Standards:*[7]

API Manual of Petroleum Measurement Standards, Chapter 3

API Manual of Petroleum Measurement Standards, Chapter 4

API Manual of Petroleum Measurement Standards, Chapter 5

API Manual of Petroleum Measurement Standards, Chapter 6

API Manual of Petroleum Measurement Standards, Chapter 10

2.3 *Gas Processors Association Standard:*[8]

GPA 2166 Obtaining Natural Gas Samples for Analysis by Gas Chromatography

[1] This practice is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.02 on Static Petroleum Measurement.

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[2] *Annual Book of ASTM Standards*, Vol 10.03.

[3] *Annual Book of ASTM Standards*, Vol 05.05.

[4] *Annual Book of ASTM Standards*, Vol 05.01.

[5] *Annual Book of ASTM Standards*, Vol 05.02.

[6] *Annual Book of ASTM Standards*, Vol 05.03.

[7] Available from American Petroleum Institute, 1220 L St., NW, Washington, DC 20005.

[8] Available from Gas Processors Assoc., 6526 E. 60th St., Tulsa, OK 14145.

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2.4 *Institute of Petroleum Standard:*[9]
IP Petroleum Measurement Manual, Part IV, Sampling Section 2, Guide to Automatic Sampling of Liquids from Pipelines, Appendix B, 34th Ed
2.5 *Government Standard:*[10]
CFR 29, Section 11910.1000

3. Terminology

3.1 *Description of Terms Specific to This Standard:*
3.1.1 *automatic sampler, n*—a device used to extract a representative sample from the liquid flowing in a pipe.
3.1.1.1 *Discussion*—The automatic sampler usually consists of a probe, a sample extractor, an associated controller, a flow measuring device, and a sample receiver.
3.1.2 *automatic sampling system, n*—a system consisting of stream conditioning, an automatic sampler, and sample mixing and handling.
3.1.3 *dissolved water, n*—water in solution in petroleum and petroleum products.
3.1.4 *emulsion, n*—a water in oil mixture, which does not readily separate.
3.1.5 *entrained water, n*—water suspended in the oil.
3.1.5.1 *Discussion*—Entrained water includes emulsions but does not include dissolved water.
3.1.6 *flow proportional sample, n*—flow taken such that the rate is proportional throughout the sampling period to the flow rate of liquid in the pipe.
3.1.7 *free water, n*—water that exists as a separate phase.
3.1.8 *grab, n*—the volume of sample extracted from a pipeline by a single actuation of the sample extractor.
3.1.9 *homogeneous, adj*—when liquid composition is the same at all points in the container, tank, or pipeline cross section.
3.1.10 *isokinetic sampling, n*—sampling in such a manner that the linear velocity through the opening of the sample probe is equal to the linear velocity in the pipeline at the sampling location and is in the same direction as the bulk of the liquid approaching the sampling probe.
3.1.11 *Newtonian fluid, n*—a liquid whose viscosity is unaffected by the order of magnitude or agitation to which it may be subjected as long as the temperature is constant.
3.1.12 *power mixer, n*—a device which uses an external source of power to achieve stream conditioning.
3.1.13 *primary sample receiver/container, n*—a vessel into which all samples are initially collected.
3.1.14 *probe, n*—the portion of the automatic sampler that extends into the pipe and directs a portion of the fluid to the sample extractor.
3.1.15 *profile testing, n*—a procedure for simultaneously sampling at several points across the diameter of a pipe to identify the extent of stratification.
3.1.16 *representative sample, n*—a portion extracted from a total volume that contains the constituents in the same proportions as are present in the total volume.
3.1.17 *sample, n*—a portion extracted from a total volume that may or may not contain the constituents in the same proportions as are present in that total volume.
3.1.18 *sample controller, n*—a device which governs the operation of the sample extractor.
3.1.19 *sample extractor, n*—a device which removes a sample (grab) from a pipeline, sample loop, or tank.
3.1.20 *sample handling and mixing, n*—the conditioning, transferring and transporting of a sample.
3.1.21 *sample loop (fast loop or slip stream), n*—a low volume bypass diverted from the main pipeline.
3.1.22 *sampling, n*—all the steps required to obtain a sample that is representative of the contents of any pipe, tank, or other vessel and to place that sample into a container from which a representative test specimen can be taken for analysis.
3.1.23 *sampling system proving, n*—a procedure used to validate an automatic sampling system.
3.1.24 *sediment and water (S&W), n*—material which coexists with, but is foreign to, a petroleum liquid.
3.1.24.1 *Discussion*—S&W may include dissolved water, free water and sediment, and emulsified and entrained water and sediment.
3.1.25 *static mixer, n*—a device which utilizes the kinetic energy of the flowing fluid to achieve stream conditioning.
3.1.26 *stream condition, n*—the distribution and dispersion of the pipeline contents, upstream of the sampling location.
3.1.27 *stream conditioning, n*—the mixing of a flowing stream so that a representative sample can be extracted.
3.1.28 *time proportional sample, n*—a sample composed of equal volume grabs taken from a pipeline at uniform time intervals during the entire transfer.
3.1.29 *worst case conditions, n*—the operating conditions for the sampler that represent the most uneven and unstable concentration profile at the sampling location.

4. Significance and Use

4.1 Representative samples of petroleum and petroleum products are required for the determination of chemical and physical properties, which are used to establish standard volumes, prices, and compliance with commercial and regulatory specifications.

5. Representative Sampling Criteria

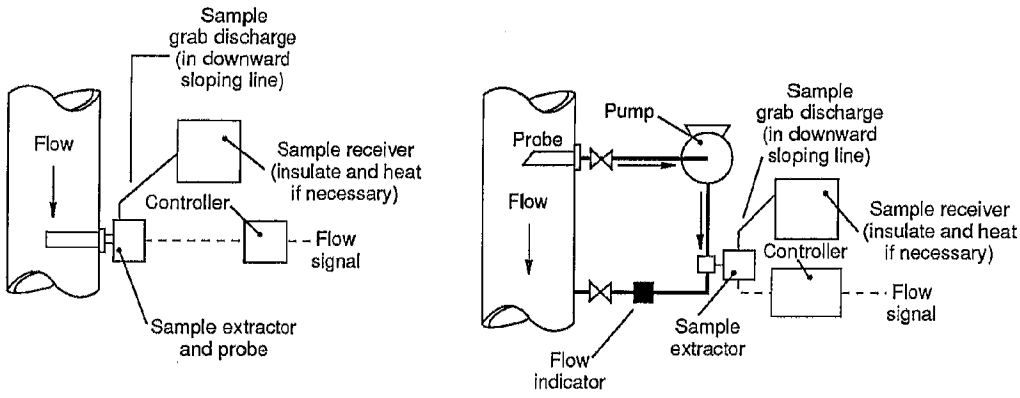
5.1 The following criteria must be satisfied to obtain a representative sample from a flowing stream.
5.1.1 For non-homogeneous mixtures of oil and water, free and entrained water must be uniformly dispersed at the sample point.
5.1.2 Grabs must be extracted and collected in a flow proportional manner that provides a representative sample of the entire parcel volume.
5.1.3 Grabs must be a consistent volume.
5.1.4 The sample must be maintained in the sample receiver without altering the sample composition. Venting of hydrocarbon vapors during receiver filling and storage must be minimized. Samples must be mixed and handled to ensure a representative test specimen is delivered into the analytical apparatus.

6. Automatic Sampling Systems

6.1 An automatic sampling system consists of stream

[9] Available from The Institute of Petroleum, 61 New Cavendish St., London WIM 8AR, England.
[10] Available from Supt. of Documents, U.S. Government Printing Office, Washington, DC 20402.

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NOTE—Arrow does not indicate piping orientation.

FIG. 1 Typical Automatic Sampling Systems

conditioning upstream of the sampling location, a device to physically extract a grab from the flowing stream, a flow measurement device for flow proportioning, a means to control the total volume of sample extracted, a sample receiver to collect and store the grabs and, depending on the system, a sample receiver/mixing system. Unique properties of the petroleum or petroleum product(s) being sampled may require the individual components or the entire system be insulated or heated, or both. Appendix X1 references many of the design consideration that should be taken into account.

6.2 Grabs must be taken in proportion to flow. However, if the flow rate, during the total parcel delivery (week, month, etc.) varies less than ±10 % from the average flow rate, a representative sample may be obtained by the time proportional control of the grabs.

6.3 There are two types of automatic sampling systems (see Fig. 1). Both systems can produce representative samples if properly designed and operated. One system locates the extracting device directly in the main line, whereas the other system locates the extracting device in a sample loop.

6.4 In a sample loop type system, a probe is located in the main pipeline and directs a portion of the fluid flow into the sample loop. This probe may be a 90° elbow or a 45° level facing upstream (see 10.2). The average flow velocity through the sample loop shall be near the maximum average velocity expected in the main pipeline, but not less than 2.5 m/s (8 ft/s).

6.5 The controller which operates the sample extractor in the sample loop receives its flow proportional signal from the flow meter(s) in the main line. For sample loop installations, a flow indicator must also be installed in the sample loop.

6.6 If circulation in the sample loop stops and sampling continues, a non-representative sample will result. A low-flow alarm should be installed to alert the operator of a loss of flow. In no case shall a filter be installed in a sample loop, upstream of the sample extractor, as it may alter the representativeness of the sample.

7. Sampling Frequency

7.1 Guidelines for sampling frequency can be given in terms of "grab per lineal distance of pipeline volume." For marine and pipeline service this minimum guideline can be related to barrels per grab using the following equation:

$$\text{BBL/grab} = .0001233 \times D^2 \text{ or } .079548 \times d^2 \quad (1)$$

where:

D = nominal pipe diameter, mm and

d = nominal pipe diameter, in.

7.2 This formula equates to one grab for every 25 lineal metres (approximately 80 ft) of pipeline volume.

7.3 Sampling frequency should be based on maximizing grabs for the available receiver size. Typically, Lease Automatic Custody Transfer (LACT) or Automatic Custody Transfer (ACT) units are paced at one grab per one to ten barrels.

7.4 The optimum sampling frequency is the maximum number of grabs which may be obtained from any parcel operating within the grab frequency and grab volume limitations of the equipment. The completed sample should be of sufficient volume to mix and properly analyze while not over filling the sample receiver.

8. Stream Conditioning

8.1 The sampler probe must be located at a point in the pipe where the flowing stream is properly conditioned. This conditioning may be accomplished with adequate flow velocity through the piping system or mixing elements may be added to supplement mixing provided by the basic piping. Petroleum that contains free or entrained sediment and water (S&W) requires adequate mixing energy to create a homogeneous mixture at the sample point.

8.2 Petroleum products are generally homogeneous and usually require no special stream conditioning. Exceptions to this may occur if free water is present or if a product is exiting a blending system.

8.3 *Velocities and Mixing Elements:*

8.3.1 Figure 2, based on tests, provides a guideline for minimum velocities versus mixing elements for pipes 50 mm (2 in.) in diameter and larger. Stream conditioning can be accomplished with pressure reducing valves, metering manifolds, lengths of reduced diameter piping, or piping elements

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Mixing Element	Piping	Minimum Pipeline Velocity, meters per second: 0	.305	.61	.91	1.22	1.52	1.83	2.13	2.44
Power mixing	Horizontal or vertical	Adequate at any velocity								
Static mixing	Vertical	Stratified	Not Predictable	Adequately dispersed						
Static mixing	Horizontal	Stratified		Not predictable		Adequately dispersed				
Piping elements	Vertical	Stratified		Not predictable			Adequately dispersed			
Piping elements	Horizontal	Stratified				Not predictable			Adequately dispersed	
None	Horizontal or vertical	Stratified or not predictable								
		0	1	2	3	4	5	6	7	8
		Minimum Pipeline Velocity, feet per second								

FIG. 2 General Guidelines for Minimum Velocities Versus Mixing Elements

(valves, elbows, tees, piping, or expansion loops).

8.3.2 Where the flow velocity at the automatic sampler probe location falls below the minimum levels detailed in Table 1, additional means will be required to provide adequate stream conditioning such as power mixers or static mixers. The effect of viscosity, density, water content, as well as the relative position of the mixing element(s) and sample probe should also be considered.

8.3.3 Specific calculation procedures for estimating the acceptability of a proposed or existing sampling location are detailed in Annex A2.

8.3.4 Again it should be remembered that petroleum products are assumed to be homogeneous at the point of sampling and require no additional stream conditioning unless specifically sampling for water content, or where the sampler is downstream of a blending manifold.

9. Special Considerations for Marine Applications

9.1 When pumping from a shore tank or from a vessel, a significant amount of free water may be transferred during a short period of time (see Appendix X2). This may occur when the pumping rate is low and the oil/water mixture is stratified. The stream conditioning may not be adequate to provide a representative sample. To help minimize this condition, a tank that does not contain free water should be utilized first. Tanks containing free water can be discharged when the pumping rate is normal.

9.2 If the sampler is located some distance from the point of load/discharge, operating procedures should account for the line fill between those two points.

10. Probes

10.1 *Probe Location and Installation:*

10.1.1 The recommended sampling area is approximately the center one-third of the pipeline cross-section area as shown in Fig. 3.

10.1.2 The probe opening must face upstream and the external body of the probe should be marked with the direction of flow to verify that the probe is installed correctly.

TABLE 1 Typical Receiver Sizes

Lease automatic custody transfer	10–60 L (3–15 gal)
Pipelines (crude petroleum)	20–60 L (5–15 gal)
Pipelines (products)	4–20 L (1–5 gal)
Portable sampler	1–20 L (1 qt–5 gal)
Tanker loading/unloading	20–75 L (5–20 gal)

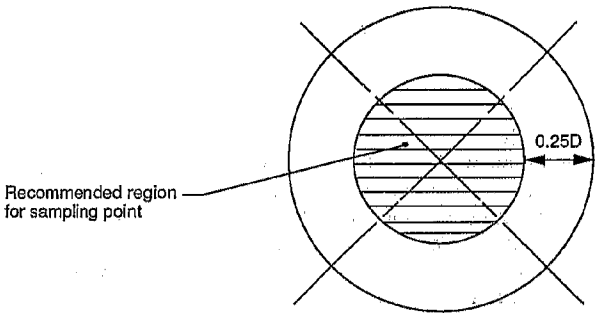


FIG. 3 Recommended Sampling Area

10.1.3 The probe must be located in a zone where sufficient mixing results in adequate stream conditioning. This zone is generally from 3 to 10 diameters downstream of piping elements, .5 to 4 diameters from static mixers, and 3 to 10 diameters from power mixers. When static or power mixers are used, the manufacturer of the device should be consulted for the probe's optimum location.

10.1.4 The line from the outlet of the extractor to the sample receiver must continuously slope downward from the extractor to the receiver and contain no dead space.

10.1.5 The preferred installation of a combined probe-extractor is in the horizontal plane.

10.1.6 If a vertical piping loop is used for stream conditioning, locate the probe in the downflow section of the loop to obtain the benefit of the additional stream conditioning provided by the three 90° elbows. Locate the probe a minimum of three pipe diameters downstream of the top 90° elbow and not closer than one-half pipe diameter upstream of the final exiting elbow (see Fig. 4).

10.1.7 According to tests sponsored by the American Petroleum Institute (API), locating a sample probe downstream of a single 90° bend is not recommended because of inadequate stream conditioning.

10.2 *Probe Design:*

10.2.1 The mechanical design of the probe should be compatible with the operating conditions of the pipeline and the fluid being sampled. There are three basic designs shown in Fig. 5. Probe openings should be in the center third of the

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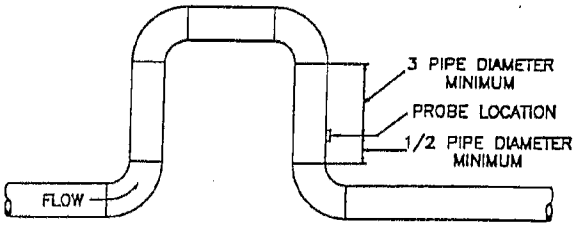


FIG. 4 General Vertical Piping Loop Configuration

cross sectional area of the pipe.

10.2.2 Probe designs commonly used are described as follows:

10.2.2.1 A closed end probe equipped with an open orifice (see Fig. 5A).

10.2.2.2 A short-radius elbow or pipe bend facing upstream. The end of the probe should be chamfered on the inside diameter to give a sharp entrance (see Fig. 5B).

10.2.2.3 A tube cut at a 45° angle with the angle facing upstream (see Fig. 5C).

11. Automatic Sampling Components

11.1 *Extractor*—An automatic sample extractor is a device that extracts a sample (grab) from the flowing medium. The extractor may or may not be an integral part of the probe. The sample extractor should extract a consistent volume that is repeatable within ±5 % over the range of operating conditions and sampling rates.

11.2 *Controller*—A sample controller is a device which governs the operation of the sample extractor. The sample controller should permit the selection of the sampling frequency.

12. Sampler Pacing

12.1 *Custody Transfer Meters*—Custody transfer meters should be used to pace the sampler where available. When flow is measured by multiple meters, the sampler should be paced by the combined total flow signal. Alternatively, a separate sampler may be installed in each meter run. The sample from each meter run must be considered a part of the total sample and in the same proportion as that meter's volume is to the total volume.

12.2 *Special Flow Meters*—When custody transfer is by tank measurements, a flow signal must be provided to the sample controller. This signal may be provided by an add-on flow metering device. These devices should have an accuracy of ±10 % or better, over the total volume of the parcel.

12.3 *Time Proportional Sampling*—An automatic sampler should preferably operate in proportion to flow. However, sampling in a time proportional mode is acceptable if the flow rate variation is less than ±10 % of the average rate over the entire parcel.

13. Primary Sample Receivers

13.1 A sample receiver/container is required to hold and maintain the composition of the sample in liquid form. This includes both stationary and portable receivers, either of which may be of variable or fixed volume design. If the loss of vapors will significantly affect the analysis of the sample, a variable volume type receiver should be considered. Materials of construction should be compatible with the petroleum or petroleum product sampled.

13.2 *Stationary Receivers:*

13.2.1 *General Design Features*—These features may not be applicable to some types of receivers, that is, variable volume receivers.

13.2.1.1 Receiver design must allow for preparation of a homogeneous mixture of the sample.

13.2.1.2 The bottom of the receiver must be continuously sloped downward toward the drain to facilitate complete liquid withdrawal. There should be no internal pockets or dead spots.

13.2.1.3 Internal surfaces of the receiver should be designed to minimize corrosion, encrustation, and clingage.

13.2.1.4 A means should be provided to monitor filling of the receiver. If a sight glass is used, it must be easy to clean and not be a water trap.

13.2.1.5 A relief valve should be provided and set at a pressure that does not exceed the design pressure of the receiver.

13.2.1.6 A means to break vacuum should be provided to permit sample withdrawal from the receiver.

13.2.1.7 A pressure gage should be provided.

13.2.1.8 Receivers should be sheltered from adverse ambient conditions when in use.

13.2.1.9 Receivers may need to be heat traced or insulated, or both, when high pour point or high viscosity petroleum or petroleum products are sampled. Alternatively, they may be housed in heated and insulated housing. Exercise caution to ensure added heating does not affect the sample.

13.2.1.10 Use of multiple sample receivers should be considered to allow flexibility in sampling sequential parcels and line displacements. Exercise care in the piping design to prevent contamination between samples of different parcels. See Fig. 6.

13.2.1.11 Receivers should have an inspection cover or closure of sufficient size to facilitate easy inspection and cleaning.

13.2.1.12 Facilities for security sealing should be provided.

13.2.1.13 The system must be capable of completely draining the receiver, mixing pump, and associated piping.

13.2.1.14 The circulating system shall not contain any dead legs.

13.3 *Portable Receivers*—In addition to considerations outlined in 13.2, portable receivers may include the following additional features:

13.3.1 Light weight,

13.3.2 Quick release connections for easy connection/disconnect to the probe/extractor and the laboratory mixer (see Fig. 7), and

13.3.3 Carrying handles.

13.4 *Receiver Size*—The receiver should be sized to match its intended use and operating conditions. The size of the receiver is determined by the total volume of sample required, the number of grabs required, the volume of each grab and, transportability of the receiver if portable. Typical sample receiver sizes are shown in Table 1.

14. Sample Mixing and Handling

14.1 Sample in the receiver must be properly mixed to

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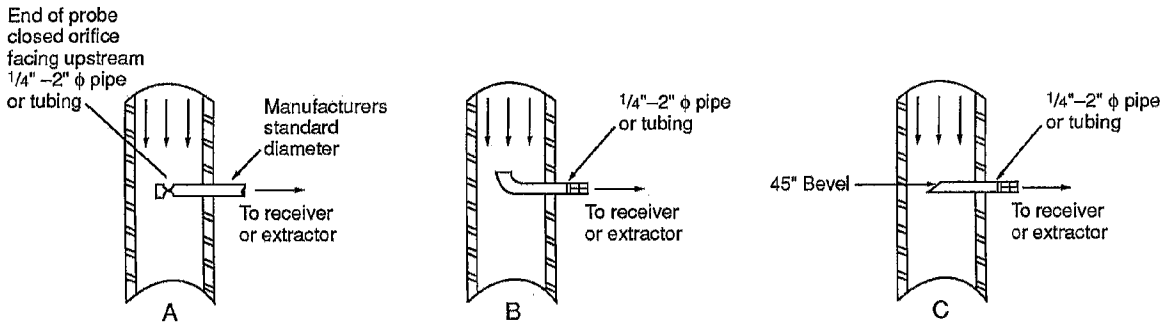
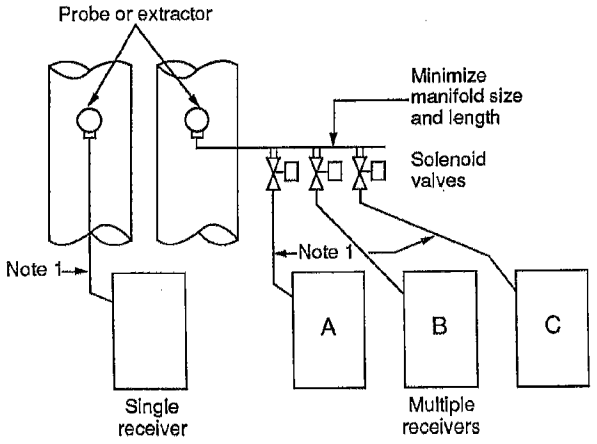
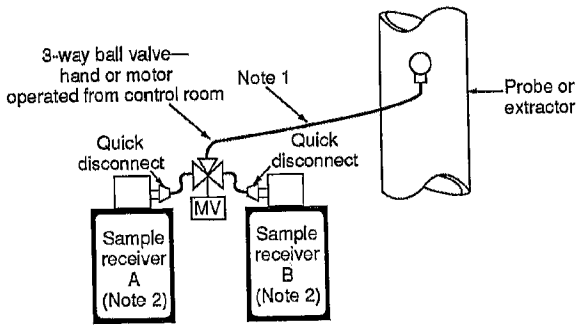


FIG. 5 Probe Designs



NOTE—6.4 or 9.5 mm (¼ or ⅜ in.) tubing, as short as possible and sloping continuously toward the sample receiver, should be used. 9.5 mm (⅜ in.) tubing should be used where long sampling lines cannot be avoided or in crude oil service. Heat trace and insulate these lines when necessary.

FIG. 6 Receiver(s) Installation



Installation Showing Portable Receivers

NOTE 1—6.4 or 9.5 mm (⅜ in.) tubing, as short as possible and sloping continuously toward the sample receiver should be used. Three-eighths inch tubing should be considered where long sampling lines cannot be avoided or the crude oil is viscous. Heat trace and insulate these lines when necessary.

NOTE 2—Sample should flow into a connection at the top of the container. In warm climates, a sun shield should be provided to avoid excessive temperature changes in sample receivers.

NOTE 3—In warm climates, a sun shield should be provided to avoid excessive temperature changes in sample receivers.

NOTE 4—In cold climates, consider placing sample receivers in a heated housing or heat trace and insulate the receivers and sample lines.

FIG. 7 Portable Receiver(s) Installation

ensure a homogenous sample. Transfer of samples from the receiver to another container or the analytical glassware in which they will be analyzed requires special care to maintain their representative nature. See Practice D 5854 for detailed procedures.

15. Portable Samplers

15.1 A typical application of a portable sampling system is on board a marine vessel. There are also occasional applications on shore. The same criteria for representative sampling applies to both portable and stationary sampling systems. Exercise caution when using portable samplers on marine vessels due to the difficulty in verifying stream conditioning during actual operations. An example of a marine application is shown in Fig. 8.

15.2 *Design Features*—Special features and installation requirements for a portable sampler are:

15.2.1 A spool assembly fitted with a sample probe/extractor and flow sensor is inserted between the ship's manifold and each loading/unloading arm or hose. If the grab size of each sampler is equal, a common receiver can be used.

15.2.2 A controller is required for each extractor. The controller must be able to record total number of grabs and total volume.

15.2.3 Piping arrangement at the ship's manifold will often distort the flow profile. The flow sensor, when operated under the piping and flow conditions at the ship's manifold, must meet the accuracy criteria in 12.2.

15.2.4 Stream conditioning is accomplished by velocity of the fluid and the piping elements ahead of the probe. The number of hoses, arms, and lines in service at any one time may need to be limited to maintain sufficiently high velocity.

15.2.5 The controller may be placed on the ship's deck, which is usually classified as a hazardous zoned area. If the controller is electronic, it should meet the requirements of the hazardous area.

15.2.6 Air supply must meet the requirements of the equipment.

15.2.7 For high pour or viscous fluids, particularly in cold climates, the line from the extractor to the receiver may require a thermally insulated high pressure hose or tubing. The receiver should be placed as close to the extractor as

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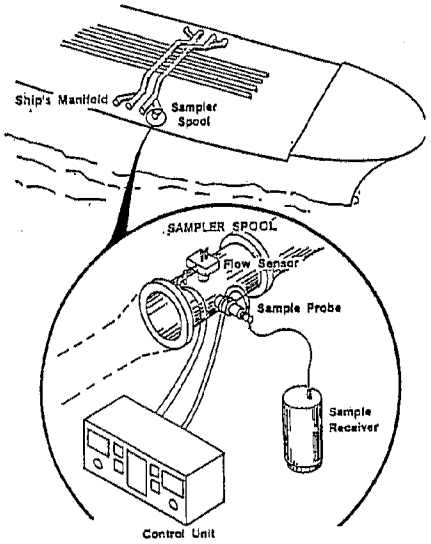


FIG. 8 Typical Portable Marine Installation

possible to minimize the hose length. The hose or tubing should have an internal diameter of 9.5 mm (3/8 in.) or more and slope continuously downward from the extractor to the receiver. The line from the extractor to the receiver may have to be heat traced.

15.2.8 Filling of receivers should be monitored to ensure that each sampler is operating properly. Frequent visual inspection, level indicators, and weighing have proven to be acceptable monitoring methods.

15.2.9 The portable sampler is used intermittently; therefore the sample probe, extractor, and flow sensor should be cleaned after every use to prevent plugging.

15.2.10 All components and installation must meet applicable regulations, that is, U.S. Coast Guard regulations.

15.3 *Operating Considerations*—The portable sampler operator must maintain operating conditions which provide adequate mixing and produce a representative sample. Performance criteria is given in Annex A5. To meet the criteria requires cooperation of the vessel crew and shore personnel. Special operating requirements are:

15.3.1 The portable sampler operator should keep the flow rate at each flow sensing device within its design range by limiting the number of loading lines or hoses in service during periods of low flow rates, for example, start-up, topping off, stripping, etc.

15.3.2 For discharge operations, the vessel compartment discharge sequence must be controlled so that the amount of free water being discharged during the start-up operation is less than 10 % of the total amount of water in the cargo.

15.3.3 For loadings, a shore tank with no free water is preferred for the initial pumping. Water drawing the tank or pumping a small portion of the tank to another shore tank prior to the opening tank gage, or both, are suggested.

16. Acceptance Tests

16.1 Testing is recommended to confirm that a sampling system is performing accurately. Annex A3 outlines methods for testing samplers that are used for the collection of S&W or free water samples. The test methods fall in two general categories; Total System Testing and Component Testing.

16.2 *Total System Testing*—This test method is a volume balance test where tests are conducted for known amounts of water. It is designed to test the total system including the laboratory handling and mixing of sample. Two procedures are outlined. One involves only the sampler under test, the other utilizes an additional sampler to measure the baseline water.

16.3 *Component Testing*—This test method involves testing individually the components that comprise a sampling system. Where applicable, some of the component tests may be conducted prior to installation of the total system. Components to be tested include:

16.3.1 Probe/extractor,

16.3.2 Profile (for stream conditioning),

16.3.3 Special flow meter, and

16.3.4 Primary sample receiver and mixer.

16.3.5 If a system design has been proven by testing, subsequent systems of the same design (for example, LACT Units), including piping configuration and operated under the same or less criterial conditions (that is, higher flow rate, higher viscosity, lower water content, etc.) need not be tested. Once a system or system design has been proven, the following checks can be used to confirm system reliability:

Component	Check
Stream conditioning	Flow rate or pressure drop if equipped with power or static mixer.
	Profile test for systems with only piping elements.
Pacing device	Compare recorded batch volume to known.
	Compare actual sample volume to expected volume.
Extractor	Compare actual sample volume to expected volume.
	Compare actual grab size to expected grab size.

16.3.6 Portable sampling systems can be tested by the component testing method except for proper stream conditioning. To compensate for this, the performance test for each operation has been designed to evaluate the operation of the sampler. This is shown in Annex A5.

16.4 *Requirements for Acceptability*—Testing by either the component or total system method requires that two out of three consecutive sets of test data repeat within the limits shown in Annex A3.

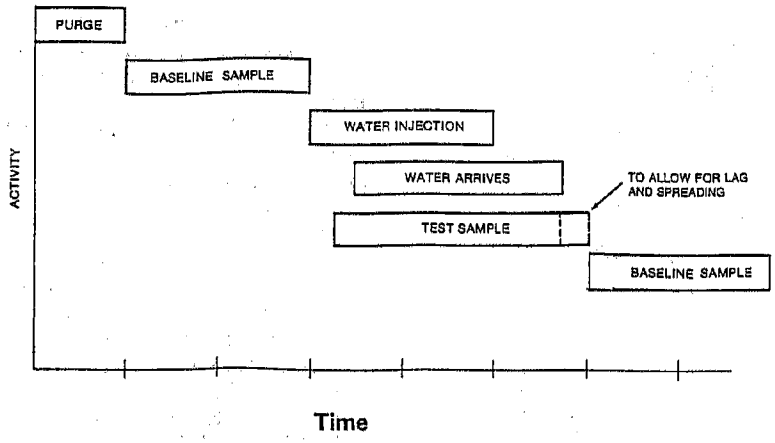
17. Operational Performance Checks/Reports

17.1 Monitoring of sampler performance is a necessary part of every sampling operation. Monitoring is required to make sure that the sample extractor is extracting a uniform grab in a flow proportional manner. This is normally accomplished by assessing the sample volume collected to ensure that it meets expectations for the equipment and transfer volume involved.

17.2 Several procedures may be used to accomplish this requirement, that is, sight glasses, gages, or weigh cells. Selection of a procedure should be based on (*1*) volume of transfer, (*2*) type of installation, (*3*) time interval of transfer, (*4*) whether the sampling facility is manned, (*5*) receiver type, (*6*) purpose of the sample, and (*7*) equipment used.

17.3 For LACT and ACT units, monitoring may consist of comparison between sample volume collected and expected sample volume. For very large transfers including marine transferee, more information may be desired as outlined in Annexes A4 and A5.

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NOTE—Times are calculated based on minimum oil flow rate and the distance between the injection and the sample point.

FIG. 9 Sequence of Acceptance Test Activities

18. Keywords

18.1 acceptance tests; automatic petroleum sampling; controllers; extractor; intermediate sampling receiver; isokinetic sampling; mixing elements; portable samplers; primary sample receiver; probe; representative sampling; representative sampling criteria; sampling handling; sample loop; sample mixing; stream conditioning

ANNEX

(Mandatory Information)

A1. PRECAUTIONARY INFORMATION

A1.1 *Physical Characteristics and Fire Considerations:*

A1.1.1 Personnel involved in the handling of petroleum-related substances (and other chemical materials) should be familiar with their physical and chemical characteristics, including potential for fire, explosion, and reactivity, and appropriate emergency procedures. These procedures should comply with the individual company's safe operating practices and local, state, and federal regulations, including those covering the use of proper protective clothing and equipment. Personnel should be alert to avoid potential sources of ignition and should keep the materials' containers closed when not in use.

A1.1.2 API Publication 2217 and Publication 2026[5] and any applicable regulations should be consulted when sampling requires entry to confined spaces.

A1.1.3 INFORMATION REGARDING PARTICULAR MATERIALS AND CONDITIONS SHOULD BE OBTAINED FROM THE EMPLOYER, THE MANUFACTURER OR SUPPLIER OF THAT MATERIAL OR THE MATERIAL SAFETY DATA SHEET.

A1.2 *Safety and Health Consideration:*

A1.2.1 *General:*

A1.2.1.1 Potential health effects can result from exposure to any chemical and are dependent on the toxicity of the chemical, concentration, and length of the exposure. Everyone should minimize his or her exposure to work place chemicals. The following general precautions are suggested:

(*a*) Minimize skin and eye contact and breathing of vapors.

(*b*) Keep chemicals away from the mouth; they can be harmful or fatal if swallowed or aspirated.

(*c*) Keep containers closed when not in use.

(*d*) Keep work areas as clean as possible and well ventilated.

(*e*) Clean spills promptly and in accordance with pertinent safety, health, and environmental regulations.

(*f*) Observe established exposure limits and use proper protective clothing and equipment.

NOTE A1.1—Information on exposure limits can be found by consulting the most recent editions of the Occupational Safety and Health Standards, 29 Code of Federal Regulations Sections 11910.1000 and following and the ACGIH publication "Threshold Limit Values for Chemical Substances and Physical Agents in the Work Environment."[11]

A1.2.1.2 INFORMATION CONCERNING SAFETY AND HEALTH RISKS AND PROPER PRECAUTIONS WITH RESPECT TO PARTICULAR MATERIALS AND CONDITIONS SHOULD BE OBTAINED FROM THE EMPLOYER, THE MANUFACTURER OR THE MATERIAL SAFETY DATA SHEET.

[11] Available from American Conference of Government Industrial Hygienists, (ACGIH), Bldg. D-7, 6500 Glenway Ave., Cincinnati, OH 45211-4438.

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A2. THEORETICAL CALCULATIONS FOR SELECTING THE SAMPLER PROBE LOCATION

A2.1 *Introduction:*

A2.1.1 This annex describes calculation procedures for estimating the dispersion of water-in-oil at a sampling location. These procedures have a very simple theoretical base with many of the equations not being strictly applicable; therefore, they should be used with extreme caution in any practical application. A conservative approach is strongly recommended when estimating the acceptable limits for adequate dispersion (steam conditioning).

NOTE A2.1—From IP Petroleum Measurement Manual, Part IV Sampling:

A2.1.2 The equations contained in this annex have been shown to be valid for a large number of field data. The range of the field data covered the following correlating parameters:

Relative density	.8927–.8550 (27°–34° API)
Pipe diameter	40 cm–130 cm (16 in.–52 in.)
Viscosity	6–25 cSt at 40°C
Flowing velocity	>0–3.7 m/s (>0–12 ft/s)
Water concentration	<5 %

NOTE A2.2—Use caution when extrapolating outside of these ranges.

A2.1.3 When evaluating if dispersion is adequate or not in a given system, using the worst case conditions is recommended.

A2.1.4 When calculating the dispersion rate E in A2.3, it should be noted that dispersion energies of different piping elements are not additive in regard to dispersion, that is, when a series of elements is present, the element that should be considered is the one that dissipates energy the most.

A2.1.5 As an aid in determining the element most likely to provide adequate dispersion, Fig. A2.2 has been developed. When using Fig. A2.2, it is important to consider it as a guide only and that particular attention should be paid to the notes. Fig. A2.2 does not preclude the need for a more detailed analysis of these elements, within a given system, shown by the table to be the most effective.

A2.2 *Symbols*—The symbols used in Annex A2 are presented in Table A2.1.

A2.3 *Dispersion Factors:*

A2.3.1 As a measure of dispersion, the ratio of water concentration at the top of a horizontal pipe C_1 to that at the bottom C_2 is used. A C_1/C_2 ratio of 0.9 to 1.0 indicates very good dispersion while a ratio of 0.4 or smaller indicates poor dispersion with a high potential for water stratification. Calculations giving ratios less than 0.7 should not be considered reliable as coalescence of water droplets invalidates the prediction technique.

A2.3.2 The degree of dispersion in horizontal pipes can be estimated by:

$$\frac{C_1}{C_2} = \exp\left(\frac{-W}{\epsilon/D}\right) \quad (1)$$

where:

C_1/C_2 = the ratio of water concentration at the top (C_1) to that at the bottom (C_2),
W = the settling rate of the water droplets, and
ϵ/D = the turbulence characteristic, where ϵ is the eddy diffusivity and D the pipe diameter.

A2.3.3 An alternative measure of dispersion, G, can be defined in Eq 2. Table A2.2 presents the relationship of C_1/C_2 with G.

$$G = \frac{\epsilon/D}{W} \quad (2)$$

A2.3.4 It is important to note that the uncertainty of the calculations is such that errors in G of more than 20 % may result at low values of G. For this reason, it is recommended that no reliance be placed upon calculated G values of less than 3 and that additional energy dissipation calculated G value.

A2.4 *Determination of Energy Dissipation:*

A2.4.1 Two different techniques are given for determining the rate of energy dissipation.

A2.4.2 Method A uses the relationship in Eq 3.

$$E = \frac{\Delta P V}{\Delta X \rho} \quad (3)$$

where:

ΔP = the pressure drop across the piping element,
V = the flow rate at the pipe section in which energy is dissipated, and

TABLE A2.1 Symbols Used in Annex A2

NOTE 1—1 Pa = 10^{-5} bar
NOTE 2—1 $m^2/s = 10^6$ cSt = 10^6 mm^2/s
NOTE 3—1 N/m = 10^3 dyn/cm

Symbol	Term	Units
C	water concentration (water/oil ratio)	dimensionless
D	pipe diameter	m
d	droplet diameter	m
E	rate of energy dissipation	W/kg
E_o	energy dissipation in straight pipe	W/kg
E_r	required energy dissipation	W/kg
G	parameter, defined in A2.3.3	dimensionless
K	resistance coefficient	dimensionless
n	number of bends	dimensionless
ΔP	pressure drop	Pa(1)
Q	volumetric flow rate	m^3/s
r	bend radius	m
V	flow velocity	m/s
V_j	flow nozzle exit velocity	m/s
W	settling rate of water droplets	m/s
ΔX	dissipation distance	m
β	parameter, defined in A2.4.3	dimensionless
γ	ratio between small and large diameters	dimensionless
ϵ	eddy diffusivity	m^2/s
θ	turn angle	degrees
ν	kinematic viscosity	m^2/s (2)
σ	surface tension	N/m (3)
ρ	crude oil density	kg/m^3
ρ_d	water density	kg/m^3
ϕ	flow nozzle diameter	m

TABLE A2.2 Dispersion Factors

G	C_1/C_2	C_2/C_1
10	0.90	1.11
8	0.88	1.14
6	0.85	1.18
4	0.78	1.28
3	0.71	1.41
2	0.61	1.64
1.5	0.51	1.96
1	0.37	2.70

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TABLE A2.3 Suggested Resistance Coefficients, K

NOTE—γ is the small diameter/large diameter and K is based on the velocity in the smaller pipe.

Contraction	$K = 0.5\,(1 - \gamma^2)$	$(0 \le K \le 0.5)$
Enlargement	$K = \frac{(1-\gamma^2)^2}{\gamma^4}$	$(0 \le K \le 0.5)$
Orifice	$K = 2.8\,(1 - \gamma^2)\left[\left(\frac{1}{\gamma}\right)^4 - \right]$	
Circular mitre bends	$K = 1.2\,(1 - \cos\theta)$ where θ = turn angle	$(0 \le K \le 1.2)$
Swing check valve	$K = 2$	
Angle valve	$K = 2$	
Globe valve	$K = 6$	
Gate valve	$K = 0.15$	

ΔX = a characteristic length which represents the distance in which energy has been dissipated. In most cases ΔX is not known with any confidence. Wherever possible, the value to be used should be supported by experimental data.

NOTE A2.3—If ΔX is not known, a substitute value of $\Delta X = 10D$ may be used as a very rough approximation for devices of low mixing efficiency such as those in Table A2.3. For specially designed high efficiency static mixers the value ΔX will be small and should be obtained from the designer.

NOTE A2.4—If ΔP is not known, calculate it from Eq 4.

$$\Delta P = \frac{K\rho V^2}{2} \tag{4}$$

where:

K = the resistance coefficient of the piping element under consideration.

Suggested values of K for different piping elements are given in Table A2.3.

A2.4.3 Method B uses the relationship $E = \beta E_0$, where β is a characteristic parameter of a mixing element and E_0 is the rate of energy dissipation in a straight pipe. E_0 is calculated from Eq 5.

$$E_0 = 0.005\nu^{0.25}D^{-1.25}V^{2.75} \tag{5}$$

where: ν is given in mm^2/s (cSt).

A2.4.4 Suggested values of β and tentative relationships for E (other than $E = \beta E_0$) are given in Tables A2.4 and A2.5 respectively.

A2.5 *Contraction:*

$$\beta = 2.5(1 - \gamma^2) \tag{6}$$

A2.5.1 Contraction effects can be calculated with Eq 6.

A2.6 *Enlargement:*

$$\beta = \frac{5(1-\gamma^2)^2}{\gamma^4} \tag{7}$$

A2.6.1 Enlargement effects can be calculated with Eq 7.

A2.7 *Mean Water Droplet Diameter:*

A2.7.1 The mean water droplet diameter d may be estimated using Eq 8.

$$d = 0.3625\left(\frac{\sigma}{\rho}\right)^{0.6}E^{-0.4} \tag{8}$$

where:

σ = the droplet surface tension between water and oil measured in N/m. All formulas and examples in this Annex A2 assume $\sigma = 0.025$ N/m.

A2.7.2 Interfacial tension values may be significantly affected by additives and contaminants. If it is known that the value is other than 0.025 N/m, the water droplet settling velocity W, given in A2.8, should be modified by multiplying by Eq 9.

$$\left(\frac{\sigma}{0.025}\right)^{0.5} \tag{9}$$

A2.8 *Water Droplet Settling Velocity:*

A2.8.1 The determination of either of the dispersion factors requires a knowledge of the water droplet settling rate, W. This can be calculated using the relationship in Eq 10.

$$W = \frac{855(\rho_d - \rho)E^{-0.8}}{\nu\rho^{2.2}} \tag{10}$$

where:

ρ_d = the water density. For salt water (from wells or tankers) a suggested value is 1025 Kg/m^3 if the actual one is not available.

A2.8.2 If the mean water concentration is higher than 5 %, multiply W by 1.2.

A2.9 *Turbulence Characteristic:*

A2.9.1 Determination of either of the dispersion factors requires the turbulence characteristics ϵ/D to be evaluated using Eq 11.

$$\frac{\epsilon}{D} = 6.313 \times 10^{-3}V^{0.875}D^{-0.125}\nu^{0.125} \tag{11}$$

A2.10 *Verification of an Existing Sampler Location*—It is important to select the worst case conditions in the following sequence:

A2.10.1 Determine the desired profile concentration ratio C_1/C_2 and, using Table A2.2, the corresponding value of G.

A2.10.2 Determine, using Fig. A2.1, which pipeline fittings within 30D upstream of the sampler are most likely to provide adequate dispersion.

A2.10.3 Estimate the energy available from each of the most likely fittings using either of the methods described in A2.4.

A2.10.4 Calculate the value of G from the highest value of available energy obtained in step (c) using the formulas presented in A2.3, A2.8, and A2.9.

A2.10.5 Obtain the C_1/C_2 ratio from Table A2.2.

A2.10.6 Check that the calculated C_1/C_2 (or G) value is higher than the desired value obtained in A2.10.1. If it is, the sampler location should prove suitable for the application. If not, remedial action should be taken.

TABLE A2.4 Dissipation Energy Factors (β) (1, 2)

r/d	1	1.5	2	3	4	5	10
$n = 1$	1.27	1.25	1.23	1.22	1.18	1.15	1.07
$n = 2$	1.55	1.50	1.48	1.45	1.38	1.30	1.13
$n = 3$	1.90	1.80	1.75	1.70	1.56	1.44	1.18
$n = 4$	2.20	2.10	2.00	1.93	1.72	1.56	1.23
$n = 5$	2.60	2.40	2.30	2.20	1.90	1.70	1.28

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TABLE A2.5 Dissipation Energy Relationships

Centrifugal pump	$E = 0.125 \frac{\Delta PQ}{\rho D^3}$
Throttling valve	$E = \frac{\Delta PV}{20\rho D}$
Flow nozzle	$E = 0.022 \frac{Vj^3}{\phi}$

A2.11 *Selection of a Suitable Sampler Location*—It is again very important to select the worst case and continuing the above sequence.

A2.11.1 Determine if the desired profile concentration ratio C_1/C_2 and, using Table A2.2, the corresponding value of G.

A2.11.2 Determine the turbulence characteristic ϵ/D as described in A2.9.

A2.11.3 Calculate the water droplet settling rate using Eq 12.

$$W = \frac{\epsilon/D}{G} \tag{12}$$

A2.11.4 Determine the energy required to produce the desired profile concentration ratio using the formula presented in A2.8 re-written in the form of Eq 13.

$$E_r = \frac{4630}{\rho^{2.75}} \left[\frac{\rho_d - \rho}{\nu W}\right]^{1.25} \tag{13}$$

A2.11.5 Select from Fig. A2.1 the available piping elements most likely to provide adequate energy dissipation.

A2.11.6 Calculate the dissipation energy E for the selected piping elements using either of the methods described in A2.4.

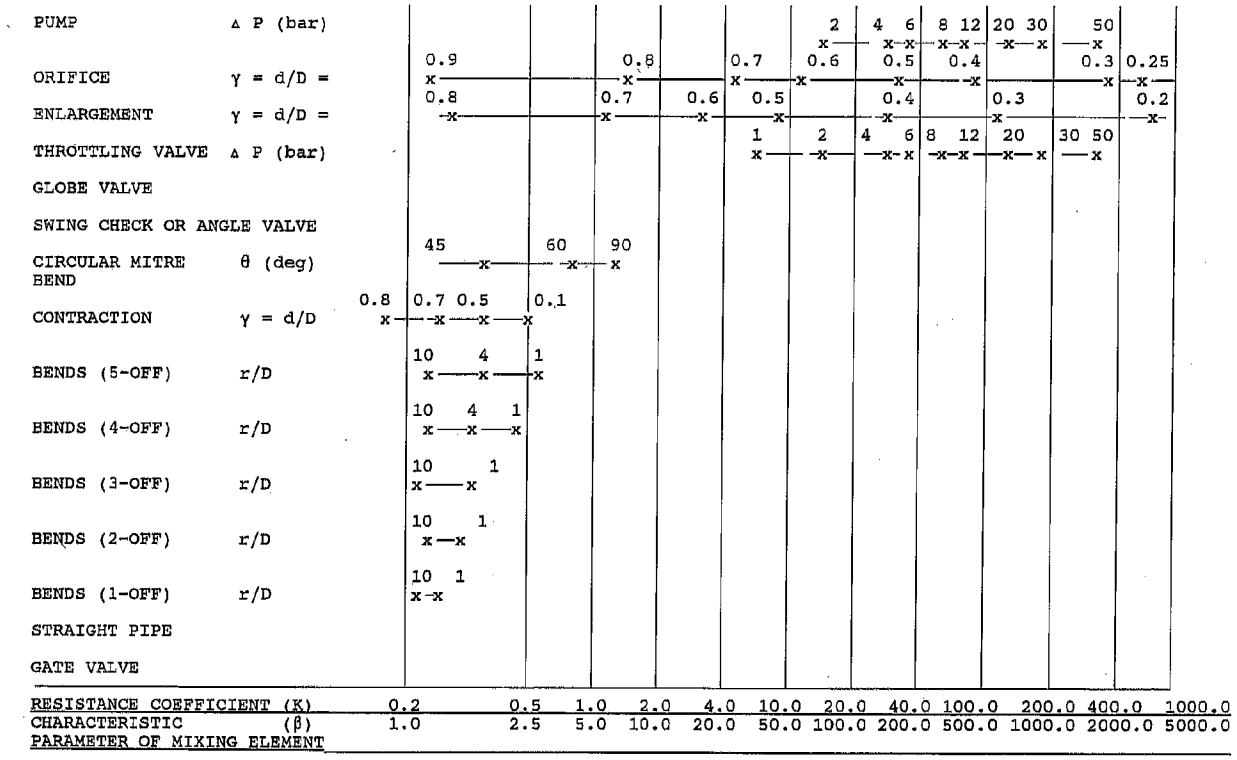
A2.11.7 Compare E_r with E to determine if an acceptable profile can be achieved. If for any piping element $E > E_r$, then a satisfactory profile can be achieved using that element. If $E < E_r$ for all piping elements, then additional dissipation energy must be provided. This can be done by reducing the pipe diameter (a length > $10D$ is recommended) by introducing an additional piping element or by incorporating a static or dynamic mixer.

A2.11.8 If the flow rate has been increased by reducing the pipe diameter, repeat steps A2.10.8 to A2.10.13.

A2.11.9 If a new piping element has been introduced into the system without changing the flow rate, check, using step A2.11.6, that its dissipation energy is larger than the best so far achieved and, if so, proceed to step A2.11.7.

A2.11.10 If a static or dynamic mixer is considered, then the manufacturer should be consulted as to its design and application.

A2.12 *Examples*—Verification of an existing sampler location:



NOTE 1—The table has been compiled assuming the same pipeline diameter downstream of any device. If the downstream diameter of any two devices is not identical, comparisons using Fig. A2.1 cannot be performed.

NOTE 2—It is not intended that Fig. A2.1 be used to ascertain β or K values but only to provide a comparison of the likely mixing effects of devices.

NOTE 3—For centrifugal pumps and throttling valves, the dissipation energies, which are defined without the use of β values (see Table A2.1), the comparison has been done using an assumed β equal to E/E_o and the following typical values—D = 0.4 m; ν = 16 cSt; ρ = 900 kg/m^3; V = 5.6 m/s.

FIG. A2.1 Comparison of Mixing Devices

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A2.12.1 Using the procedure of A2.10, for an installation in a 500 mm pipe where the most severe operating conditions are represented by:

$$V = 2 \text{ m/s}$$
$$\rho = 850 \text{ kg/m}^3$$
$$\nu = 8 \text{ cSt}$$
$$\rho_d = 1025 \text{ kg/m}^3$$

A2.12.1.1 The desired C_1/C_2 ratio is 0.9, from Table A2.2, $G = 10$.

A2.12.1.2 The pipeline fittings within $30D$ upstream of the sampler are a globe valve, an enlargement with diameter ratio, $\gamma = 0.5$ and two 90° bends. Then, from Fig. A2.1 the globe valve or the enlargement is clearly most likely to provide adequate dispersion.

A2.12.1.3 The energy available may be calculated using either Method A or B of A2.4. However, only K values are given for the globe valve, therefore, these must be used to compare the likely mixing effects of the globe valve and the enlargement.

Globe valve $K = 6$ (Table A2.3)

Enlargement $K = \dfrac{(1-\gamma^2)^2}{\gamma^4} = 9$ (Table A2.3)

The enlargement has the higher K value and should be used in the following calculations. A2.4 may be used for the rest of the calculation. (*a*) Using Method A, A2.4:

$$E = \frac{\Delta PV}{\Delta xp} \text{ W/kg} \tag{3}$$

or as:

$$\Delta P = \frac{K\rho V^2}{2} \text{ W/kg} \tag{4}$$

then:

$$E = \frac{KV^3}{2\Delta X} \text{ W/kg} \tag{12}$$

and using $\Delta X = 10D$

$$E = \frac{9 \times 2^3}{2 \times 10 \times 0.5} = 7.2 \text{ W/kg} \tag{13}$$

A2.12.1.4

$$G = \frac{\epsilon/D}{W} \tag{2}$$

$$\frac{\epsilon}{D} = 6.313 \times 10^{-3} V^{0.375} D^{-0.125} \nu^{0.125} \text{ m/s} \tag{11}$$

$$W = \frac{855(\rho_d - \rho)}{\nu\rho^{2.2}} E^{-0.8} \text{ m/s} \tag{10}$$

$$\therefore \frac{\epsilon}{D} = 6.313 \times 10^{-3} \times 2^{0.875} \times \frac{1}{0.5^{0.125}} \times 8^{0.12} \tag{14}$$

$$= 16.37 \times 10^{-3} \text{ m/s}$$

and

$$W = \frac{855(1025 - 850)}{8 \times 850^{2.2}} \times \frac{1}{7.2^{0.8}} \tag{15}$$

$$= 1.38 \times 10^{-3} \text{ m/s}$$

$$\therefore G = \frac{16.37 \times 10^{-3}}{1.38 \times 10^{-3}} = 11.83 \tag{16}$$

A2.12.1.5 From Table A2.2 the C_1/C_2 ratio is greater than 0.9.

A2.12.1.6 The calculated value of C_1/C_2 is greater than the required value, and therefore, adequate conditions for sampling exist.

A2.12.1.7 Using Method B, A2.4:

$$E = \beta E_0 \text{ W/kg} \tag{17}$$

$$\beta = \frac{5(1-\gamma^2)^2}{\gamma^4} = 45 \text{ (Table A2.3)} \tag{18}$$

$$E_0 = 0.005 \nu^{0.25} D^{-1.25} V^{2.75} \tag{19}$$

$$\therefore E = 45 \times 0.005 \times 8^{0.25} \times \frac{1}{0.5^{1.25}} \times 2^{2.75} \tag{20}$$

$$= 6.0545 \text{ W/kg}$$

A2.12.1.8

$$G = \frac{\epsilon/D}{W} \text{ (Table A2.2)} \tag{2}$$

$$\epsilon/D = 16.37 \times 10^{-3} \text{ m/s} \tag{21}$$

as calculated for Method A:

$$W = \frac{855(\rho_d - \rho)}{\nu\rho^{2.2}} E^{-0.8} \text{ m/s} \tag{10}$$

$$= \frac{855(1025 - 850)}{8 \times 850^{2.2}} \times \frac{1}{6.0545^{0.8}} \tag{22}$$

$$= 1.59 \times 10^{-3} \text{ m/s}$$

$$\therefore G = \frac{16.37 \times 10^{-3}}{1.59 \times 10^{-3}} = 10.29 \tag{23}$$

A2.12.1.9 Follow A2.12.1.5 and A2.1.1.6 as for Method A.

A2.12.2 *Selection of a Suitable Sampler Location*—Using the procedure of A2.11:

A2.12.2.1 The proposed pipeline configuration consists of a 600 mm line enlarging to 800 mm followed by a line of three 90° bends each with an r to D ratio of 1 and finally a throttling valve with the differential pressure of one bar. The most severe operating conditions are represented by the following conditions:

$$V = 1.5 \text{ m/s}$$
$$\rho = 820 \text{ kg/m}^3$$
$$\nu = 7 \text{ cSt}$$
$$\rho_d = 1025 \text{ kg/m}^3$$

A2.12.2.2 The desired C_1/C_2 ratio is 0.9; then, from Table B.2, G = 10.

A2.12.2.3 The turbulence characteristic from B.6 is:

$$\epsilon/D = 6.313 \times 10^{-3} V^{0.875} D^{-0.125} \nu^{0.125} \text{ m/s} \tag{13}$$

$$= 6.313 \times 10^{-3} \times 1.5^{0.875} \times \frac{1}{0.8^{0.125}} \times 7^{0.125} \tag{24}$$

$$= 11.81 \times 10^{-3} \text{ m/s}$$

A2.12.2.4 The water droplet settling velocity is:

$$W = \frac{\epsilon/D}{G} = \frac{11.81 \times 10^{-3}}{10} = 1.18 \times 10^{-3} \text{ m/s} \tag{25}$$

A2.12.2.5 The energy dissipation rate required per Eq 26 is:

$$E_r = \frac{4630}{\rho^{2.75}} \left[\frac{\rho_d - \rho}{\nu W}\right]^{1.25} \tag{26}$$

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$$= \frac{4630}{820^{2.75}} \left(\frac{1025 - 820}{7 \times 1.18 \times 10^{-3}} \right)^{1.25} \quad (27)$$

$$= 13.99\ W/\text{kg}$$

A2.12.2.6 From Fig. A2.1 the throttling valve is clearly the element most likely to provide sufficient energy dissipation.

A2.12.2.7 Method B is the only one to provide an energy dissipation formula for a throttling valve; see Table A2.5.

$$\therefore E = \frac{\Delta PV}{20\rho D}\ W/\text{kg} \quad (28)$$

$$= \frac{1 \times 10^5 \times 1.5}{20 \times 820 \times 0.8}\ [1\ bar = 10^5\ Pascal] \quad (29)$$

$$= 11.43\ W/\text{kg}$$

A2.12.2.8 The energy dissipation rate E provided by the throttling valve is less than required E_r. Therefore, a G value of 10 has not been achieved and sampling from this location is unlikely to prove adequate. If the enlargement from 600 to 800 mm is moved downstream of the throttling valve and sampling location, then the following recalculation applies with $D = 0.6$ m and $V = 2.67$ m/s:

A2.12.2.9

$$\frac{\epsilon}{D} = 6.313 \times 10^{-3} \times 2.67^{0.875} \times \frac{1}{0.6^{0.125}} \times 7^{0.125}\ \text{m/s} \quad (30)$$

$$= 20.25 \times 10^{-3}\ \text{m/s}$$

A2.12.2.10

$$W = \frac{\epsilon/D}{G} = \frac{20.25 \times 10^{-5}}{10} = 2.02 \times 10^{-3}\ \text{m/s} \quad (31)$$

A2.12.2.11

$$E_r = \frac{4630}{820^{2.75}} \left[\frac{1025 - 820}{7 \times 2.02 \times 10^{-3}} \right]^{1.25} W/\text{kg} \quad (32)$$

$$= 7.13\ W/\text{kg}$$

A2.12.2.12 Unchanged from previous calculation.

A2.12.2.13

$$E = \frac{\Delta PV}{20\rho D}\ W/\text{kg} \quad (33)$$

$$= \frac{10^5 \times 2.67}{20 \times 820 \times 0.6} \quad (34)$$

$$= 27.10\ W/\text{kg}$$

A2.12.2.14 The energy dissipation rate provided by the throttling valve located in the smaller diameter pipe is more than sufficient to give a G value of 10. Adequate sampling should therefore be possible.

A3. ACCEPTANCE METHODOLOGIES FOR SAMPLING SYSTEMS AND COMPONENTS

A3.1 *Descriptions of Terms Specific to This Standard*—The following definitions are included as an aid in using Tables A3.1 and A3.2 for profile test data and point averages and deviation:

A3.1.1 *minimum flow rate, n*—the lowest operating flow rate, excluding those rates which occur infrequently (that is, 1 of 10 cargoes) or for short time periods (less than 5 min).

A3.1.2 *overall profile average, n*—the average of all point averages.

A3.1.3 *point, n*—a single sample in a profile.

A3.1.4 *point average, n*—the average of the same point from all profiles (excluding profiles with less than 1.0 % water).

A3.1.5 *profile, n*—multi-point samples taken simultaneously across a diameter of the pipe.

A3.2 *Acceptance Testing—Water Injection Volume Balance Tests:*

A3.2.1 This annex describes three test methods shown to be acceptable in proving the performance of pipeline and marine automatic pipeline sampling systems, that is, single sampler, dual sampler and component testing. These methods have equal validity and the order listed should not be construed as one method having preference over another. Once a system design has been proven, subsequent systems of the same design (for example, LACT units), including piping configuration and similar service need not be tested. Refer to Section 16 for verification of systems of the same design.

A3.2.2 The following procedures are presented for the testing of systems to identify water in petroleum. The same approach may be modified to apply to petroleum blending systems.

A3.2.3 The single and dual sampler tests are designed to

TABLE A3.1 Allowable Deviations for the Single and Dual Sampler Water Injection Acceptance Tests (Volume %)

NOTE 1—The reference to tanks or meters refers to the method used to determine the volume of crude oil or petroleum in the test.

NOTE 2—Deviations shown reflect use of the Karl Fischer test method described in D 4928 for water.

NOTE 3—Interpolation is acceptable for water concentrations between values shown in the table. For example, if the total water is 2.25 % the allowable deviation using tank gages would be 0.175 % and 0.135 % if using meters.

NOTE 4—This table is based, in part, on statistical analysis of a data base consisting of 36 test runs from 19 installations. Due to the number of data, it was not possible to create separate data bases for analysis by the volume determination method, that is, by tank or meter. Therefore, it was necessary to treat the data as a whole for analysis. The data base is valid for the water range 0.5 % to 2.0 %.

NOTE 5—The reproducibility standard deviation calculated for the data, at a 95 % confidence level, has been used for the meter values shown in the table in the water range 0.5 to 2.0 %. Assigning these values to the meter is based on a model that was developed to predict standard deviations for volume determinations by tanks and meters. Values shown in the table for the tank, in the range 0.5 % to 2.0 %, were obtained by adding 0.04 % to the meter values in this water range. The value of 0.04 % was derived from the aforementioned model as the average bias between tank and meter volume determinations.

NOTE 6—As there is insufficient test data for water levels over 2.0 %, values shown in the table above 2.0 % have been extrapolated on a straight line basis using the data in the 0.5 % to 2.0 % range.

NOTE 7—In order to develop a broader data base, owners of systems are encouraged to forward a copy of test data using test data sheets as shown in Annex A6 to the American Petroleum Institute, Industry Services Department, 1220 L Street, N.W., Washington, DC 20005.

Total Water (W test)	Allowable Deviations	
	Using Tank Gages	Using Meters
0.5	0.13	0.09
1.0	0.15	0.11
1.5	0.16	0.12
2.0	0.17	0.13
2.5	0.18	0.14
3.0	0.19	0.15
3.5	0.20	0.16
4.0	0.21	0.17
4.5	0.22	0.18
5.0	0.23	0.19

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test the entire sampling system starting with the stream condition in the pipeline through collection and analysis of the sample. These are volume balance tests in which a known amount of water is injected into a known volume of oil of a known baseline water content. As these volumes pass the sampler under test, a sample is collected and the results analyzed for comparison against the known baseline water plus injected water.

A3.2.4 The single sampler test requires that an assumption be made concerning the baseline water content during the time that test water is injected. Successful tests are dependent upon a constant baseline oil throughout the test. If a constant baseline oil cannot be ensured, inconclusive results will be obtained.

A3.2.5 In the dual sampler test, the first sampler (that is, baseline sampler) is used to measure the baseline water content during the test. Test water is injected between the baseline and primary samplers. The primary sampler (one under test) is used to collect the baseline plus injected water sample. It is not necessary that the two sampling installations be of identical or similar design.

A3.3 *Preparations Prior to Acceptance Test:*

A3.3.1 Test the sample receiver and mixer as outlined in Practice D 5854, Annex A2. During the sampler acceptance test, water injection should last at least 1 h. The corresponding sample volume collected during a sampler acceptance test is usually less than the volume expected under normal conditions. Therefore, if the sample volume to be collected during the sampler acceptance test is less than the minimum volume at which the receiver and mixer have been tested, the receiver and mixer must be tested prior to the acceptance test in accordance with Annex A2 of Practice D 5854 using the oil and volume that are to be sampled.

A3.3.2 Determine the method and accuracy by which the water and oil volumes will be measured. Water injection meters should be installed and proven in accordance with API MPMS Chapters 4, 5 and 6. Oil volumes should be measured by tank gage or meter in accordance with applicable API MPMS Chapters 3, 4, 5 and 6 guidelines.

A3.3.3 Locate the water injection point upstream of the elements expected to produce the stream conditioning for the sampling system. Be aware of potential traps in the piping which may prevent all of the injected water from passing the sample point. Exercise care to ensure that the location and manner in which water is injected does not contribute additional mixing energy at the point of sampling which would distort the test results. Equipment or facilities used to inject water should be in accordance with local safety practices.

A3.3.4 Review the normal operating conditions of the pipeline in terms of flow rates and crude types. Select the most common, worst case conditions to test the sampling system. The worse case is commonly the lowest normal flow rate and the highest API gravity crude normally received or delivered.

A3.3.5 In the case of the single sampler acceptance test, a source of constant water content for oil must be identified for the test. If possible, it is suggested that this oil be isolated as changes in the baseline water content can produce inconclusive test results.

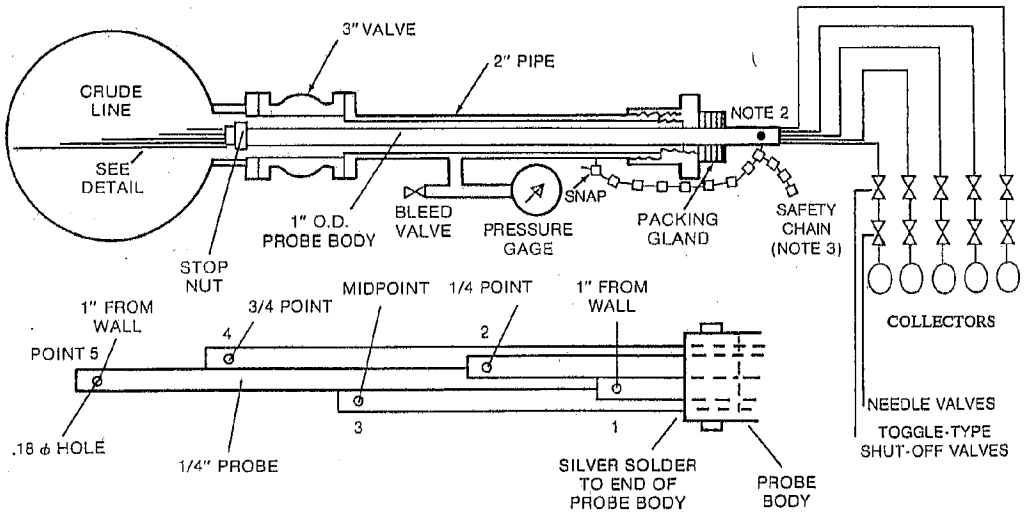
A3.4 *Single Sampler—Acceptance Test:*

A3.4.1 Purge the system at a sufficiently high flow rate to displace free water which may be laying in the pipeline system upstream of the automatic sampling system (refer to Fig. A3.1).

A3.4.2 Establish the flow rate for the test.

A3.4.3 Collect the first baseline sample(s). A baseline sample may be a composite sample collected in a separate sample receiver or several spot samples collected at intervals directly from the sample extractor.

A3.4.4 Record the initial oil volume by tank gage or



PROBE DETAIL (NOTE 4)

NOTE 1—For pipes less than 30 cm (12 in.), delete the ¼ and ¼ points.
NOTE 2—The punch mark on probe sleeve identifies the direction of probe openings.
NOTE 3—When the probe is fully inserted, take up the slack in the safety chains and secure the chains tightly.
NOTE 4—The probe is retractable and is shown in the inserted position.

FIG. A3.1 Multi Probe for Profile Testing

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meter reading and simultaneously begin collecting grabs in the sample receiver.

A3.4.5 Record the initial water meter reading. Then turn the water on and adjust injection rate.

A3.4.6 A minimum of 1 h is recommended for the water injection.

A3.4.7 Turn the water off and record the water meter reading.

A3.4.8 Continue sampling into the receiver until the injected water is calculated to have passed the sampler.

A3.4.9 Stop the collection of test sample and simultaneously record the oil volume by tank gage or meter reading.

A3.4.10 Collect the second baseline sample(s).

A3.4.11 Analyze the baseline samples.

A3.4.12 Analyze the test sample.

A3.4.13 Using the following Eq 35, calculate the deviation between the water in the test sample minus the water in the baseline, corrected to test conditions, compared to the amount of water injected.

$$\text{Dev} = (W_{\text{test}} - W_{\text{bl}}) - W_{\text{inj}} \quad (35)$$

where:

Dev = deviation, vol %,

W_{test} = water in test sample, vol %,

W_{bl} = baseline water adjusted to test conditions, vol %

$$= W_{\text{avg}} \times \frac{TOV - V}{TOV}, \quad (36)$$

W_{avg} = average measured baseline water, vol %,

TOV = total observed volume (test oil plus injected water) that passes the sampler (barrels),

V = volume of injected water in barrels (Note A), and

W_{inj} = water injected during test, vol %

$$= \frac{V}{TOV} \times 100 \quad (37)$$

A3.4.14 Repeat A3.4.3 through A3.4.13 until two consecutive tests that meet the criteria in A3.6 have been obtained.

A3.4.15 When production water is used, make correction for dissolved solids as applicable.

A3.5 *Dual Sampler—Proving Test:*

A3.5.1 The dual sampler test is a two-part test. In the first part, the two samplers are compared to one another at the baseline water content. In part two of the test, water is injected between the two samplers to determine if the baseline water plus injected water is detected by the primary sampler. Refer to Annex A6.

A3.5.2 *Baseline Test Procedure:*

A3.5.2.1 Purge system to remove free water.

A3.5.2.2 Establish steady flow in line.

A3.5.2.3 Start baseline sampler. Record tank gage or meter reading.

A3.5.2.4 Start primary sampler after pipeline volume between samplers has been displaced.

A3.5.2.5 Stop baseline sampler after collecting targeted sample volume. A minimum of 1 h is recommended. Record tank gage or meter reading.

A3.5.2.6 Stop primary sampler after pipeline volume between baseline and primary samplers has been displaced.

A3.5.2.7 Analyze test samples.

A3.5.2.8 Compare results and make sure they are within acceptable tolerance as per Table A3.1 before proceeding.

A3.5.3 *Water Injection Test:*

A3.5.3.1 Record water meter reading.

A3.5.3.2 Start baseline sampler, injection of water and record tank gage or meter reading all in rapid succession.

A3.5.3.3 Start primary sampler immediately prior to arrival of injected water.

A3.5.3.4 Collect targeted sample volume with baseline sampler.

A3.5.3.5 Stop baseline sampler, record tank gage or meter reading and shut off water injection all in rapid succession.

A3.5.3.6 Record water meter reading.

A3.5.3.7 Stop primary sampler after displacement of pipeline volume between baseline and primary samplers.

A3.5.3.8 Analyze test samples.

A3.5.3.9 Repeat A3.5.2.2 through A3.5.3.6 until two consecutive tests that meet the criteria in A3.6 have been obtained for both parts of the test.

A3.6 *Approval for Custody Transfer:*

A3.6.1 The acceptance test is valid and the automatic sampling system is acceptable for custody transfer if two consecutive test runs meet the following criteria:

A3.6.2 *Single Sampler Test:*

A3.6.2.1 The difference in the percent water in the beginning and ending baselines is 0.1 % or less, and

A3.6.2.2 The deviation between the test sample and the known baseline plus injected water is within the limits shown in Table A3.1.

A3.6.3 *Dual Sampler Test:*

A3.6.3.1 The difference between the two samplers during the baseline test must be within 0.1 %, and

A3.6.3.2 The difference between the second sampler (test sampler) and the baseline sampler plus injected water must be within the limits shown in Table A3.1.

A3.6.4 *Procedures to Follow if the Acceptance Test Fails:*

A3.6.4.1 Ensure volume of oil was calculated and recorded correctly.

A3.6.4.2 Ensure volume of water was calculated and recorded correctly. Ensure scaling factor is correct or the meter factor has been applied to obtain correct volume, or both.

A3.6.4.3 If inadequate stream conditioning in the pipeline is suspected, validate the sample point by one of the following:

(*a*) Annex A2 to estimate the water-in-oil dispersion

(*b*) A multiple point profile test as described in A3.7.1.

A3.7 *Component Performance Test:*

A3.7.1 *Profile Test to Determine Stream Condition*—The extent of stratification or non-uniformity of concentration can be determined by taking and analyzing samples simultaneously at several points across the diameter of the pipe. The multipoint probe shown in Fig. A3.1 is an example of a profile probe design. This test should be conducted in the same cross-section of pipe where the sample probe will be installed.

A3.7.1.1 *Criteria for Uniform Dispersion and Distribution*—A minimum of five profile tests meeting criteria in A3.8.2. If three of those profiles indicate stratification, the mixing in the line is not adequate.

A3.7.1.2 *Profile Probe*—A probe with a minimum of five sample points is recommended for 30 cm (12-in.) pipe or

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TABLE A3.2 Typical Profile Test Data, in Percent Volume of Water

NOTE—For invalid sample or missed data point, the point should be shown as missing data and the remaining data averaged.

Profile	Point (% volume – water)				
	A Bottom	B ¼ Point	C Midpoint	D ¾ Point	E Top
1	0.185	0.096	0.094	0.096	0.096
2	0.094	0.182	0.135	0.135	0.135
3	13.46	13.72	13.21	12.50	12.26
4	8.49	7.84	8.65	8.65	8.33
5	6.60	7.69	7.69	6.60	8.00
6	6.73	7.02	6.48	6.73	5.38
7	7.88	6.73	6.73	7.27	5.96
8	2.78	3.40	3.27	3.08	2.88
9	1.15	1.36	1.54	1.48	1.32
10	0.58	0.40	0.48	0.55	0.47

larger. Below 30 cm (12-in.) pipe size, three sample points are adequate.

A3.7.1.3 *Sampling Frequency*—Profile samples should not be taken more frequently than at 2 min intervals.

A3.7.1.4 *Probe Orientation*—Profiles in horizontal lines must be taken vertically, where as profiles in vertical lines should be taken horizontally.

A3.7.1.5 *Test Conditions*—The test should be set up to measure the worst case conditions including the minimum flow rate and lowest flow viscosity and density or other conditions as agreed upon.

A3.7.1.6 *Water Injection*—The water injection method described in testing automatic sampling systems (see A3.2 and A3.3.3) is recommended.

A3.7.1.7 *Sampling*—Sampling should begin 2 min before the calculated water arrival time and continue until at least ten profiles have been taken.

NOTE A3.1—Probe installation and operation are covered in A3.9. As a safety precaution, the probe should be installed and removed during low pressure conditions. However, the probe should be equipped with safety chains and stops to prevent blow-out should it be necessary to remove it during operation conditions.

A3.8 *Application of Dispersion Criteria:*

A3.8.1 Table A3.2 lists data accumulated during a typical profile test. Units are percent volume of water detected. Approximately 1000 barrels of seawater were added to a center compartment of a 76 000 dead weight ton crude oil tanker. The quantity of water was verified by water cut measurements shortly before the loading operation.

A3.8.2 To apply the dispersion criteria, it is best to eliminate all profiles with less than 0.5 % water and the profile taken in the leading edge of the water (which occurs in Profile 3 of Table A3.2). Typically, a profile of the leading edge is erratic with respect to water dispersion. While it is a useful means of verifying arrival time, it hinders evaluation of profile data and can cause an unnecessarily reduced profile test rating. Calculate the point average and deviation for all other profiles with 1 % or more water. (See Table A3.3.)

A3.9 *Water Profile Test Procedures*—Refer to Fig. A3.1 while following the steps of this procedure.

TABLE A3.3 Calculation of Point Averages and Deviation

NOTE 1—The system is rated with respect to the worst point average in the test: point average E has the largest deviation (–0.28).

NOTE 2—For representative sampling, the allowable deviation is 0.05 % water for each 1 % water in the overall profile average. In this example, the allowable deviation is given by the (5.69 × 0.05) % W = ±0.28 % W.

	Point (% volume – water)					Average E %
	A	B	C	D	E	
Average of profiles 4 through 9	5.61	5.67	5.73	5.64	5.31	5.59
Deviation from overall profile average (Note 1) (% water)	+0.02	+0.08	+0.14	+0.05	–0.28	
Allowable deviation (Note 2)	(5.59 × 0.05) % water = ±0.28 % water					

A3.9.1 Install profile probe in line. Check that the probe is properly positioned and safely secured.

A3.9.2 Position a slop can under the needle valves. Open the shut-off and needle valves and purge the probes for one minute (or sufficient time to purge 10 times the volume in the probe line).

A3.9.3 Adjust needle valves so that all sample containers fill at equal rates.

A3.9.4 Close shut-off valves.

A3.9.5 Open the shut-off valves, purge the probe lines, and quickly position the five sample containers under the needle valves. Close shut-off valves.

A3.9.6 Repeat A3.9.5 at intervals of not less than 2 min until a minimum of ten profiles have been obtained.

A3.10 *Sample Probe/Extractor Test:*

A3.10.1 The grab size should be repeatable within ±5 % over the range of operating conditions. Operating parameters that may affect grab size are sample viscosity, line pressure, grab frequency and back pressure on the extractor.

A3.10.2 Test the sample probe/extractor by collecting 100 grabs in a graduated cylinder and calculate the average grab size. Perform the test at the highest and the lowest oil viscosity, pressure and grab frequency.

A3.10.3 The average grab size will determine if the target number of grabs will exceed filling the sample receiver above the proper level. The average grab size is also used in determining the sampler performance (see Annexes A4 and A5).

A3.11 *Special Flow Meter Test:*

A3.11.1 If custody transfer meters are used, verification of the flow meter calibration is not necessary.

A3.11.2 Special types of meters, such as those described in 12.2, can be verified by comparing the meter pacing the extractor with tank gages or custody transfer meters. Conditions for the test are:

A3.11.2.1 The test should be conducted at the average flow rate experienced during normal operations.

A3.11.2.2 The flow meter must be tested in its normal, operating location to determine if piping configuration affects its accuracy.

A3.11.2.3 When using tank gages as a reference volume, the tank level changes must be large enough to give accurate volume readings.

A3.11.3 Flow meters used for pacing sample extractors should be within ±10 % of the volume measured by tank gaging or custody transfer meters.

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A4. PERFORMANCE CRITERIA FOR PERMANENT INSTALLATIONS

A4.1 *Calculations Prior to Operation:*

PV_e Expected parcel volume, m^3
b Expected extractor grab size, mL
SV_e Expected sample volume, mL (normally 80 % of receiver capacity)
n Number of sample grabs expected

$$n = \frac{SV_e}{b} \tag{38}$$

B Frequency of sampling, m^3/grab (Controller input)

$$B = \frac{PV_e}{n} \tag{39}$$

A4.2 *Data from the Sampling Operation:*

N Total number of grabs ordered by the controller
SV Sample volume collected, mL
SV_c Sample volume calculated, mL
PV_s Parcel volume measured by sampler flow sensing device, m^3
PV_{co} Custody transfer or outturn parcel volume, m^3

A4.3 *Calculation of Performance Report*—The following calculations can be helpful in evaluating if a sample is representative:

A4.3.1 *Grab Factor (GF):*

$$GF = \frac{SV}{N \times b} = 1 \pm 0.05 \tag{40}$$

A4.3.1.1 Components and variables involved:
(*a*) Average grab size,
(*b*) Controller-to-probe link, and
(*c*) Probe operation.

A4.3.2 *Performance Factor (PF):*

$$PF = \frac{SV}{SV_c} 1 \pm 0.10 \tag{41}$$

$$= \frac{SV}{\frac{PV_s}{B} \times b} = 1 \pm 0.10 \tag{42}$$

A4.3.3 *Flow Sensor Accuracy (SA):*

$$SA = \frac{PV_{co}}{PV_s} = 1 \pm 0.10 \tag{43}$$

A4.3.4 *Sampling Time Factor (SF):*

$$\text{Sampling Factor} = \frac{\text{Total sampling time}}{\text{Total parcel time}} = 1 \pm 0.05 \tag{44}$$

Time parcel began _____
Time parcel completed _____
Total parcel time _____
Time sampler begins operation _____
Intermittent outages _____
Time sampler stops operation _____
Total sampling time _____

Note: Record actual times sampler is not in service.

A4.3.5 Sampler installation was tested according to Practice D 4177

Yes _____ No _____ Date tested _____

A4.3.5.1 Components and variables involved are (*a*) average grab size, (*b*) flow sensor-to-controller link, (*c*) controller, (*d*) controller-to-probe link, (*e*) probe operation, and (*f*) flow sensor accuracy.

A5. PERFORMANCE CRITERIA FOR PORTABLE SAMPLING UNITS

A5.1 Representative sampling is more difficult to document and verify when a portable sampler is used. The flow sensing device is usually limited in accuracy and turndown. Stream conditioning is usually limited to piping elements and flow velocity. The sampler controller data logging is usually limited. Special precautions and operating procedures with additional record keeping by the operator can overcome these limitations.

A5.2 *Calculations Prior to Operation:*

PV_e Expected parcel volume, m^3
b Expected extractor grab size, mL
SV_e Expected sample volume, mL (normally 80 % of receiver capacity)
n Number of sample grabs expected

$$n = \frac{SV_e}{b} \tag{38}$$

B Frequency of sampling, m^3/grab (Controller input)

$$B = \frac{PV_e}{n} \tag{39}$$

A5.3 *Data from the Sampling Operation:*

N Total number of grabs ordered by the controller
SV Sample volume collected, mL
PV_s Parcel volume measured by sampler flow sensing device, m^3
PV_{co} Custody transfer or outturn parcel volume, m^3

A5.4 *Calculation of Performance Report*—The following calculations can be helpful in evaluating if a sample is representative:

A5.4.1 *Grab Factor (GF):*

$$GF = \frac{SV}{N \times b} = 1 \pm 0.05 \tag{40}$$

A5.4.2 *Modified Performance Factor (PF_m):*

$$PF_m = \frac{SV}{\frac{PV_s}{B} \times b} = 1 \pm 0.10 \tag{45}$$

PV_s is normally not available. When this is the case, use PV_{co} which excludes the effect of flow sensor malfunction or inaccuracy on PF_m. If PV_s is available from the controller, calculate PF as in Annex A4.

A5.4.3 *Flow Sensor Accuracy (SA)*—The volume as measured by the sampler(s) flow sensor(s) is normally not available. The volume measured by the flow sensor(s) is calculated from the number of grabs ordered by the controller(s).

$$SA = \frac{N \times B}{PV_{co}} = 1 \pm 0.10 \tag{46}$$

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VESSEL _____ LOCATION _____

LOADING _____ DISCHARGE _____ TIME PUMPING BEGINS ___ ENDS ___

DATE PUMPING BEGINS _____

Date	Time	Probe ID (1)		Line No. (1)		Parcel	Calculation (2)	
		Into Service	Out of Service	Into Service	Out of Service	Flow Rate	Velocity at Probe	Velocity Thru Line

NOTE 1—Line No. = identification letter or number from Figs. A5.1 or A5.2.

NOTE 2—Velocities should be calculated for lines A to D in Fig. A5.1 as major rate changes occur and arms/hoses are added or removed from service. The same applies to spools I to IV on the vessel. The same applies for line and spools designated I to IV in Fig. A5.2.

FIG. A5.1 Portable Sampler Operational Data Confirmation of Mixing and Flow Sensor Velocity

A5.4.4 *Sampling Factor (SF):*

$$\text{Sampling Factor} = \frac{\text{Total sampling time}}{\text{Total parcel time}} = 1 \text{ at } \pm 0.05 \quad (44)$$

A5.4.5 *Stream Conditioning:*

A5.4.5.1 For 95 % of the parcel volume, the flow rate in piping ahead of the sampler(s) was a minimum of 2 m/s (6.6 ft/s) Yes _____ No _____

A5.4.5.2 No more than 10 % of the total free water in the tanks/compartments was pumped at flow rates of less than 2 m/s. Yes _____ No _____ The criteria for stream conditioning is met if both answers are "Yes."

A5.5 *Line and Manifold Data*—Complete forms as outlined in Tables A5.1 through A5.4 for each sample.

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VESSEL _____ LOCATION _____ DATE _____

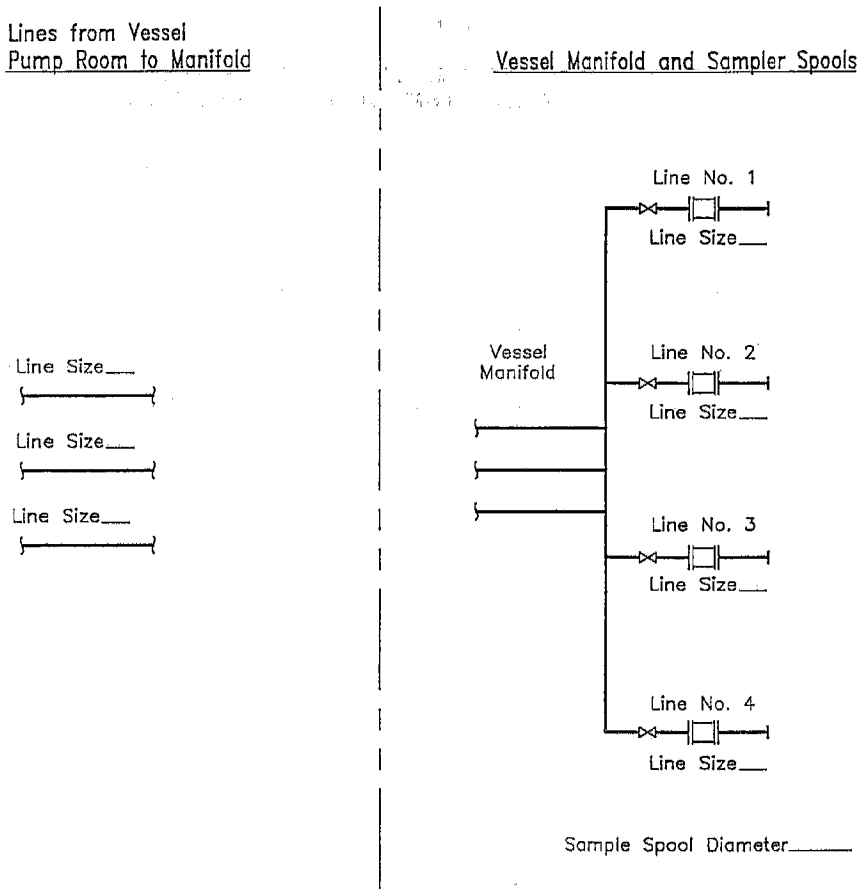
TABLE G2 PORTABLE SAMPLER OPERATIONAL DATA
CONFIRMATION OF MIXING AND FLOW SENSOR VELOCITY

Tank or Compartment Number	Initial Free Water		Pumping Begins		Pipe Velocity at Sampler	Calculations for Pipe Velocity at Sampler When Pumping Begins
	Volume	%	Date	Time		
Total						

NOTE 1—Free water is assumed to be pumped from a tank or compartment with the initial 5 % of the volume pumped.
NOTE 2—A sample cannot be judged representative if more than 10 % of the water found in the total parcel after the operation is complete is pumped as free water and the velocity in the piping ahead of the sampler at the time of pumping is less than 2.44 m/s (8 ft/s).

FIG. A5.2 Portable Sampler Operational Data Confirmation of Free Water Sampled

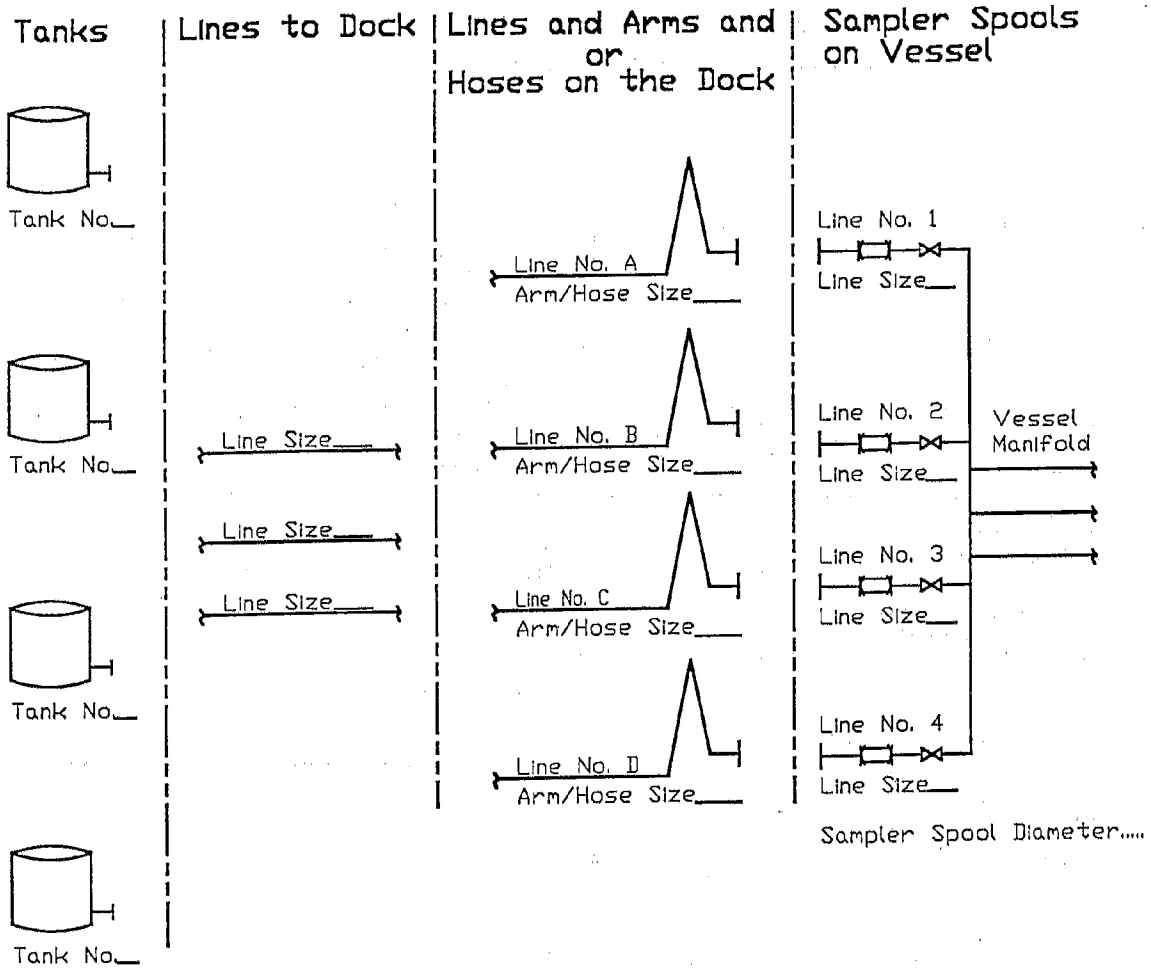
PRO_00104377



NOTE—In the spaces provided, enter the tank numbers and lines sizes used during loading.

FIG. A5.3 Typical Piping Schematic to Be Recorded for Loading

PRO_00104378



NOTE—In the spaces provided, enter the line sizes used during discharge.

FIG. A5.4 Typical Piping Schematic to be Recorded for Discharges

PRO_00104379

A6. SAMPLER ACCEPTANCE TEST DATA

A6.1 Figure A6.1 is an example of the sampler acceptance test data sheet.

Company: _____ Location: _____ Sampler ID: _____ Test # ____of ____

Date: _____ Company Witness: _____ Other Witness: _____

SYSTEM DATA

Crude Grade: _____ _____ | Viscosity: _____ cts @ 40C | API: ____ | Flow Rate: _____ bph/m3 Flow Temp: _____ F/C | Velocity ___ fps/mps | Line Size: ____in.

Crude Volume Determination by:	Probe Design:	Probe Orientation:	Stream Conditioning:	Laboratory Analysis:
___ Meter ___ Tank Tank Increment Vol. _____ bbls/m3 Sample Receiver Volume: _____ gal/l Test Sample Volume _____ gal/l	___ Isokinetic ___ Ell ___ Beveled ___ Plain ___ Other ___ Grab Size(ml)	___ Top ___ Side ___ Bottom ___ Sample Loop	___ Power Mixing ___ Static Mixer–Vertical ___ Static Mixer–Horizontal ___ Piping Element–Vertical ___ Piping Element–Horizontal ___ None	___ Centrifuge ___ Distillation ___ Karl Fischer ___ Mass ___ Volume

Test Water: _____ Fresh; _____ Brackisk; _____ Sea; _____ Production

TEST DATA

Baseline Test Data

1. Single Sampler Method Baseline Test:
   (Wavg) = (1st baseline _____ % + 2nd baseline _____ %) / 2 = _____ %

2. Dual Sampler Method Baseline Test:
   a. Before Water Injection Comparison Test
      (Baseline Sampler _____ % – Primary Sampler _____ %) = _____ %
      Maximum Deviation From Table A.1 = _____ %
   b. During Water Injection Test: (Wavg) = _____ %

Water Injection and Crude Volumes:

3. Water Injected (V)
   Stop Meter Totalizer _____ gal/l
   Start Meter Totalizer _____
   V = Difference _____ gal/l x _____ (Meter Factor) x _____ (0.0238 gal/bbl or 0.001 l/m3) = _____ bbls/m3

4. Crude Volume
   Stop Tank or Meter Totalizer _____ bbl/m3
   Start Tank or Meter Totalizer _____
   Difference _____ bbl/m3 x _____ (Meter Factor, as applicable) = _____ bbls/m3

5. TOV (line 3 + line 4) = _____ bbls/m3

CALCULATIONS:

Dev = (Wtest – Wbl) – Winj
Where:
Wtest = Percent water in test sample

6. Wbl = Wavg x [(TOV – V) / TOV]
   = _____ (line 1 or 2b) x [(_____ (line 5) – _____ (line 3)) / _____ (line 5)] = _____ %

7. Winj = (V / TOV) x 100
   = (_____ (line 3) / _____ (line 5)) x 100 = _____ %

   Dev = (_____ (Wtest) – _____ (line 6)) – _____ (line 7) = _____ %
   Maximum Deviation From Table A.1 = _____ %

NOTES:
– All percent figures are % Volume.
– Correct the volume of water injected for solids content,as applicable, if production water is used.
– Deviations must be within limits outlined in MPMS Chapter 8.2, Table A.1.
– Note below any physical or procedural changes made between consecutive test runs.
– Attach copy of sampler receiver–mixer proving test report. See MPMS Chapter 8.3.

COMMENTS:

FIG. A6.1 Sampler Acceptance Test Data Sheet

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APPENDIXES

(Nonmandatory Information)

X1. DESIGN DATA SHEET FOR AUTOMATIC SAMPLING SYSTEM

X1.1 Figure X1.1 is a sample of the design data sheet for an automatic sampling system.

PROCESS DATA	DESIGN DATA
Type of Product _____	Pipeline I.D. _____
Specific Gravity or API _____	Design pressure _____
Viscosity _____	Operating pressure _____
Vapor Pressure _____	Other _____
Expected water content (%) _____	Flow Rate
H2O (%) _____	Maximum _____ Mininum _____
Other physical properties _____	Normal _____
Sediment (%)	Parcel or batch size _____
SAMPLER DATA	**SAMPLE RECEIVER**
Grab size (ml/grab)	Total Volume _____
Collection period: Hours__ Days ___ Weeks__	Design pressure _____
Probe insertion length required	Design temperature _____
Maximum grab rate required	Material of construction _____
Air _____(Pressure)	Internal coating _____
Electricity _____(Voltage)	Portable ____ Fixed ____
Proportion to time ____, Flow ____	Accessories:
Meter manufacturer	Pressure relief valve ____ (settings)
Type _____	Vacuum relief ____ (settings)
Signal _____	Pressure gauge ____ Level gauge ____
Sampler Controller alarms: _____	Volume weight/indicator _____
	Other _____
SYSTEM SPECIFICATIONS	
INSTALLATION:	AVAILABLE UTILITIES:
Permanent ____ Portable ____	Electrical: Voltage ____ Hz ____
Electrical Classifications at proposed installation site_____	Phase
	Air: Pressure ____ Instrument ____
	Steam: Pressure ____ Temperature ____
NOTES: _____	
COMPANY _____	PROJECT _____
ADDRESS _____	
DATE PREPARED _____	DATE REQUIRED _____

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FIG. X1.1 Design Data Sheet for Automatic Sampling System

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X2. COMPARISON OF PERCENT SEDIMENT AND WATER VERSUS UNLOADING TIME PERIOD

X2.1 Figure X2.1 presents a comparison of percent sediment and water versus unloading time period.

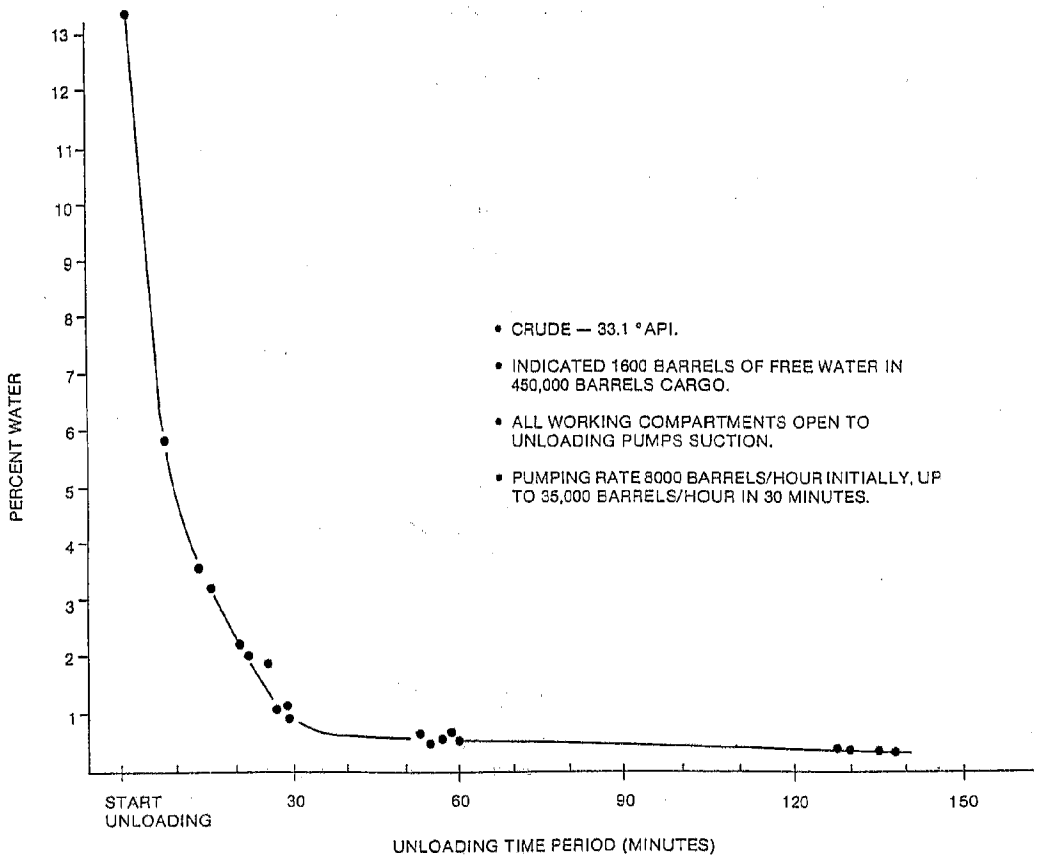


FIG. X2.1 Comparison of Percent Sediment and Water Versus Unloading Time Period

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Document Name: ASTM D4239: Standard Test Methods for Sulfur in the Analysis Sample of Coal and Coke Using High Temperature Tube Furnace Combustion Methods

CFR Section(s): 40 CFR 60, Appendix A-7

Standards Body: American Society for Testing and Materials

APPROVED

Official Incorporator:
THE EXECUTIVE DIRECTOR
OFFICE OF THE FEDERAL REGISTER
WASHINGTON, D.C.

Designation: D 4239 – 97$^{\epsilon 1}$

Standard Test Methods for Sulfur in the Analysis Sample of Coal and Coke Using HighTemperature Tube Furnace Combustion Methods[1]

This standard is issued under the fixed designation D 4239; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

ε[1] NOTE—Section 18.4 has been editorially corrected in June 1999.

1. Scope

1.1 These test methods cover three alternative procedures using high-temperature tube furnace combustion methods for the rapid determination of sulfur in samples of coal and coke.

1.2 These test methods appear in the following order:

	Sections
Method A—High-Temperature Combustion Method with Acid Base Titration Detection Procedures	6-9
Method B—High-Temperature Combustion Method with Iodimetric Titration Detection Procedures	10-13
Method C—High-Temperature Combustion Method with Infrared Absorption Detection Procedures	14-16

1.2.1 When automated equipment is used to perform any of the three methods of this test method, the procedures can be classified as instrumental methods. There are several manufacturers that offer to the coal industry equipment with instrumental analysis capabilities for the determination of the sulfur content of coal and coke samples.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* See 7.8 and 15.2.

2. Referenced Documents

2.1 *ASTM Standards:*

D 346 Practice for Collection and Preparation of Coke Samples for Laboratory Analysis[2]

D 1193 Specification for Reagent Water[3]

D 2013 Method of Preparing Coal Samples for Analysis[2]

D 2361 Test Method for Chlorine in Coal[2]

D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke[2]

D 3176 Practice for Ultimate Analysis of Coal and Coke[2]

D 3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases[2]

D 4208 Test Method for Total Chlorine in Coal by the Oxygen Bomb Combustion/Ion Selective Electrode Method[2]

D 4621 Guide for Accountability and Quality Control in the Coal Analysis Laboratory[2]

D 5142 Test Methods for the Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures[2]

3. Summary of Test Methods

3.1 *Method A—High-Temperature Combustion Method with Acid-Base Titration Detection Procedures*—A weighed sample is burned in a tube furnace at a minimum operating temperature of 1350°C in a stream of oxygen. During combustion, all sulfur contained in the sample is oxidized to gaseous oxides of sulfur (sulfur dioxide, SO_2, and sulfur trioxide, SO_3) and the chlorine in the sample is released as Cl_2. These products are then absorbed into a solution of hydrogen peroxide (H_2O_2) where they dissolve forming dilute solutions of sulfuric (H_2SO_4) and hydrochloric (HCl) acids. The quantities of both acids produced are directly dependent upon the amounts of sulfur and chlorine present in the original coal sample. Once the amounts of each acid present have been determined, the percentage of sulfur contained in the coal may be calculated.

3.1.1 This method is written to include commercially available sulfur analyzers that must be calibrated with appropriate standard reference materials (SRMs) to establish recovery factors or a calibration curve based on the range of sulfur in the coal or coke samples being analyzed.

NOTE 1—Elements ordinarily present in coal do not interfere in Method A (3.1), with the exception of chlorine; results must be corrected for chlorine content of the samples (9.1).

3.2 *Method B—High-Temperature Combustion Method with Iodimetric Detection Procedures*—A weighed sample is burned in a tube furnace at a minimum operating temperature of 1350°C in a stream of oxygen to ensure the oxidation of sulfur. The combustion products are absorbed in an aqueous solution that contains iodine. When sulfur dioxide is scrubbed by the diluent, the trace iodine originally present in the solution is reduced to iodide, thus causing an increase in resistance. The detection system of the instrument consists of a polarized dual platinum electrode. Any change in resistance of the solution in

[1] This test method is under the jurisdiction of ASTM Committee D-5 on Coal and Coke and is the direct responsibility of Subcommittee D05.21 on Methods of Analysis.

Current edition approved June 10, 1997. Published May 1998. Originally published as D 4239 – 83. Last previous edition D 4239 – 94.

[2] *Annual Book of ASTM Standards*, Vol 05.05.

[3] *Annual Book of ASTM Standards*, Vol 11.01.

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the vessel is detected. Iodine titrant is then added proportionally to the reaction vessel until the trace excess of iodine is replenished and the solution resistance is reduced to its initial level. The volume of titrant expended is used to calculate the sulfur concentration of the sample. The method is empirical; therefore, the apparatus must be calibrated by the use of standard reference material (SRM).

3.2.1 This method is designed to be used with commercially available sulfur analyzers, equipped to perform the preceding operation automatically, and must be calibrated with an appropriate sample (5.4) based on the range of sulfur in each coal or coke sample analyzed.

NOTE 2—Nonautomatic systems may be used with the titration procedures and calculations performed manually by qualified laboratory technicians. The resulting loss in accuracy or speed, or both, would then negate the advantages of using the fully automated instrumental approach.

3.3 *Method C—High-Temperature Combustion Method with Infrared Absorption Detection Procedures*—The sample is burned in a tube furnace at a minimum operating temperature of 1350°C in a stream of oxygen to oxidize the sulfur. Moisture and particulates are removed from the gas by traps filled with anhydrous magnesium perchlorate. The gas stream is passed through a cell in which sulfur dioxide is measured by an infrared (IR) absorption detector. Sulfur dioxide absorbs IR energy at a precise wavelength within the IR spectrum. Energy is absorbed as the gas passes through the cell body in which the IR energy is being transmitted: thus, at the detector, less energy is received. All other IR energy is eliminated from reaching the detector by a precise wavelength filter. Thus, the absorption of IR energy can be attributed only to sulfur dioxide whose concentration is proportional to the change in energy at the detector. One cell is used as both a reference and a measurement chamber. Total sulfur as sulfur dioxide is detected on a continuous basis. This method is empirical; therefore, the apparatus must be calibrated by the use of SRMs.

3.3.1 This method is for use with commercially available sulfur analyzers equipped to carry out the preceding operations automatically and must be calibrated using standard reference material (coal) of known sulfur content based on the range of sulfur in each coal or coke sample analyzed.

4. Significance and Use

4.1 Determination of sulfur is, by definition, part of the ultimate analysis of coal.

4.2 Results of the sulfur analysis are used to serve a number of interests: evaluation of coal preparation, evaluation of potential sulfur emissions from coal combustion or conversion processes, and evaluation of the coal quality in relation to contract specifications, as well as other scientific purposes.

4.3 The instrumental analysis provides a reliable, rapid method for determining the concentration of sulfur in a lot of coal or coke and are especially applicable when results must be obtained rapidly for the successful completion of industrial, beneficiation, trade, or other evaluations.

5. Sample

5.1 The sample shall be the material pulverized to pass No. 60 (250-μm) sieve and mixed thoroughly in accordance with Method D 2013 or Practice D 346.

NOTE 3—It may be difficult to meet the precision statements of Section 18 when high mineral content coals are ground to pass 60 mesh. When the precision of analysis required cannot be obtained, it is recommended that the coals be ground to pass through a No. 100 (150-μm) sieve. The reduced particle size should result in a more homogeneous sample.

5.2 A separate portion of the analysis sample should be analyzed for moisture content in accordance with Test Method D 3173, so that calculation to other than the as-determined basis can be made.

5.3 Procedures for converting as-determined sulfur values obtained from the analysis sample to other bases are described in Practices D 3176 and D 3180.

5.4 Standard Reference Material (SRM) such as SRM Nos. 2682 through 2685–*Sulfur in Coal*[4] which consist of four different coals that have been individually crushed and ground to pass a 60-mesh sieve, and bottled in 50-g units, or other commercially available reference coals with a certified sulfur content.

METHOD A—HIGH-TEMPERATURE COMBUSTION METHOD WITH ACID-BASE TITRATION DETECTION PROCEDURES[5]

6. Apparatus

6.1 *Tube Furnace*—Capable of heating 150- to 175-mm area (hot zone) of the combustion tube (6.2) to at least 1350°C. It is usually heated electrically using resistance rods, a resistance wire, or molybdenum disilicide elements. Specific dimensions may vary with manufacturer's design.

NOTE 4—Induction furnace techniques may be used provided it can be shown that they meet the precision requirements of Section 18.

6.2 *Combustion Tube*—Approximately 28-mm internal diameter with a 3-mm wall thickness and 750 mm in length made of porcelain, zircon, or mullite. It must be gastight at working temperature. The combustion may be carried out in a tapered-end tube that is closely connected to the gas absorber by high temperature tubing with gastight joints. Acceptable configurations include connecting the tapered-end tube directly to the elbow of the fritted gas bubbler or to a 10/30, standard taper-ground joint that is attached to a heat resistant glass right angle bend. The temperature at the tapered end of the tube should be maintained high enough to prevent condensation in the tube itself.

6.2.1 Alternatively, a high-temperature straight refractory tube may be used, if available. It requires a silica adaptor (6.11) with a flared end that fits inside the combustion tube and serves as an exit for the gases.

6.3 *Flowmeter*, for measuring an oxygen flow rate up to 2.0 L/min.

6.4 *Sample Combustion Boats*, must be made of iron-free material and of a convenient size suitable for the dimensions of

[4] Available from the Office of Standard Reference Materials, Room B314, Chemistry Bldg., National Bureau of Standards, Washington, DC 20234.

[5] Based on the method of Mott, R. A., and Wilkinson, H. C., "Determination of Sulfur in Coal and Coke by the Sheffield High Temperature Method," *Fuel*, Fuel B, Vol. 35, 1956, p. 6. This method is designed for the rapid determination of sulfur in coal and coke. It is not applicable to coals or coal density fractions that have been subjected to treatment with chlorinated hydrocarbons because of the potentially high acidity of the combustion gases.

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the instrument being used.

6.5 *Boat Puller*—Rod of a heat-resistant material with a bent or disk end to insert and remove boats from the combustion tube.

6.5.1 If the boat puller is to remain within the combustion tube while the boat is moved into the hot zone, it is necessary to pass the puller through a T-piece that is fitted into a rubber stopper at the inlet of the combustion tube. The open end of the T-piece is sealed with a rubber stopper to permit movement of the pusher and prevent escape of the oxygen that enters at the side limb of the T. The rubber stopper or tube should be checked often to avoid leakage.

6.6 *Gas Absorber or Analyzer Titration Vessel*—A narrow vessel of such diameter that the end of the tube from which the gasses exit is inside the vessel and submerged to a depth of at least 90 mm, when 200 mL of the peroxide solution (7.4) is added to the vessel.

6.6.1 Alternatively, 125-mL capacity bottles with fritted disk can be used for gas absorption. The bottles should be of such a diameter that the fritted end is covered by the peroxide solution to a depth of at least 50 mm. The fritted glass end porosity should be 15 to 40 μm. The bottles are fitted in a series of two to the outlet end of the combustion tube.

6.7 *Gas-Purifying Train*—Designed to be used with specific instruments, or a U-tube packed with soda asbestos may be used. See configuration in Fig. 1.

6.8 *Vacuum Source*—Needed if a negative pressure is used to transport the gasses and combustion products through the system.

6.9 *Vacuum Regulating Bottle*, containing mercury with an open-ended tube dipping into the mercury, used with a vacuum source.

6.10 *Silica Adaptor*, 300 mm long by 8 mm in outside diameter and flared at one end to 26 mm. To be used with a straight refractory combustion tube.

6.11 *Other Configurations of Apparatus*—Complete sulfur analyzer assembly units designed to perform functions similar to this method, with automated features that perform the sulfur analysis in a more rapid manner are commercially available. These instruments may have combustion tube dimensions and oxygen purifying apparatus that differ slightly from those described in this method, but are acceptable, provided equivalent values within the precision statement of Section 18 are obtained. (See Fig. 2 and Fig. 3.)

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Available Reagents of the American Chemical Society, where such specifications are available.[6] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water, Type IV, conforming to Specification D 1193.

7.3 *Aluminum Oxide (Al_2O_3)*—finely divided and dried at 1350°C.

7.4 *Hydrogen Peroxide (H_2O_2) Solution*—One volume percent (50 mL of 30 % H_2O_2 with 1450 mL of water). The pH is adjusted (using NaOH or H_2SO_4 as appropriate) to that which is used for the end point in the titration. Solutions should be discarded after two or three days.

7.5 *Indicator*—Indicators that change color (titration end point) between pH 4 and 5 are recommended, but in no case should the pH exceed 7. Adequate lighting and stirring to ensure proper detection of the end point is essential. A choice of indicators or use of a pH meter is permitted (Note 5). Directions for preparing two acceptable mixed indicators are as follows:

7.5.1 Mix 1 part methyl red solution (dissolve 0.125 g in 60 mL of ethanol and dilute to 100 mL with water) with 3 parts bromcresol green solution (dissolve 0.083 g in 20 mL of ethanol and dilute to 100 mL with water). Discard the mixed solution after one week.

7.5.2 Mix equal volumes of methyl red solution (dissolve 0.125 g in 60 mL of ethanol and dilute to 100 mL with water) and methylene blue solution (dissolve 0.083 g in 100 mL of

[6] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

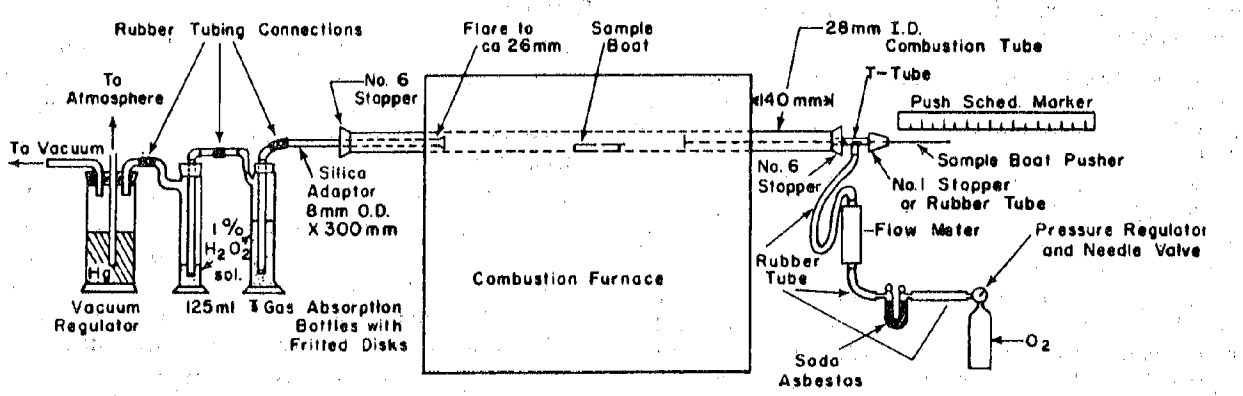


FIG. 1 Apparatus for the Determination of Sulfur Using Acid-Base Titration

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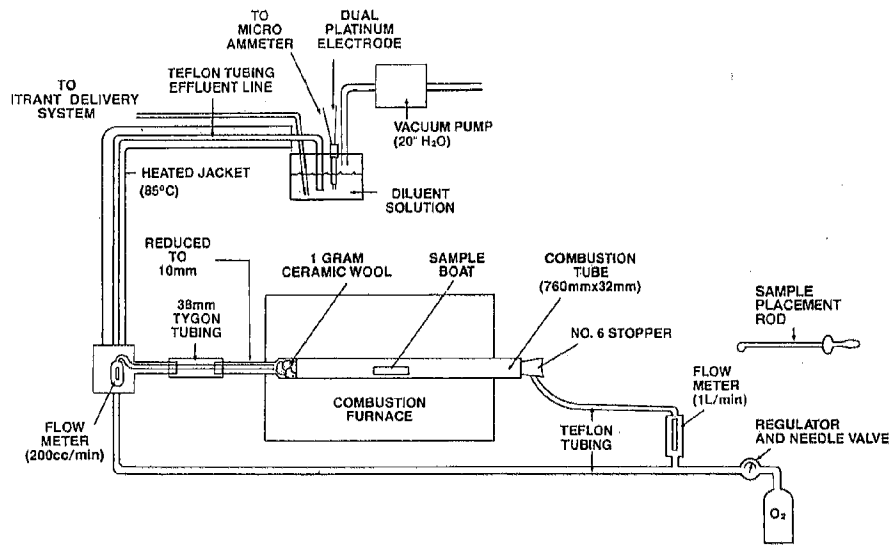


FIG. 2 Apparatus for the Determination of Sulfur by the Iodimetric Detection Method

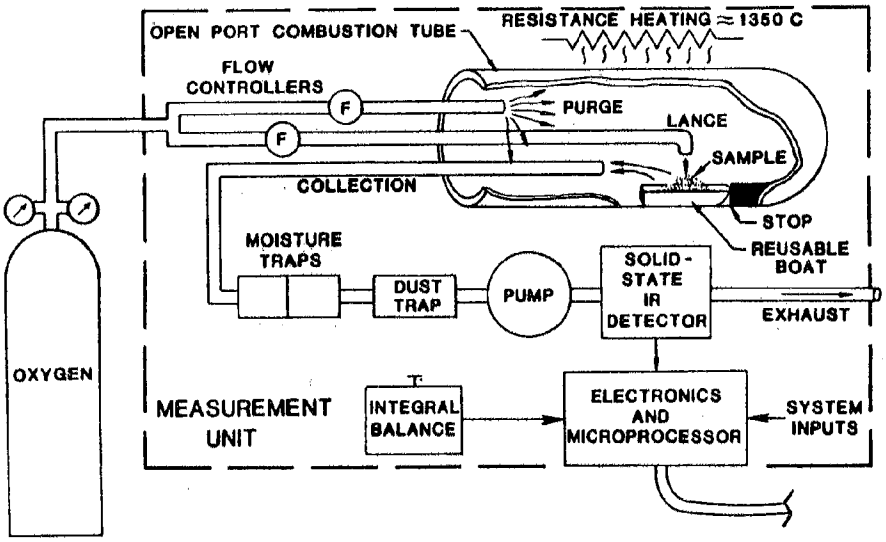


FIG. 3 Apparatus for the Determination of Sulfur by the Infrared Detection Method

ethanol and store in a dark glass bottle). Discard the mixed solution after one week.

NOTE 5—Although two end-point indicators or a pH meter method are described, the use of the pH meter is accepted as more definitive of the end point of the titration process and considered to give more reproducible results.

7.6 *Soda-Asbestos*, 8 to 20 mesh, if a U-tube is used.

7.7 *Sodium Hydroxide, Standard Solution, 0.05N*—Dissolve 2.05 g of sodium hydroxide (NaOH) in water and dilute to 1 L. Standardize against a primary standard.

7.8 *Oxygen, 99.5 % Pure*—Compressed gas contained in a cylinder equipped with a suitable pressure regulator and a needle valve to control gas flow. **Warning**—Pure oxygen vigorously accelerates combustion. All regulators, lines, and valves should be free of grease and oil.

8. Procedure

8.1 Assemble the apparatus, as directed, by the instructions of the instrument manufacturer. Alternatively, the apparatus shown in Fig. 1 can be assembled except do not initially connect the rubber tube from the oxygen supply to the soda asbestos U-tube.

8.2 *Calibration*—Sulfur analyzers must be calibrated at least once on each day they are used, following the analysis procedure outlined in Section 8, using coal or coke standards (5.4) with sulfur values in the range of the samples being analyzed. A recovery factor (F) or calibration curve must be established and appropriately used in each calculation.

$$F = \frac{\text{Actual Sulfur in Standard, Dry Basis}}{\text{Analyzed Sulfur in Standard, Dry Basis}} \quad (1)$$

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8.3 *Furnace Adjustment*—Raise the temperature of the furnace to at least 1350°C. Bring the temperature up slowly, allowing approximately 3 to 4 h in advance, to allow sufficient time to come to a stable temperature. Be sure to check the manufacturer's instructions for raising the temperature of the furnace and heed any precautions for protecting heating elements from deterioration or thermal shock.

8.4 *Titration Vessel Preparation*—Fill the titration vessel in accordance with the manufacturer's instructions with approximately 200 mL of the gas absorption fluid (hydrogen peroxide) (7.4). Adjust the pH of the solution to make it definitely acidic by adding dilute sulfuric acid. If chemical indicators (instead of a pH meter) are used, add five or six drops of the indicator and then add a very small quantity (as required) of dilute sodium hydroxide (NaOH) to reach the end point color that will be developed in the sulfur analysis.

8.4.1 If the apparatus with two gas absorption bottles is used, add 100 mL of 1 % H_2O_2(7.4) to the bottles so that at least 50 mm of the fritted disk is covered in the first bottle.

8.5 *Oxygen Flow*—Connect the oxygen supply and adjust the oxygen flow to approximately 2 L/min with the oxygen baffle inserted in the entrance end of the combustion tube. Be sure to check manufacturer's instructions. The flow rate at the temperature of 1350°C should be sufficient to prevent the formation of oxides of nitrogen. Allow the oxygen to flow through the combustion tube for at least 1 min before inserting any sample. Check the system for any possible leaks.

8.5.1 If a vacuum source is used, draw air through the apparatus at about 350 mL/min, then connect the oxygen supply to the U-tube and adjust the rate of flow of the oxygen to 300 mL/min. The flow rate is adjusted by changing the depth of the penetration into the mercury of the open-ended glass tube in the vacuum regulating bottle. The preliminary adjustment to 350 mL/min of air ensures that the connections at the outlet end of the combustion tube are under slightly reduced internal pressure and no leak of combustion products should occur.

NOTE 6—A gastight combustion train must be established with an adequate flow of approximately 300 mL/min of pure acid-free oxygen before analyzing samples on the equipment. This is best accomplished during the period the high-temperature tube furnace is brought to its operating temperature of 1350°C. The required gas flow may be established by the use of reduced internal pressure, or should the manufacturer specify or the operator prefer, it can be obtained by the use of a positive pressure train operated at slightly above atmospheric pressure to obtain the required oxygen flow rate. In all cases, the instructions of the manufacturer of the equipment should be followed. This also applies to the addition of sufficient gas absorption fluid as well as to the assembly of the apparatus.

8.6 *Analysis Sample Size*—Weigh out 0.5 g of the analysis sample to the nearest 0.1 mg for coals containing up to 4.0 % sulfur and 0.25 g to the nearest 0.1 mg of analysis sample for coals containing over 4.0 % sulfur. Spread the sample evenly in a combustion boat.

8.6.1 A thin layer of Al_2O_3 can be used to line the sample boat and cover the sample to ensure complete combustion and reduce splattering or loss of sample.

8.7 *Sample Combustion*—Remove the oxygen baffle or rubber stopper or both from the combustion tube and put the charged sample boat into the inlet end of the combustion tube approximately 270 mm from the center of the combustion tube hot zone. Close the combustion tube by replacing the oxygen baffle or rubber stopper or both and, if necessary, readjust the rate of flow of the oxygen. Leave the boat in this position for 1 to 3 min until the volatiles have been driven off. This will also eliminate the "popping" and soot accumulation in the right angle bend. Remove the oxygen baffle or rubber stopper and move the sample boat slowly forward until the boat is in the center of the hot zone, approximately 30 mm at the beginning of each minute for 6 min is the suggested schedule to ensure a slow heating rate. Be sure to remove the boat puller from the hot zone and replace the baffle or stopper after each movement. Allow the sample to burn in the hot zone for approximately 3 to 4 min until all sulfur in the sample is oxidized to sulfur dioxide (SO_2) or sulfur trioxide (SO_3). The complete sample burning time is not more than 14 to 15 min. This heating program has been established for all types of coal. Where it is shortened for a particular coal or by instruction of the manufacturer of a particular sulfur analyzer, results should be checked against those obtained by using the longer heating schedule.

8.7.1 If the rubber stopper with the T-piece is used (6.5.1), the rubber stopper remains in the end of the combustion tube and the boat puller is permitted movement into the furnace through the T-piece. See Fig. 1.

8.8 *Titration*—The gasses of combustion leave the combustion tube through the exit end and are dissolved in the hydrogen peroxide in the gas absorption bottles or analyzer titration vessel forming a dilute sulfuric acid. Titrate the contents of this vessel with 0.05*N* sodium hydroxide (7.7), backwashing the titration vessel and inlet tubes according to manufacturer's instructions. The total acidity, because of oxides of sulfur and chlorine, is given according to the following reactions:

$$SO_2 + H_2O_2 \rightarrow H_2SO_4$$

$$Cl_2 + H_2O_2 \rightarrow 2HCl + O_2$$

8.8.1 If the contents of the gas absorption bottles must be transferred to a suitable titration flask, be sure to wash the bottles and inlet tube or silica adaptor with water (7.2) and add these washings and five or six drops of indicator to the titration flask before titrating with the 0.05*N* NaOH solution (7.7).

8.8.2 High-temperature combustion acid/base titration sulfur analyzers may be designed to give a buret reading directly in percent sulfur content of the coal sample, but a correction still must be made for acidity caused by chlorine present in the sample using Test Methods D 2361 or D 4208.

NOTE 7—Often *no* correction is made for the presence of chlorine in the sample, or a percentage value (found as a relatively invariant value based upon prior knowledge of the coals being analyzed) is subtracted from the percent sulfur determined. This method can be acceptable for coals of known chlorine content; however, for work of the highest accuracy, the percentage of chlorine present in the sample must be determined analytically, and correction for its presence made by subtracting an equivalent value from a value equivalent to the total acidity determined by the sulfur titration.

9. Calculations

9.1 Some sulfur analyzers are designed to give buret readings in percent sulfur if the titrant is adjusted and standardized

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to exactly 0.05*N* and the sample weight is exactly 0.500 g. After the observed percent sulfur has been adjusted using the recovery factor or calibration curve, then it must be corrected for chlorine using the following calculation:

$$S_c = 1.603\ (S_b/1.603 \times F - \text{Cl, \%}/3.546) \quad (2)$$

where:

S_c = sulfur corrected for chlorine (as determined), %;
S_b = sulfur from buret reading, %;
F = the recovery factor or factor taken from a calibration curve for the analyzer; and
Cl, % = chlorine in sample (as determined), %.

9.2 On analyzers that are designed to give buret readings in percent sulfur, but where the normality of the titrant or sample weight may vary from that prescribed, the following calculation must be used:

$$S_c = 1.603\ [(S_b \times N_1 \times F \times 10) - \text{Cl, \%}/3.546]/W \quad (3)$$

where:

S_c = sulfur corrected for chlorine (as determined), %;
S_b = sulfur taken from buret reading, %;
N_1 = normality of the sodium hydroxide;
F = recovery factor or factor taken from a calibration curve for the analyzer;
Cl,% = chlorine in sample (as determined), %; and
W = weight of sample, g.

9.3 When sulfur analyzers are used that have buret readings in millilitres of titrant, the following calculation will apply:

$$S_c = 1.603\ [(V_1 \times N_1 \times F) - \text{Cl, \%}/3.546]/W \quad (4)$$

where:

S_c = sulfur corrected for chlorine (as determined), %;
S_b = sulfur taken from buret reading, %;
V_1 = sodium hydroxide, mL;
N_1 = normality of sodium hydroxide;
Cl, % = chlorine in sample (as determined), %;
F = the recovery factor or factor taken from a calibration curve for the analyzer; and
W = weight of sample, g.

METHOD B—HIGH-TEMPERATURE COMBUSTION METHOD WITH IODIMETRIC TITRATION DETECTION PROCEDURES

10. Apparatus

10.1 *Analytical Apparatus*—Designed to perform the analysis procedure described in 3.2 automatically.

NOTE 8—It is recommended that the analytical equipment be an automated sulfur analyzer. Otherwise, the restrictions and limitations given in Note 3 for nonautomated systems apply.

10.2 *Tube Furnace*—See 6.1.

10.3 *Combustion Tube*—Made of mullite, porcelain, or zircon, approximately a 27-mm inner diameter, a 33-mm outer diameter, and 750 mm in length, with the last 23 mm of the exit end reduced to 10-mm outer diameter and 5-mm inner diameter to facilitate exit and collection of the gases in the titration vessel.

10.4 *Sample Combustion Boats*—See 6.4.

10.5 *Boat Puller*—See 6.5.

11. Reagents

11.1 *Purity of Reagents*—See 7.1.

11.2 *Purity of Water*—See 7.2.

11.3 *Iodine Titrant*—Dissolve 2.5 g of iodine in 280 mL of pyridine. Mix well and be certain all iodine is dissolved. Add 700 mL of methanol and 20 mL of water. (See Note 9.)

11.4 *Diluent*—Mix 280 mL of pyridine with 700 mL of methanol and 20 mL of water. Mix well.

NOTE 9—Alternative formulations may be substituted to the extent that they can be demonstrated to yield equivalent results in regard to accuracy and precision.

11.5 *Oxygen*—See 7.8.

12. Procedure

12.1 *Instrument Preparation*:

12.1.1 Assemble the analytical apparatus according to the manufacturer's instructions. Check all connections carefully to avoid leaks.

12.1.2 Set furnace temperature to 1350°C.

12.1.3 Set oxygen flow rate according to manufacturer's instructions.

12.1.4 Place approximately 150 mg of a coal sample in a boat and insert into the 1350°C region of the furnace. Sample boat should remain within the hot zone of the furnace for at least 2 min or until sample is completely burned. This action will serve to condition the apparatus in all functions.

12.2 *Calibration*:

12.2.1 Select a coal standard reference material (SRM), as described in 5.4, which has a sulfur value in the range of the sample to be analyzed. Weigh out about 150 mg of this previously dried coal standard and record the weight to the nearest 0.1 mg.

12.2.2 Enter the weight and sulfur content of the standard reference material sample into the memory of the analyzer.

12.2.3 Insert SRM sample into the 1350°C region of the furnace.

12.2.4 After endpoint is reached, not less than 2 min, record the titrant factor as milligrams sulfur per millilitre of titrant (mgS/mL). If analyzer does not have an integral computer, record the volume of titrant used and calculate titrant factor as instructed in 13.1.

12.2.5 Remove sample boat and repeat Steps 12.2.1-12.2.4 two more times.

12.2.6 If analyzer does not automatically average the titrant factors obtained in the calibration step and enter the average into the microprocessor, then do so manually. Successive calibrations should yield titrant factors within 0.01 mgS/mL of each other.

12.3 *Analysis Procedure*:

12.3.1 Use an instrument that has been conditioned and calibrated according to 12.1 and 12.2.

12.3.2 Weigh to the nearest 0.1 mg, approximately 150 mg of the coal analysis sample into a boat.

12.3.3 Enter the sample weight into the sulfur analyzer memory.

12.3.4 Insert the coal sample into the 1350°C region of the furnace.

12.3.5 After the endpoint is reached (not less than 2 min)

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record the sulfur concentration of the sample. If analyzer does not have an integral computer, record the volume of titrant used and calculate the sulfur concentration as instructed in 13.2.

13. Calculations

13.1 On analyzers that do not calculate the titrant factor automatically, the following calculation must be used:

$$T = S_s \times W/100 \times V_t \quad (5)$$

where:
T = titrant factor, mg of sulfur/mL;
S_s = sulfur concentration of standard, dry basis;
W = weight of standard, mg; and
V_t = volume of titrant, mL.

13.2 On analyzers that do not calculate the percent sulfur in the analysis sample automatically, the following calculation must be used:

$$S = 100\,(T \times V_t)/W \quad (6)$$

where:
S = percent sulfur (as determined),
T = titrant factor (see 13.1),
V_t = volume of titrant, mL, and
W = weight of sample, mg.

METHOD C—HIGH-TEMPERATURE COMBUSTION METHOD WITH INFRARED ABSORPTION PROCEDURE

14. Apparatus

14.1 *Measurement Apparatus*—Equipped to combust the sample as described in 3.3 automatically. (See Note 8.)

14.2 *Tube Furnace*—See 6.1.

14.3 *Combustion Tube*—Made of mullite, porcelain, or zircon with provisions for routing the gasses produced by combustion through the infrared cell.

14.4 *Sample Combustion Boats*—See 6.4.

14.5 *Boat Puller*—See 6.5.

15. Reagents

15.1 *Purity of Reagents*—See 7.1.

15.2 *Magnesium Perchlorate*—**Warning**: Magnesium perchlorate is a strong oxidizing agent. Do not try to regenerate the absorbent. Do not allow contact with organic materials or reducing agents.

15.3 *Oxygen*—See 7.8.

15.4 *Standard Reference Material (SRM)*—Such as SRM Nos. 2682 through 2685—*Sulfur in Coal*,[7] reference coals or calibrating agents with certified dry-basis sulfur values must be used. The materials must be supplied by or have traceability to internationally recognized certifying organizations, such as the National Institute of Standards and Technology.

15.4.1 All SRMs, reference coals, or calibrating agents must have precision values of less than or equal to method repeatability. Such SRMs, reference coals, or calibrating agents must be stable with respect to moisture and be pulverized to pass 100 % through a 0.250-mm (No. 60) USA Standard Sieve. SRMs, reference coals, or calibrating agents must be mixed thoroughly before each use.

16. Procedure

16.1 *Instrument Preparation*—Perform system update checks in accordance with manufacturer's instructions.

16.1.1 *Balance Calibration*—Calibrate internal balance in accordance with manufacturer's instructions.

16.2 *Calibration of the Infrared Detection System*—Select SRMs, reference coals, or calibrating agents with known dry-basis sulfur values in the range of the samples to be analyzed. For the initial calibration and periodic verification of instrument linearity, at least three such SRMs, reference coals, or calibrating agents are recommended for each range of sulfur values to be tested. When performing a single-point calibration (Note 10) the SRM, reference coal, or calibrating agent containing the highest sulfur value for the expected range should be used for calibration. The other two SRMs, reference coals, or calibrating agents should represent the low and midpoints of the expected range. When performing a multiple point calibration, two of the SRMs, reference coals, or calibrating agents should bracket the range of sulfur values to be tested with the third falling within the range. All results obtained must be within the allowable limits of the SRMs, reference coals, or calibrating agents. Records for all calibrations will be maintained in accordance with Guide D 4621.

16.2.1 All SRMs, reference coals, or calibrating agents used for calibrating the instrument should comply with the provisions of 15.4. **CAUTION**—An indicated problem with linearity of the instrument during calibration could result from contamination of the SRM, reference coal, or calibrating agent as the container becomes depleted. It is, therefore, suggested that extreme care be used in mixing the SRM, reference coal, or calibrating agent before removing any sample from the container and that it be discarded when less than 5 g remain in the container.

NOTE 10—When performing a single-point calibration, the technique of calibrating the instrument with the SRM, reference coal, or calibrating agent corresponding to the highest sulfur value expected for the range uses the optimum linear range available for calibration. Single-point calibration is most linear from the point of calibration to zero.

16.2.2 *Calibration Procedure*—Make a minimum of two determinations to condition the equipment before calibrating the system. The as-determined sulfur value of the SRM, reference coal, or calibrating agent used for calibration of the instrument must have been previously calculated from the certified dry-basis sulfur value and residual moisture determined using either Test Methods D 3173 or D 5142. Alternately, a quantity of the SRM, reference coal, or calibrating agent allocated to be used within a normal production period (Note 11) can be dried using either Test Methods D 3173 or D 5142, in which case, the dry basis sulfur value will be used. The dried material must be stored in a desiccator, and any remaining at the end of the normal production period must be discarded. Weigh five samples of the SRM, reference coal, or calibrating agent (Note 12) chosen to represent the range of sulfur values being tested. Follow the calibration procedure

[7] Available from the Office of Standard Reference Materials, Room B314, Chemistry Bldg., National Institute of Standards and Technology, Washington, DC 20234.

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recommended by the manufacturer. For verification of the calibration curve, use SRMs, reference coals, or calibrating agents that bracket the range of values to be tested. All results obtained must be within the allowable limits of the SRMs, reference coals, or calibrating agents. Records for all calibrations will be maintained in accordance with Test Method D 4621.

NOTE 11—A normal production period would routinely be considered an 8-h shift. Dried SRMs, reference coals, or calibrating agents should not be maintained beyond one day for the purposes of instrument calibration. **CAUTION**—Previously dried material should not be redried as oxidation can readily occur.

NOTE 12—Weigh to the nearest 1.0 mg. Since the sulfur content of the SRMs, reference coals, or calibrating agents bracket the range of sulfur values being determined from the samples, the mass of the SRM, reference coals, or calibrating agents used for calibration and the samples to be analyzed should be approximately the same so that both materials produce about the same amount of infrared cell saturation (60 to 70 %).

16.2.3 *Periodic Calibration Verification*—On a periodic basis, verify the stability of the instrument and its calibration by analyzing a portion of the SRM, reference coal, or calibrating agent used to calibrate the instrument. The value determined for this material, when used as an unknown sample, must be within the certified value plus or minus the stated precision limits of the material. If the criteria for a successful verification of calibration in accordance with Test Method D 4621 is not met, the calibration procedure of 16.2.1 must be repeated and samples analyzed since the last successful verification must be repeated.

16.3 *Analysis Procedure*—Stabilize and calibrate the analyzer (see 16.2).

16.3.1 Raise the furnace temperature as recommended by the manufacturer to at least 1350°C. Weigh the sample (Note 12). Spread the sample evenly in a combustion boat and use a boat puller to position the sample in the hot zone of the furnace for at least 2 min (Note 13) or until completely combusted.

NOTE 13—The analytical cycle should begin automatically as soon as sulfur is detected.

16.3.2 When the analysis is complete, the instrument should indicate the sulfur value. Refer to the manufacturer's recommended procedure.

17. Report

17.1 The percent sulfur value obtained using any of the described methods is on an as-determined basis.

17.2 The results of the sulfur analysis may be reported on any of a number of bases, differing from each other in the manner by which moisture is treated.

17.3 Use the percentage of moisture in the sample passing a No. 60 (250-μm) sieve to calculate the as-determined results of the analysis sample to a dry basis.

17.4 Procedures for converting the value obtained on the analysis sample to other bases are described in Practices D 3176 and D 3180.

18. Precision and Bias

18.1 These are empirical methods that are highly dependent upon the calibration of the equipment; the closeness of the standards to the samples in sulfur content, chlorine content, iron content, and so forth.

18.2 *Precision Statement for High-Temperature Combustion Method Using Acid Base Titration Detection Procedures*—The relative precision of this method for the determination of total sulfur covers the concentration range from 0.5 to 6.0 %.

18.2.1 *Repeatability*—The difference in absolute value between two consecutive test results carried out on the same sample of 60-mesh pulp, in the same laboratory, by the same operator, using the same apparatus, should not exceed the repeatability interval $I(r)$ more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the repeatability interval, there is reason to question one or both of the test results. The repeatability interval may be calculated by use of the following equation:

$$I(r) = 0.06 + 0.03\,\bar{x} \quad (7)$$

where $\bar{x}$ is the average of the two test results.

NOTE 14—This equation applies to the relative spread of a measurement that is expressed as a percentage and is derived from the statistical evaluation of the round-robin analytical results. *Example:* Duplicate analysis for total sulfur gave values of 1.52 and 1.57 %. The average sulfur of the duplicate analysis value is 1.55 % and the calculated repeatability $I(r)$ is 0.11. The difference between the two sulfur values is 0.05 and does not exceed the $I(r)$ of 0.11; therefore, these two values are acceptable at the 95 % confidence level.

18.2.2 *Reproducibility*—The difference in absolute value between the averages of replicate determinations, carried out in different laboratories on representative 60-mesh samples, prepared from the same bulk sample after the last stage of reduction, should not exceed the reproducibility interval $I(R)$ more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the reproducibility interval, there is reason to question one, or both, of the test results. The reproducibility interval may be calculated by the use of the following equation:

$$I(R) = 0.03 + 0.11\,\bar{x} \quad (8)$$

where $\bar{x}$ is the average of between-laboratory results.

NOTE 15—This equation applies to the relative spread of a measurement that is expressed as a percentage and is derived from the statistical evaluation of the round-robin analytical results. *Example:* Duplicate analysis for total sulfur in one laboratory gave an average value of 3.81 %, and a value of 4.00 % was obtained in a different laboratory. The between-laboratory average sulfur value is 3.91 %, the calculated $I(R)$ interval is 0.46 %, and the difference between the different laboratory values is 0.19 %. Since this difference is less than the $I(R)$, these two values are acceptable at the 95 % confidence level.

18.3 *Precision Statement for High-Temperature Combustion Method Using Iodimetric Detection Procedures*—The relative precision of this method for the determination of total sulfur covers the concentration range from 0.5 to 6.0 %.

18.3.1 *Repeatability*—The difference in absolute value between two consecutive test results carried out on the same sample of 60-mesh pulp, in the same laboratory, by the same operator, using the same apparatus should not exceed the repeatability interval $I(r)$ more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the repeatability interval, there is reason to question one, or both, of the test results. The repeatability interval may be determined by use of the following equation:

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$$I(r) = 0.08\,\bar{x} \quad (9)$$

where $\bar{x}$ is the average of the two test results.

NOTE 16—This equation applies to the relative spread of a measurement that is expressed as a percentage and is derived from the statistical evaluation of the round-robin analytical results. *Example:* Duplicate analysis for total sulfur gave values of 1.52 and 1.57 %. The average sulfur of the duplicate analysis value is 1.55 %, and the calculated repeatability interval $I(r)$ is 0.12. The difference between the two sulfur values is 0.05 and does not exceed the $I(r)$ of 0.12; therefore, these two values are acceptable at the 95 % confidence level.

18.3.2 *Reproducibility*—The difference in absolute value between the averages of replicate determinations, carried out in different laboratories on representative 60-mesh samples prepared from the same bulk sample after the last stage of reduction, should not exceed the reproducibility interval $I(R)$ more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the reproducibility interval, there is reason to question one, or both, of the test results. The reproducibility interval may be determined by use of the following equation:

$$I(R) = 0.08 + 0.09\,\bar{x} \quad (10)$$

where $\bar{x}$ is the average of the between-laboratory results.

NOTE 17—This equation applies to the relative spread of a measurement that is expressed as a percentage and is derived from the statistical evaluation of the round-robin analytical results. *Example:* Duplicate analysis for total sulfur in one laboratory gave an average value of 3.81 %, and a value of 4.00 % was obtained in a different laboratory. The between-laboratory average sulfur value is 3.91 %, the calculated $I(R)$ interval is 0.43 %, and the difference between the different laboratory values is 0.19 %. Since this difference is less than the $I(R)$, these two values are acceptable at the 95 % confidence level.

18.4 *Precision Statement for High-Temperature Combustion Method Using Infrared Absorption Detection Procedures*—

18.4.1 *Precision—250-μm (No. 60) Samples*—The relative precision of this test method for the determination of sulfur covers the concentration range from 0.28 to 5.61 %.

18.4.1.1 *Repeatability*—The difference in absolute value between two consecutive test results, carried out on the same sample in the same laboratory by the same operator using the same apparatus, should not exceed the repeatability interval (limit) $I(r)$ more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the repeatability interval (limit), there is reason to question one or both of the test results. The repeatability interval on a dry basis may be determined by use of the following equation:

$$I(r) = 0.02 + 0.03\,\bar{x} \quad (11)$$

where $\bar{x}$ is the average of the two test results (see Note 18).

18.4.1.2 *Reproducibility*—The difference in absolute value of replicate determinations, carried out in different laboratories on representative samples prepared from the same bulk sample after the last stage of reduction, should not exceed the reproducibility interval (limit) $I(R)$ more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the reproducibility interval (limit), there is reason to question one or both of the test results. The reproducibility interval on a dry basis may be determined by use of the following equation:

$$I(R) = 0.02 + 0.09\,\bar{x} \quad (12)$$

where $\bar{x}$ is the average of the two test results (see Note 18).

NOTE 18—These equations apply to the relative spread of a measurement that is expressed as a percentage as derived from a statistical evaluation of the round-robin results.

18.4.2 *Precision—2.36-mm (No. 8) Samples*—The relative precision of this test method for determination of sulfur covers the concentration range from 0.2 to 3.0 %.

18.4.2.1 *Repeatability*—The difference in absolute value between test results obtained in the same laboratory, by the same operator, using the same apparatus, determined on a single test specimen of two separate 2.36-mm (No. 8) test units of coal reduced entirely to 250-μm (No. 6) and prepared from the same bulk sample, should not exceed the repeatability interval for more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the repeatability interval, there is reason to question one or more of the test results. The repeatability interval for this method is as follows:

Bituminous coals	0.05 %
Subbituminous and lignite coals	0.08 %

18.4.2.2 *Reproducibility*—The difference in absolute value between test results obtained in laboratories calculated as the average of determinations on single test specimens of two separate 2.36-mm (No. 8) test units of coal reduced entirely to 250-μm (No. 60) and prepared from the same bulk sample, should not exceed the reproducibility interval for more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the reproducibility interval, there is reason to question one or more of the test results. The reproducibility interval for this test method is as follows:

Bituminous coals	0.09 %
Subbituminous and lignite coals	0.13 %

NOTE 19—Supporting data for 2.36-mm (No. 8) coal has been filed at ASTM Headquarters and may be obtained by requesting RR: D05-1015.

18.5 *Bias*—Bias is eliminated when the instrument is properly calibrated against certified reference standards. Proper calibration includes comparison of instrumental results to certified sulfur values. Results for certified standards above and below anticipated analysis sample results should be within certified precision levels for all standards over the calibration range for the instrument.

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Standard Test Methods for Testing Fiber Ropes[1]

This standard is issued under the fixed designation D 4268; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 These test methods specify procedures to determine diameter and circumference (Section 8), linear density (Section 14), breaking force (Section 21), and elongation (Sections 28 and 36)) of fiber ropes except those ropes incorporating steel wire. (See MIL-STD-191)

1.2 The values stated in SI units are to be regarded as standard. The values provided in parentheses are provided for information purposes only.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Additional precautions for these test methods are given in Section 5.

2. Referenced Documents

2.1 *ASTM Standards:*

D 76 Specification for Tensile Testing Machines for Textiles[2]

D 123 Terminology Relating to Textiles[2]

E 4 Practices for Force Verification of Test Machines[3]

E 74 Practice for Calibration of Force Measuring Instruments for Verifying the Load Indication of Testing Machines[3]

2.2 *Military Standard*[4]*:*

MIL-STD-191

3. Terminology

3.1 *Definitions:*

3.1.1 *braided rope, n*—a cylindrically produced rope made by intertwining, maypole fashion, several to many strands according to a definite pattern with adjacent strands normally containing yarns of the opposite twist.

3.1.2 *cycle length n—in braided rope*, the distance, parallel to the rope axis, of the strand to make one revolution around the rope.

3.1.2.1 *Discussion*—pick count is reported in picks per metre, picks per foot, picks per inch, etc.

3.1.3 *pick count n—in braided rope*, the number of strands rotating in one direction in one cycle length.

3.1.4 *elongation, n*—the ratio of the change in length of a rope during application of tension to the original length of the rope when new.

3.1.4.1 *non-elastic elongation (NE) n—of rope*, elongation after cyclic tensioning the rope to a specified force for a specified number of cycles.

3.1.4.2 *recoverable elongation (CE) n—of rope*, elongation which may be reclaimed following a period of rope relaxation after the rope was cyclic tensioned.

3.1.4.3 *residual elongation (RE) n—of rope*, elongation after cyclic tensioning the rope to a specified force for a specified number of cycles and allowing the rope to relax for a specified period of time.

3.1.4.4 *working elongation (WE) n—of rope*, elongation which is immediately recoverable when tension is removed from the rope.

3.1.4.5 *total elongation (TE) n—of rope*, the entire elongation at any given applied force.

3.1.5 *extension, n*—the ratio of the change in length of a rope during application of tension to the length of the rope immediately before application of that load.

3.1.6 *fiber rope, n*—a rope produced primarily from textile fibers.

3.1.7 *fid, n*—a wooden or hard plastic tapered tool used as an aid in rope splicing.

3.1.7 *hockle, n—in rope*, a strand kink in a rope causing yarn displacement in the strand resulting in rope deformation and damage.

3.1.8 *kink, n—in rope*, an abrupt bend or loop in the rope which is the result of an unbalanced twist relationship in the rope structure.

3.1.9 *plaited rope, n*—rope made from eight strands arranged in four pairs in which one strand is placed adjacent to the second in each pair and in which each strand in each pair has been twisted in one direction while each strand in each alternate pair has been twisted in the opposite direction and the four pairs of strands are intertwined maypole fashion in a manner such that each pair of strands passes over and under adjacent pair of strands (syn. eight strand rope)

3.1.10 *tuck, n—in rope*, a free strand of the rope placed between rope strands during rope splicing.

3.1.11 *reference tension, n*—a low tensile force, generally about 1 % of the rope breaking strength, calculated in accordance with 11.2, and used for initial rope tension determinations.

3.1.12 *rope, n*—a compact and flexible, generally torsionally balanced continuous structure, greater than 4 mm (5/32″) diameter capable of applying or transmitting tension between two points.

3.1.13 *strand, n—in fiber rope*, an ordered assemblage of

[1] These test methods are under the jurisdiction of ASTM Committee D-13 on Textiles and are the direct responsibility of Subcommittee D13.16 on Ropes and Cordage.

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[2] *Annual Book of ASTM Standards*, Vol 07.01.

[3] *Annual Book of ASTM Standards*, Vol 03.01.

[4] Available from Standardization Documents Order Desk, Bldg. 4 Section D, 700 Robbins Ave., Philadelphia, PA 19111-5094, Attn: NPODS.

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textile yarns used to make fiber rope.

3.1.14 *twisted or laid rope, n*—rope made from three or more strands which are twisted or laid together in a twist direction opposite to the twist in the strands.

3.1.15 For definitions of other textile terms used in these test methods, refer to Terminology D 123.

4. Significance and Use

4.1 Test Methods D 4268 for the determination of size, linear density, breaking force, and elongation may be used for acceptance testing of commercial shipments of fiber ropes, but caution is advised since information on between-laboratories precision is not complete.

4.1.1 In case of dispute arising from differences in reported results when using Test Methods D 4268 for acceptance testing of commercial shipments, the purchaser and the supplier should conduct comparative tests to determine if there is a statistical bias between their laboratories. Competent statistical assistance is recommended for the investigation of bias. As a minimum the two parties should take a group of test specimens which are as homogeneous as possible and which are from a lot of material of the type in question. The test specimens should then be randomly assigned in equal numbers to each laboratory for testing. The average test results from the two laboratories should be compared using Student's T-Test for unpaired data with an acceptable probability level chosen by the two parties before the testing is begun. If a bias is estimated, either its cause must be found and corrected or the purchaser and supplier may agree to interpret further results in relation to the observed differences between the average test results.

4.1.2 The final decision to use a specified method for acceptance testing of commercial shipments must be made by the purchaser and the supplier and will depend on considerations other than the precision of the method, including the cost of sampling and testing and the value of the lot of material being tested. For very large ropes, where the cost for testing such ropes may be prohibitive, an extrapolation method for determining the rope characteristics may be a viable alternative when such methods are agreed upon by the purchaser and the supplier.

5. Hazards

5.1 Rope testing for breaking force and elongation can be dangerous and even lethal. It is important that persons witnessing such rope testing, including the testing machine operator, be made aware of the dangers involved and the precautions necessary to avoid injury. The test machine containing the rope specimen should be remote from observers or should be enclosed with an anchored cover or net that will contain the rope after it breaks. Persons witnessing the tests and the machine operator must be either far enough away from the testing machine or be behind barriers that will protect them if the broken rope should snap back and whiplash out of the test machine.

5.2 One can not expect a fiber rope that breaks at a specific force as determined using this test procedure to break at that same force if the rope is subjected to a sudden force such as while arresting a falling mass or if the rope is distorted by a knot, a kink or other such distortion. A knot, kink or other such distortion of the rope structure may reduce the breaking force as much as 60 %.

6. Sampling

6.1 *Lot Sample*—As a lot sample for acceptance testing, take at random the number of spools, reels, coils, or other shipping units directed in an applicable material specification or other agreement between the purchaser and supplier. Consider spools, reels, coils, or other shipping units to be the primary sampling units.

NOTE 1—An adequate specification or other agreement between the purchaser and the supplier requires taking into account the variability between shipping units and between specimens from a single shipping unit so as to provide a sampling plan which, at the specified level of the property of interest, has a meaningful producer's risk, acceptable quality level and limiting quality level.

6.2 *Test Specimens*—Rope specimens for laboratory testing shall be taken from the lot sample units in lengths directed in the sections on procedure for individual properties.

6.2.1 To remove a specimen for testing from a spool or reel, insert a pipe or solid round bar through the center holes of the spool or reel and support the pipe or bar ends so that the spool or reel can rotate as the specimen is pulled off the spool or reel. Do not remove the rope specimen over the spool or reel flange as this will distort the rope construction by adding or removing twist from the rope. If the shipping unit is a coil, remove each rope specimen according to the manufacturer's instructions.

6.2.2 Using a crayon or other suitable marking device, mark a line parallel to the rope axis along the rope specimen surface. The mark can be placed on the rope surface while the rope is on the spool or reel or the marking can be done as the rope is removed from the spool or reel. If the rope is in a coil, the marking should be done as the rope is removed from the coil.

7. Conditioning

7.1 Unless specified, standard conditioning of the rope specimen is not required.

DIAMETER AND CIRCUMFERENCE

8. Scope

8.1 This test method determines the diameter and circumference of fiber rope.

9. Significance and Use

9.1 Rope specifications indicate nominal diameter or nominal circumference or both. The nominal diameter must be known to calculate the Reference Tension to apply to the rope for test purposes. The actual diameter should be determined when the end use of the rope requires that the rope be threaded through sized holes or other sized hardware.

10. Apparatus

10.1 *Tensioning Device*, for applying the reference tension. Use calibrated masses or a calibrated force mechanism.

10.2 *Measuring Material*, for circumference determination shall have zero or very low stretch while under slight tension, such as manila or sisal fibers or 2 mm (1/16 in.) wide strip of kraft paper or bonded paper.

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10.3 *Measuring Devices.*

10.3.1 For circumference determination.

10.3.1.1 A narrow flexible tape having zero to very low stretch, calibrated in 1 m (1/32 in.) increments.

10.3.2 For diameter determination.

10.3.2.1 *A narrow flexible Pi tape*, having zero to very low stretch, calibrated to measure diameter directly when wrapped around a cylinder. The Pi tape should indicate diameter in millimetres (0.01 in.). This tape is called a Pi tape because of its scaling.

10.3.2.2 *Calipers*, calibrated to measure diameter directly in 1 m (0.01 in.) increments. The caliper pressing feet should cover the width of two strands.

11. Procedure

11.1 If the nominal diameter is known, use it to calculate the initial rope tension for determination of linear density and elongation. If the diameter is not known, measure it with calipers or diameter tape while the rope is under zero tension. If circumference is measured, divide the measurement by 3.14 (Pi). Use this result for the nominal diameter and calculate the initial rope tension.

11.2 Calculate the Reference Tensions using eqs 1 & 2:

$$\text{SI Units: Reference Tension} = N = 1.38\ D^2 \quad (1)$$

$$\text{Inch-Pound Units: Reference Tension} = P = 200\ d^2 \quad (2)$$

where:

N = reference tension in newtons,
P = reference tension in pounds,
D = diameter in millimetres, and
d = diameter in inches.

11.3 From the laboratory sample, prepare a test specimen at least 1800 mm (6 ft) long between grips, knots or ends of splices. (See 6.21.)

11.4 Place the rope in the tensioning device with the marked line on the rope (see 6.2.2) parallel with the rope axis.

11.5 Apply the reference tension (see 11.2) to the specimen.

11.6 While the rope is under this tension, measure the diameter or circumference directly using one of the measuring devices specified in 10.3.

11.7 Repeat the measurement as described in 11.3.4 at two more points along the specimen of rope with no two points closer than 300 mm (1 ft) from each other or from the grips, knots or ends of the splice. Average the three determinations.

11.7.1 If calipers are used, the caliper feet should span and contact at least two strand crowns and a moderate compression applied. Secure the caliper feet, remove the caliper and read and record the dimension obtained.

11.7.2 If the flexible tape is used, wrap it around the rope, apply a moderate tension, read the circumference directly and record the result.

11.7.3 If a low stretch measuring material is used, wrap it around the rope and apply a moderate tension, cut or mark the measuring material at a point of overlap, measure the resulting length of the material and record the result as the circumference.

11.7.4 If a direct diameter measuring tape is used, wrap it around the rope and apply a moderate tension. Read the diameter directly from the tape and record the result.

12. Report

12.1 State that the specimens were tested as directed in Test Method D 4268 for Measuring Diameter and Circumference. Identify the rope specimen, the type of measuring devices used and method of sampling used.

12.2 Report the following information:

12.2.1 The average diameter and/or circumference in millimetres or inches, as required by the purchase order or contract.

12.2.2 The purchase order or contract number.

12.2.3 When required the ambient temperature and relative humidity prevalent during the test.

13. Precision and Bias

13.1 *Precision*—The precision of the procedure in Test Methods D 4268 for determining diameter and circumference is being determined and it is anticipated that the interlaboratory testing and statistical analysis will be completed by 1994.

13.2 *Bias*—The value of the diameter or circumference of rope can only be defined in terms of a specified test method. Within this limitation, the procedure in Test Method D 4268 for determining rope diameter and circumference has no known bias.

LINEAR DENSITY

14. Scope

14.1 This test method determines the linear density of fiber rope.

15. Significance and Use

15.1 Fiber ropes are usually specified and evaluated on a linear density and strength basis.

16. Apparatus

16.1 *Tensioning Device*—See 10.1.

16.2 *Weighing Device*—Balance or scale to measure the specimen mass to an accuracy of 0.25 % of its total mass.

16.3 *Measuring Device*—A graduated tape which will measure the required length of rope specimen to the nearest 1 mm (1/32 in.).

17. Procedure

17.1 The test specimen shall be at least 1800 mm (6 ft) between the holding clamps or other means used to terminate the rope, with the rope line parallel to the rope axis (see 6.2.2). Then the specimen shall be tensioned to the Reference Tension of 11.2.

17.2 Measure a minimum of 1500 mm (5 ft) of undisturbed rope in the specimen and mark the length on the rope carefully while the specimen is under the Reference Tension.

17.3 Remove the tension from the rope specimen, wrap adhesive tape tightly around the rope adjacent to the marks to prevent the specimen from unravelling when cut, and then cut the test length at the marks and perpendicular to the rope axis. Remove the tapes used to secure the specimen.

17.4 Weigh the rope specimen on the weighing device.

18. Calculation

18.1 Calculate the linear density of the specimen to the

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nearest 1 % of its specification linear density in kg/100 m (lb/100 ft) using equation 3 or 4:

$$\text{SI Units: } A = K/M \times 100 \quad (3)$$

$$\text{Inch-Pound Units: } B = P/F \times 100 \quad (4)$$

where:

A = linear density in kilograms per 100 metres,
B = linear density in pounds per 100 feet,
K = mass in kilograms,
P = mass in pounds,
M = length in metres, and
F = length in feet.

19. Report

19.1 State that the specimens were tested as directed in ASTM Test Method D 4268 for Determination of Rope Linear Density. Describe the rope tested and the method of sampling used.

19.2 Report the following information:

19.2.1 The linear density in kilograms per 100 metres or pounds per 100 ft as required by the purchase order or contract.

19.2.2 The purchase order or contract number.

19.2.3 When required the ambient temperature and relative humidity prevalent during the test.

20. Precision and Bias

20.1 *Precision*—The precision of the procedure in Test Methods D 4268 for determining linear density of fiber rope is being determined and it is anticipated that the interlaboratory testing and statistical analysis will be completed by 1995.

20.2 *Bias*—The value of linear density of fiber rope can only be defined in terms of a specified test method. Within this limitation, the procedure in Test Method D 4268 for determining rope diameter and circumference has no known bias.

BREAKING FORCE

21. Scope

21.1 This test method determines the breaking force of a fiber rope.

22. Significance and Use

22.1 The breaking force of a rope is a major property to gage its serviceability. When comparing the breaking forces of two or more ropes having the same construction or different constructions, it is important to know their comparative linear densities; for although ropes may appear the same size in diameter or circumference, their linear densities may be different enough to affect their breaking force.

22.2 Published specifications of fiber rope properties usually cover new and unused ropes. Used ropes may be tested using these methods, but test results may be different than published specifications depending on how the rope was used and how long it was used. Most used ropes do suffer a strength loss due to damage from abrasion, cuts, misuse due to mishandling, improper storage or over tensioning. It can be expected that strength loss will occur depending on the severity of the rope use. The degree of rope deterioration may be significant enough to warrant replacing the rope. When in doubt, consult with the manufacturer.

23. Apparatus

23.1 *Tensile Testing Machine* meeting the following requirements:

23.1.1 The rate of travel of the pulling cross head during the breaking force test shall be such that, after precycling the rope as described in 25.4, the rope is loaded to 20 % of its estimated breaking force in not less than 20 sec nor more than 200 sec. The rate of travel of the pulling head may be adjusted during the precycling to achieve this rate.

23.1.2 The stroke and bed length of the testing machine shall be long enough to extend the rope specimen to rupture in one continuous pull without interruption. With prior agreement of the purchaser and supplier, the splice procedure and splice eye size may be modified, if this will allow the test machine to accommodate the prescribed length of rope between splices.

23.1.3 The holding and pulling ends of the testing machine shall have pins or posts whose diameters are no less than one and one half times the diameter of the rope being tested when using eye splice terminations.

23.1.4 The stroke of the testing machine (the total distance the cross head will move) must be long enough to extend the rope specimen to rupture in one continuous pull.

23.1.5 The testing machine shall be equipped with a force indicating device such as a dial, digital read-out, or digital recorder, so that the maximum force required to rupture the specimen will remain on the indicator.

23.1.6 The testing machine shall be calibrated at least once a year. The method of verification and pertinent data should be in accordance with Specification E 4 with force measuring instruments certified in accordance with Practice E 74 and is directly traceable to the National Institute of Standards and Technology.

23.2 *Fids*, of appropriate design and size to aid in eye splicing of the rope specimen.

24. Precautions

24.1 See 1.3, 5.1 and 5.2.

25. Procedure

25.1 The length of undisturbed rope between the splices or other terminations shall be a minimum of 1500 mm (5 ft) for ropes up to 125 mm (5 in.) circumference and a minimum of at least 12 times the rope circumference for larger ropes.

25.1.1 For splicable ropes, the test specimens shall be terminated with splices. For three-strand laid ropes, the minimum number of tucks for each splice shall of four full tucks, one ⅔ tuck and one ⅓ tuck. For eight-strand plaited ropes, the minimum number of tucks for each splice shall consist of two double and two single tucks. For braided ropes and any special rope constructions, consult with the rope manufacturer or the Cordage Institute for the necessary splicing instructions.

NOTE 4—Poor splicing can result in poor test results which do not reflect the actual breaking force of the rope. It is essential that the person or persons preparing the specimen for test be trained properly and be experienced in the art of splicing rope so that the splicing is done properly and with good workmanship.

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25.1.2 The inside length of each eye splice, measured with the insides of the eyes in contact, shall be at least twice the pin diameter around which the eye will be placed on the test machine. The results of a rope break which occurs in the tucked portion of the rope specimen may be disregarded and another rope tested.

25.1.3 If agreed to in advance by the purchaser and supplier, blocks, clamps, grips, or any other suitable means may be used in the above procedure instead of eye splices and pins to hold the test specimen while subjecting the rope to the test break. If a dispute arises concerning the test results using blocks, grips or any other holding mechanism, make the test with eye spliced rope.

25.4 Cycle the rope ten times from the Reference Tension of 11.2 to 20 % of the estimated breaking force. During this precycling, the rate of travel of the testing machine moving cross head may be adjusted to achieve the required rate of travel prescribed in 23.1.1.

25.5 At the beginning of cycling, during the tenth cycle, after the tenth cycle, and after the 30 minute waiting period, carry out the measurements prescribed in Parts 36 through 40.

25.6 Increase the force in the rope from the reference force calculated in 11.2 until it breaks, at the rate of moving cross head travel prescribed in 23.1.1. Record the force at which the rope breaks and the maximum force applied to the rope, if higher than this breaking force.

25.7 Carry out the calculations called for in Section 41.

26. Report

26.1 State that the break test was made as directed in Test Methods D 4268. Describe the rope tested and the method of sampling used.

26.2 Report the following information:

26.2.1 The specific method used for holding the specimen in the testing machine, the type of straining mechanism used and the rate of travel of the cross head.

26.2.2 The purchase order or contract number.

26.2.3 The number of cycles, applied load, elongations and extension called for in Part 42.

26.2.4 The breaking force of the specimen in kilonewtons or pounds force.

26.2.5 The ambient temperature and per cent relative humidity prevalent during testing when required by 7.1.

27. Precision and Bias

27.1 *Precision*—The precision of the procedure in Test Methods D 4268 for determining breaking force is being determined and it is anticipated that the interlaboratory testing and statistical analysis will be completed by 1995.

27.2 *Bias*—The value of the breaking force of fiber rope can only be defined in terms of a specified test method. Within this limitation, the procedure in Test Method D 4268 for determining breaking force is a function of the rate of the force application, condition and size of the holding mechanisms, splicing quality and technique, and other factors.

ELONGATION OF NEW ROPE, INITIAL TENSION APPLICATION

28. Scope

28.1 This method determines the elongation of new fiber rope during the initial application of force.

29. Significance and Use

29.1 Some end uses of fiber rope require information concerning the increase in rope length when initial forces are applied and other end users require information on the potential energy absorption ability of the fiber rope when used the first time. Both requirements can be calculated from a force-extension curve which can be created from information that can be obtained using this test method.

30. Apparatus

30.1 *Tensile Test Machine*—see 23.1.

30.2 *Fids*—see 23.3.

30.3 *Measuring Scale*, accurate to at least 1.0 mm (1/32 in.).

30.4 *Marking Device*—a pen or soft lead pencil that can clearly mark the rope surface.

31. Precaution

31.1 See 1.3, 5.1 and 5.2.

32. Procedure

32.1 Prepare the rope specimen as directed in 25.1.

32.2 If the breaking strength of the rope is not known, for safety sake, a specimen should be tested for breaking force before the elongation measurement is made.

32.3 Place the rope specimen in the testing machine and apply the Reference Tension determined in 11.2.

32.4 While the specimen is under Reference Tension, measure and clearly make two marks around the circumference of the rope beyond the effect of the splices such that the length of rope between the marks is a minimum of 1500 mm (5 ft) for ropes up to 125 mm (5 in.) circumference and a minimum of at least 12 times the rope circumference for larger ropes. This is distance A.

32.5 Apply 75 % of the breaking strength of the rope and remeasure the distance between the marks on the specimen. This is distance B.

33. Calculations

33.1 Calculate the elongation to the nearest 0.1 % using eq 5:

$$\text{Elongation} = 100\,(B - A)/A \qquad (5)$$

where:

A = original distance measured at reference tension, and

B = distance measured at tension equal to 75 % breaking strength.

33.2 If the percentage elongation at the breaking strength or any other lesser applied force is required, measure distance at several applied force levels up to 75 % breaking strength. Plot a force extensive curve accordingly, and then extrapolate the curve to the rope's breaking strength.

NOTE 5—There are other ways of measuring the specimen's elongation during continuous tensioning of the rope and right up to rope rupture using mechanical or electronic devices, such methods are safer and are acceptable as long as all other requirements of this test method are met. When such other methods are used, they must be described fully and be acceptable to both purchaser and supplier.

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34. Report

34.1 Identify the rope specimen, method of sampling used, lot number from which rope was sampled, and purchase or contract number.

34.2 Report the percent elongation at 75 % breaking strength to the nearest 0.1 %, and at other applied forces specified and agreed upon between the purchaser and seller. State that the specimen was tested as directed in ASTM Test Method D 4268, for determining elongation of new rope during its initial tension application.

35. Precision and Bias

35.1 *Precision*—The precision of the procedure in Test Methods D 4268 for determining percentage elongation of a new rope specimen during its initial exposure to tensioning is being established. It is anticipated that the interlaboratory testing and statistical analysis will be completed by 1994.

35.2 *Bias*—The value of elongation of new rope during its initial exposure to tension can only be defined in terms of a specified test method. Within this limitation, the procedure in Test Method D 4268 for determining this type of elongation has no known bias.

ELONGATION AND EXTENSION AFTER CYCLIC TENSIONING TO A SPECIFIED APPLIED FORCE

36. Scope

36.1 This test method determines elongation and extension after cycling fiber rope to any specific applied force.

37. Significance and Use

37.1 This test method provides elongation and extension information which can be used to predict the suitability and serviceability of a fiber rope in an operation requiring the fiber rope to support repeated applied forces on a continuous or intermittent basis.

38. Apparatus

38.1 *Tensile Test Machine*—described in 23.1, except that for the purposes of conducting long cyclic load testing the moving cross head rate of travel may be increased to a rate agreed to by the purchaser and shipper.

38.2 *Fids*—described in 23.2.

38.3 *Measuring Scale*—described in 30.3.

38.4 *Marking Device*—described in 30.4.

39. Precaution

39.1 See 1.3, 5.1 and 5.2.

40. Procedure

40.1 Prepare the specimen as directed in 25.1.

40.2 Place the specimen in the testing machine and apply the Reference Tension determined in 11.2.

40.3 While the specimen is under Reference Tension, make two marks around the circumference of the rope beyond the effect of splices such that the length of rope between the marks is a minimum of 1500 mm (5 ft) for ropes up to 125 mm (5 in.) circumference and a minimum of at least 12 times the rope circumference for larger ropes. This is distance *A*.

40.4 Cycle tension the specimen for the prescribed number of cycles to the prescribed applied force. When conducting this test in conjunction with Breaking Force Testing, that prescribed number of cycles is ten and that prescribed applied force is 20 % of the estimated breaking force. For other testing, the prescribed number of cycles and the applied force shall be as agreed upon by the purchaser and seller. Apply the prescribed number of tensioning cycles continuously.

40.5 Before the last of the prescribed number of cycles, with the rope at the Reference Tension, measure the distance between marks at the prescribed applied force. This is Distance *C*.

40.5 On the last of the prescribed number of cycles, measure the distance between marks at the prescribed applied force. This is Distance *D*.

40.6 When the last prescribed cycle has decreased to the Reference Force, again measure the distance between marks at this Reference Force. This is Distance *E*.

40.7 Immediately after distance E is determined, reduce tension to 0 and leave the rope in a relaxed state (0 tension condition) for 30 plus or minus min. After the relaxation time, reapply the Reference Force and remeasure the distance between the marks. This is distance *F*.

41. Calculation

41.1 Using Equation 6, calculate the non-elastic elongation to the nearest 0.1 %.

$$NE = 100\ (E - A)/A \tag{6}$$

where: NE = nonelastic elongation.

41.2 Using Equation 7, calculate the residual elongation to the nearest 0.1 %.

$$RE = 100 - (F - A)/A \tag{7}$$

where: RE = residual elongation.

41.3 Using equation 8 calculate the recoverable elongation to the nearest 0.1 %.

$$CE = NE - RE \tag{8}$$

where: CE = recoverable elongation.

41.4 Using Equation 9, calculate the total elongation to the nearest 0.1 %.

$$TE = 100\ (D - A)/A \tag{9}$$

where: TE = total elongation.

41.5 Using equation 10 calculate the working elongation to the nearest 0.1 %.

$$WE = TE - WE$$

where: WE = working elongation.

41.6 Using Equation 11 calculate the Extension to the nearest 0.1 %.

$$EX = 100\ (D - C)/C$$

where: EX = extension.

42. Report

42.1 State that the tests for Elongations and Extension after cyclic tensioning were made as directed in Test Methods D 4268.

42.2 Describe the rope specimen tested and method of sampling used.

42.3 Report the number of cycles and the applied force.

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42.4 Report the elongations and the extensions after cyclic tensioning of the rope specimen.

42.5 The purchase order or contract number.

42.5 When required the ambient temperature and relative humidity prevalent during the testing.

43. Precision and Bias

43.1 *Precision*—The precision of the procedure in Test Methods D 4268 for determining elongation and extension after cyclic tensioning of the rope specimen to any specified applied force is being established and it is anticipated that the interlaboratory testing and statistical analysis will be completed by 1994.

43.2 *Bias*—The values of the elongations and extension after cyclic tensioning of the rope specimen to any specified applied force can only be defined in terms of a specified test method. Within this limitation, the procedures in Test Methods D 4268 for determining elongation after cyclic tensioning of the rope specimen at a given applied force has no known bias.

44. Keywords

44.1 breaking force; cyclic tensioning; elongation; extension; fiber rope; linear density; rope

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Standard Test Method for Sulfur in Petroleum and Petroleum Products by Energy-Dispersive X-ray Fluorescence Spectrometry[1]

This standard is issued under the fixed designation D 4294; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the measurement of sulfur in hydrocarbons, such as diesel, naphtha, kerosine, residuals, lubricating base oils, hydraulic oils, jet fuels, crude oils, gasoline (all unleaded), and other distillates. In addition, sulfur in other products, such as M-85 and M-100, may be analyzed using this technique. The applicable concentration range is 0.0150 to 5.00 mass % sulfur.

1.2 The values stated in SI units are to be regarded as the standard. The preferred concentration units are mass % sulfur.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific precautionary statements, see Section 7.

2. Referenced Documents

2.1 *ASTM Standards:*

D 3120 Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry[2]

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products[2]

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products[2]

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications[3]

3. Summary of Test Method

3.1 The sample is placed in the beam emitted from an X-ray source. The resultant excited characteristic *X* radiation is measured, and the accumulated count is compared with counts from previously prepared calibration samples to obtain the sulfur concentration in mass %. Two groups of calibration samples are required to span the concentration range 0.015 to 5 mass % sulfur—0.015 to 0.1 % and 0.1 to 5.0 %.

4. Significance and Use

4.1 This test method provides rapid and precise measurement of total sulfur in petroleum products with a minimum of sample preparation. A typical analysis time is 2 to 4 min per sample.

4.2 The quality of many petroleum products is related to the amount of sulfur present. Knowledge of sulfur concentration is necessary for processing purposes. There are also regulations promulgated in federal, state, and local agencies that restrict the amount of sulfur present in some fuels.

4.3 This test method provides a means of compliance with specifications or limits set by regulations for sulfur content of petroleum products.

4.4 If this test method is applied to petroleum matrices with significantly different composition than the white oil calibration materials specified in this test method, the cautions and recommendations in Section 5 should be observed when interpreting the results.

4.5 Compared to other test methods for sulfur determination, Test Method D 4294 has high throughput, minimal sample preparation, good precision, and is capable of determining sulfur over a wide range of concentrations. The equipment specified is in most cases less costly than that required for alternative methods. Consult the ASTM Subject Index[4] for names of alternative test methods.

5. Interferences

5.1 Spectral interferences result when some sample component element or elements emit X-rays that the detector cannot resolve from sulfur X-ray emission. As a result, the lines produce spectral peaks that overlap with each other. Spectral interferences may arise from samples containing water, lead alkyls, silicon, phosphorus, calcium, potassium, and halides if present at concentrations greater than one tenth of the measured concentration of sulfur, or more than a few hundred milligrams/kilogram. Follow the manufacturer's operating-guide to compensate for the interferences.

5.2 Matrix effects are caused by concentration variations of the elements in a sample. These variations directly influence X-ray absorption and change the measured intensity of each element. For example, performance enhancing additives, such as oxygenates in gasoline, can affect the apparent sulfur

[1] This test method is under the jurisdiction of Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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[2] *Annual Book of ASTM Standards*, Vol 05.02

[3] *Annual Book of ASTM Standards*, Vol 14.02

[4] *Annual Book of ASTM Standards*, Vol 00.01.

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reading. These types of interferences are always present in X-ray fluorescence analysis and are completely unrelated to spectral interferences.

5.3 Both types of interferences are compensated for in contemporary instruments with the use of built-in software. It is recommended that these interferences be checked from time to time and that the software corrections offered by the manufacturer not be accepted at face value. Corrections should be verified for new formulations.

5.4 M-85 and M-100 are fuels containing 85 and 100 % methanol, respectively. As such, they have a high oxygen content, hence, absorption of sulfur Kα radiation. Such fuels can, however, be analyzed using this test method provided that the calibration standards are prepared to match the matrix of the sample. There may be a loss of sensitivity and precision. The repeatability, reproducibility, and bias obtained in this test method did not include M-85 and M-100 samples.

5.5 In general, petroleum materials with compositions that vary from white oils as specified in 9.1 may be analyzed with standards made from base materials that are of the same, or similar, composition. Thus, a gasoline may be simulated by mixing *iso*octane and toluene in a ratio that approximates the true aromatic content of the samples to be analyzed. Standards made from this simulated gasoline will produce results that are more accurate than results obtained using white oils.

NOTE 1—In the case of petroleum materials that contain suspended water, it is recommended that the water be removed before testing or that the sample be thoroughly homogenized and immediately tested. The interference is greatest if the water creates a layer over the transparent film as it will attenuate the X-ray intensity for sulfur. One such method to accomplish the removal of water is to centrifuge the sample first under ambient sealed conditions, taking care that the sample integrity is not compromised.

6. Apparatus

6.1 *Energy-dispersive X-ray Fluorescence Analyzer*—Any energy dispersive X-ray fluorescence analyzer may be used if its design incorporates, as a minimum, the following features:

6.1.1 *Source of X-ray Excitation*, X-ray source with energy above 2.5 keV

NOTE 2—**Precaution:** In addition to other precautions, if a radioactive source is used, it must be well shielded to international standard requirements and, therefore, not present any safety hazard. However, attention to the source is only to be carried out by a fully trained and competent person using the correct shielding techniques.

NOTE 3—Operation of analyzers using X-ray tube sources is to be conducted in accordance with the manufacturer's safety instructions and local regulations.

6.1.2 *Sample Cell*, providing a sample depth of at least 4 mm and equipped with a replaceable X-ray transparent plastic film window.

6.1.3 *X-ray Detector*, with sensitivity at 2.3 keV and a resolution value not to exceed 800 eV. A gas filled proportional counter has been found to be suitable to use.

6.1.4 *Filters*, or other means of discriminating between sulfur Kα radiation and other X-rays of higher energy.

6.1.5 Signal conditioning and data handling electronics that include the functions of X-ray intensity counting, a minimum of two energy regions (to correct for background X-rays), spectral overlap corrections, and conversion of sulfur X-ray intensity into percent sulfur concentration.

6.1.6 *Display or Printer*, that reads out in mass % sulfur.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[5] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Di-n-Butyl Sulfide (DBS)*, a high purity standard with a certified analysis for sulfur content. Use the certified sulfur content when calculating the exact concentrations of the calibration standards (9.1.7).

NOTE 4—**Warning:** Di-*n*-butyl sulfide is flammable and toxic.

NOTE 5—It is essential to know the concentration of the sulfur in the di-*n*-butyl sulfide, not the purity, since impurities may also be sulfur containing compounds.

7.3 *Mineral Oil, White (MOW)*, ACS reagent grade or less than 2 mg/kg sulfur.

7.4 *X-ray Transparent Film*, any film that resists attack by the sample, is free of sulfur, and is sufficiently X-ray transparent may be used. Films found to be suitable are polyester, polypropylene, polycarbonate, and polyimide films.

7.4.1 Samples of high aromatic content may dissolve polyester and polycarbonate films. In these cases, other materials besides these films may be used for X-ray windows, provided that they do not contain any elemental impurities. An optional window material is polyimide foil. Although polyimide foil absorbs sulfur X-rays more than other films, it may be a preferred window material as it is much more resistant to chemical attack by aromatics and exhibits higher mechanical strength.

7.5 *Sample Cells*, resistant to sample attack and meet geometry requirements of spectrometer.

8. Sampling and Specimen Preparation

8.1 Samples shall be taken in accordance with the instructions in Practice D 4057 or D 4177, where appropriate. Samples should be analyzed immediately after pouring into a sample cell and allowing for the escape of the air bubbles caused by mixing.

8.2 If using reusable sample cells, clean and dry cells before use. Disposable sample cells are not to be reused. A new piece of X-ray film on a reused sample cell is required prior to analyzing the sample. Avoid touching the inside of the sample cell or portion of the window film in the cell or in the instrument window that is exposed to X-rays. Oil from fingerprints can affect the reading when analyzing for low

[5] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "*Analar Standards for Laboratory* U.K., Chemicals," BDH Ltd., Poole, Dorset, and the *United States Pharmacopeia, and National Formulary*, U.S. Pharmacopeial Convention, Inc., (USPC), Rockville, MD.

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levels of sulfur. Wrinkles in the film will affect the intensity of sulfur X-rays transmitted. Therefore, it is essential that the film be taut and clean to ensure reliable results. The analyzer will need recalibration if the type or thickness of the window film is changed.

8.3 Impurities or thickness variations, which may affect the measurement of low levels of sulfur, have been found in polyester films and may vary from lot to lot. Therefore, the calibration shall be verified after starting each new roll of film.

9. Calibration and Standardization

9.1 *Preparation of Calibration Standards*:

9.1.1 Although it is possible to make a single calibration to measure sulfur in a variety of matrices, it is strongly recommended that, whenever possible, the calibration is matrix specific, that is, a diesel calibration should be based on diesel standards. This is especially true for the analysis of sulfur at low levels. Hence, the matrix diluent should be as close to the form of the matrix being analyzed as possible. White mineral oil (see 7.3) is acceptable as an alternative matrix diluent.

9.1.2 Make primary standards independently at 0.1 and 5 mass % sulfur and not by serial dilution from a single concentrate. The exact sulfur content in each standard is to be calculated to four decimal places.

9.1.3 Accurately weigh the nominal quantity of matrix diluent to the nearest 0.1 mg, as shown in Table 1, into a suitable, narrow-necked container and then accurately weigh in the nominal quantity of di-*n*-butyl sulfide. Mix thoroughly (a PTFE-coated magnetic stirrer is advisable) at room temperature.

9.1.4 Prepare calibration standards with the nominal concentration ranges identified in Table 2 for the two ranges by diluting each primary standard with the applicable matrix diluent.

9.1.5 Alternatively, National Institute of Standards and Technology (NIST) traceable certified standards, prepared as described above or composed of the matrix to be analyzed, can be used.

9.1.6 If the matrix diluent being used for the preparation of standards contains sulfur, add this value to the calculated sulfur content of the prepared standards (consult your supplier for a certified sulfur concentration or test the mineral oil using Test Method D 3120 or any other equivalent low level sulfur analyzing method with an MDL no higher than 1 ppm).

9.1.7 Weigh the DBS and matrix diluent to the recommended mass to the nearest 0.1 mg. It is important that the actual mass is known; thus, the actual concentration of the prepared standards is calculated and entered into the instrument for calibration purposes. The concentration of sulfur can be calculated using the following equation:

$$S=[DBS \times S_{DBS})+(MO \times S_{MO})]/(DBS + MO) \quad (1)$$

TABLE 1 Composition of Primary Standards

Sulfur Content, mass %	Mass of Matrix Diluent, g	Mass of Di-*n*-Butyl Sulfide, g
5.0	48.6	14.4
0.10	43.6	0.200

TABLE 2 Calibration Standards

Range	1	2
Sulfur mass %	0.0020 - 0.1	0.1 - 5.0
Std 1	0.0000	0.00
Std 2	0.0020	0.10
Std 3	0.0050	0.50
Std 4	0.0100	1.00
Std 5	0.0300	2.50
Std 6	0.0600	5.00
Std 7	0.1000	

where

S = mass % sulfur of the prepared standards,
DBS = actual mass of DBS, g,
S_{DBS} = the mass % sulfur in DBS, typically 21.91 %,
MO = actual mass of mineral oil, g,
S_{MO} = mass % sulfur in the mineral oil.

9.2 *Certified Calibration Standards*—Calibration standards, which are certified by a national standards organization, may be used in place of some or all of the standards prescribed in 9.1 when of similar matrix to the sample of interest. Such standards include Standard Reference Materials (SRM) prepared and certified by the National Institute of Standards and Technology (NIST), that is, SRM 2724 for sulfur in diesel. The standards used must cover the nominal concentrations ranges identified in Table 2.

9.3 *Calibration Check Standards*—Several additional standards (calibration check standards) that were not used in generating the calibration curve can be used to check the validity of the calibration. Calibration check standards may be independently prepared according to 9.1, or certified standards according to 9.2. The concentration of the calibration check standards shall be near the expected concentration of the samples being analyzed.

9.4 *Quality Control Samples*—Stable petroleum or product samples (that is, quality control samples) representative of the samples of interest may be run on a regular basis to verify that the system is in statistical control (see Section 14).

9.5 *Storage of Standards and Quality Control Samples*—Store all standards in glass bottles, either dark or wrapped in opaque material, closed with glass stoppers, inert plastic lined screw caps, or other equally inert, impermeable closures, in a cool, dark place until required. As soon as any sediment or change of concentration is observed, discard the standard.

10. Preparation of Apparatus

10.1 Set up the apparatus in accordance with the manufacturer's instructions. Whenever possible, the instrument should remain energized to maintain optimum stability.

11. Procedure

11.1 Although X-radiation penetrates only a short distance into the sample, scatter from the sample cell and the sample may vary. Consequently, the analyst must ensure that the sample cell is filled with sample above a minimum depth, at which point, further filling causes an insignificant change in the counting rate. Generally speaking, filling the sample cup to at least three-fourths the capacity of the sample cell will be sufficient. Prepare the sample cell by providing adequate head

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space. Provide a vent hole in the top to prevent bowing of the X-ray film during measurement of volatile samples.

NOTE 6—**Warning:** Avoid spilling flammable liquids inside the analyzer

11.2 *Instrument Calibration*—Calibrate the instrument for the appropriate range as listed in Table 2, following manufacturer's instructions. Typically, the calibration procedure involves setting up the instrument for recording of net sulfur X-ray intensity, followed by the measurement of known standards. Obtain two readings on the standard using the recommended counting time for the instrument according to Table 3. With minimal delay, repeat the procedure using freshly prepared cells and fresh portions of the standard. Once all the standards have been analyzed, follow the manufacturer's instructions for generating the optimum calibration curve based on the net sulfur counts for each standard that has been analyzed four times. Immediately upon completion of the calibration, determine the sulfur concentration of one or more of the calibration check samples (see 9.3). The measured values should be within 3 % relative of the certified values. If this is not the case, the calibration or calibration standards are suspect and corrective measures should be taken and the calibration rerun. The degree of matrix mismatch between samples and standards should also be considered when evaluating a calibration.

11.3 *Analysis of Unknown Samples*—Fill the cell with the sample to be measured as described in 11.1. Before filling the cell, it may be necessary to heat viscous samples so that they are easy to pour into the cell. Ensure that no air bubbles are present between the cell window and the liquid sample. Measure each sample (see Table 3 for the recommended counting times for the specific concentration ranges). With minimal delay, repeat the measurement using a freshly prepared cell and a fresh portion of the sample. Obtain the average of the two readings for the sulfur content in the unknown sample. If the average reading is not within the concentration range for that calibration, repeat the sample measurement in duplicate using the range that brackets the sample average determined.

12. Calculation

12.1 The concentration of sulfur in the sample is automatically calculated from the calibration curve.

13. Report

13.1 Report the result as the total sulfur content, mass %, rounding to three significant figures using Practice E 29, and state that the results were obtained according to Test Method D 4294.

14. Quality Control

14.1 The use of quality control programs, such as the one described in 14.1.1, can assist in maintaining statistical control of this test method.

TABLE 3 Counting Times For Sulfur Content Analysis

Sulfur Content Range, % mass	Counting Time, s
0.0000 to 0.1000	200 to 300
0.1000 to 5.0	100

NOTE 7—Verification of system control through the use of QC samples and control is highly recommended. It is recognized that QC procedures are the province of the individual laboratory.

14.1.1 For the purpose of establishing the statistical control status of the testing process since the last valid calibration, quality control samples prepared from material(s) selected and stored according to 9.3 and 9.4 are to be regularly tested as if they were unknown production samples. Results are recorded and immediately analyzed by control charts[6] or other statistically equivalent techniques to ascertain the statistical control status of the total testing process. Any out of control data shall trigger investigation for root cause(s). The outcome of the investigation may result in instrument recalibration. Depending on the criticality of the quality being measured and the demonstrated stability of the testing process, the frequency of quality control sample testing can range from once each day the test apparatus is in use to twice per week. It is recommended that at least one type of quality control sample be analyzed that is representative of samples routinely analyzed (as in 9.3.1).

15. Precision and Bias [7]

15.1 *Precision*—The precision of this test method as obtained by statistical analysis of interlaboratory test results is as follows:

15.1.1 *Repeatability*—The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

$$0.02894(X + 0.1691) \quad (2)$$

where X is the sulfur concentration in mass %.

15.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, exceed the following values only in one case in twenty:

$$0.1215\ (X + 0.05555) \quad (3)$$

where X is the sulfur concentration in mass %.

15.2 *Bias*—The interlaboratory study included eight NIST reference materials. The certified values and bias are given in Table 4.

[6] ASTM MNL 7, *Manual on Presentation of Data and Control Chart Analysis*, Section 3, Control Charts for Individuals.

[7] Supporting data are available from ASTM Headquarters. Request RR:D02-1418.

TABLE 4 Bias

NIST Standard	Sulfur mass %	Bias	Significant
SRM 1616a	0.0146	0.0009	No
SRM 2724a	0.0430	0.0008	No
SRM 1617a	0.173	0.0003	No
SRM 1623c	0.381	-0.0119	Yes
SRM 1621e	0.948	-0.0198	No
SRM 2717	3.02	0.0072	No

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16. Keywords

16.1 analysis; energy dispersive; petroleum; spectrometry; sulfur, X-ray

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CERTIFICATE

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Standard Practice for Fluorescent UV Exposure of Plastics[1]

This standard is issued under the fixed designation D 4329; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope *

1.1 This practice covers specific procedures and test conditions that are applicable for fluorescent UV exposure of plastics conducted in accordance with Practices G 151 and G 154. This practice also covers the preparation of test specimens, the test conditions best suited for plastics, and the evaluation of test results.

NOTE 1—Previous versions of this practice referenced fluorescent UV devices described by Practice G 53, which described very specific equipment designs. Practice G 53 is being replaced by Practice G 151, which describes performance criteria for all exposure devices that use laboratory light sources and by Practice G 154, which gives requirements for exposing nonmetallic materials in fluorescent UV devices. Practice G 53 will be balloted for withdrawl before December 2000.

1.2 The values stated in SI units are be regarded as standard. The values given in parentheses are for information only.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

NOTE 2—This practice is technically equivalent to ISO 4892-3.

2. Referenced Documents

2.1 *ASTM Standards:*

D 3980 Practice for Interlaboratory Testing of Paint and Related Materials[2]

D 5870 Practice for Calculating Property Retention Index of Plastics[3]

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[4]

G 53 Practice for Operating Light- and Water-Exposure Apparatus (Fluorescent UV-Condensation Type) for Exposure of Nonmetallic Materials[4]

G 113 Terminology Relating to Natural and Artificial Weathering Tests of Nonmetallic Materials[4]

G 141 Guide for Addressing Variability in Exposure Testing on Nonmetallic Materials[4]

G 147 Practice for Conditioning and Handling of Nonmetallic Materials for Natural and Artificial Weathering Tests[4]

G 151 Practice for Exposing Nonmetallic Materials in Accelerated Test Devices That Use Laboratory Light Sources[4]

G 154 Practice for Operating Fluorescent Light Apparatus for UV Exposure of Nonmetallic Materials[4]

2.2 *ISO Standard:*[5]

ISO 4892-3 Plastics—Methods of Exposure to Laboratory Light Sources — Part 3, Fluorescent UV Lamps

3. Terminology

3.1 The definitions in Terminology G 113 are applicable to this practice.

4. Significance and Use

4.1 The ability of a plastic material to resist deterioration of its electrical, mechanical, and optical properties caused by exposure to light, heat, and water can be very significant for many applications. This practice is intended to induce property changes associated with end-use conditions, including the effects of sunlight, moisture, and heat. The exposure used in this practice is not intended to simulate the deterioration caused by localized weather phenomena, such as, atmospheric pollution, biological attack, and saltwater exposure.

4.2 **Caution**—Variation in results may be expected when operating conditions are varied within the accepted limits of this practice. Therefore, no reference to the use of this practice should be made unless accompanied by a report prepared in accordance with Section 8 that describes the specific operating conditions used. Refer to Practice G 151 for detailed information on the caveats applicable to use of results obtained in accordance with this practice.

NOTE 3—Additional information on sources of variability and on strategies for addressing variability in the design, execution, and data analysis of laboratory-accelerated exposure tests is found in Guide G 141.

4.3 Reproducibility of test results between laboratories has been shown to be good when the stability of materials is

[1] This practice is under the jurisdiction of ASTM Committee D-20 on Plastics and is the direct responsibility of Subcommittee D20.50 on Permanence Properties.
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[2] *Annual Book of ASTM Standards*, Vol 06.01.

[3] *Annual Book of ASTM Standards*, Vol 08.03.

[4] *Annual Book of ASTM Standards*, Vol 14.02.

[5] Available from American National Standards Institute, 11 W. 42nd St., 13th Floor, New York, NY 10036.

***A Summary of Changes section appears at the end of this standard.**

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evaluated in terms of performance ranking compared to other materials or to a control.[6,7] Therefore, exposure of a similar material of known performance (a control) at the same time as the test materials is strongly recommended. It is recommended that at least three replicates of each material be exposed to allow for statistical evaluation of results.

4.4 Test results will depend upon the care that is taken to operate the equipment in accordance with Practice G 154. Significant factors include regulation of line voltage, temperature of the room in which the device operates, temperature control, and condition and age of the lamp.

5. Apparatus

5.1 Use of fluorescent UV apparatus that conforms to the requirements defined in Practices G 151 and G 154 is required to conform to this practice.

5.2 Unless otherwise specified, the spectral power distribution of the fluorescent UV lamp shall conform to the requirements in Practice G 154 for a UVA 340 lamp.

5.3 *Test Chamber Location:*

5.3.1 Locate the apparatus in an area maintained between 18 and 27°C (65 and 80°F). Measure ambient temperature at a maximum distance of 150 mm (6 in.) from the plane door of the apparatus. Control of ambient temperature is particularly critical when one apparatus is stacked above another, because the heat generated from the lower unit can interfere with the operation of the units above.

5.3.2 Place the apparatus at least 300 mm from walls or other apparatus. Do not place the apparatus near a heat source such as an oven.

5.3.3 Ventilate the room in which the apparatus is located to remove heat and moisture.

6. Test Specimen

6.1 The size and shape of specimens to be exposed will be determined by the specifications of the particular test method used to evaluate the effects of the exposure on the specimens; the test method shall be determined by the parties concerned. Where practical, it is recommended that specimens be sized to fit specimen holders and racks supplied with the exposure apparatus. Unless supplied with a specific backing as an integral part of the test, specimens shall be mounted so that only the minimum specimen area required for support by the holder shall be covered. This unexposed surface must not be used as part of the test area.

6.2 For specimens of insulating materials, such as foams, maximum specimen thickness is 20 mm in order to allow for adequate heat transfer for condensation.

6.3 To provide rigidity, attach flexible specimens to a backing panel made of aluminum, 0.635 mm (0.025 in.) thick. Suggested aluminum alloys are 5052, 6061, or 3003.

6.4 Seal any holes in specimens larger than 2 mm and any openings larger than 1 mm around irregularly shaped specimens to prevent loss of water vapor. Attach porous specimens to a solid backing such as aluminum that can act as a vapor barrier.

6.5 Unless otherwise specified, expose at least three replicate specimens of each test and control material.

6.6 Follow the procedures described in Practice G 147 for identification, conditioning, and handling of specimens of test, control, and reference materials prior to, during, and after exposure.

6.7 Do not mask the face of a specimen for the purpose of showing on one panel the effects of various exposure times. Misleading results may be obtained by this method, since the masked portion of the specimen is still exposed to temperature and humidity cycles that in many cases will affect results.

6.8 Since the thickness of a specimen may markedly affect the results, thickness of test and control specimens shall be within ±10 % of the nominal dimensions.

NOTE 4—This is especially important when mechanical properties are being investigated.

6.9 Incident energy at the extremes of the specimen exposure area in older equipment may be only 70 % of that at the center. If the irradiance at any position within the exposure area is less than 90 % of the peak irradiance, follow one of the procedures outlined in Practice G 154 to ensure either equal radiant exposure or compensation for differences in radiant exposure.

6.10 Retain a supply of unexposed file specimens of all materials evaluated.

6.10.1 When destructive tests are run, ensure that sufficient file specimens are retained so that the property of interest can be determined on unexposed file specimens each time exposed materials are evaluated.

6.11 Specimens should not be removed from the exposure apparatus for more than 24 h and then returned for additional tests, since this does not produce the same results on all materials as tests run without this type of interruption. When specimens are removed from the exposure apparatus for 24 h or more and then returned for additional exposure, report the elapsed time as noted in accordance with Section 9.

NOTE 5—Since the stability of the file specimen may also be time-dependent, users are cautioned that over prolonged exposure periods, or where small differences in the order of acceptable limits are anticipated, comparison of exposed specimens with the file specimen may not be valid. Instrumental measurements are recommended whenever possible.

7. Procedure

7.1 When the test and control specimens do not completely fill the specimen racks, fill all empty spaces with blank panels to maintain the test conditions within the chamber.

7.2 Unless otherwise specified, program the device to one of the following test cycles. Operate the device continuously.

7.2.1 *Cycle A:*

8 h UV with uninsulated black panel temperature controlled at 60 ± 3°C
4 h condensation with uninsulated black panel temperature controlled at 60± 3°C
(Used for most general applications)

[6] Fischer, R., "Results of Round Robin Studies of Light- and Water-Exposure Standard Practices," *Accelerated and Outdoor Durability Testing of Organic Materials, ASTM STP 1202*, Warren D. Ketola and Douglas Grossman, eds., American Society for Testing and Materials, Philadelphia, 1993.

[7] Ketola, W., and Fischer, R., "Characterization and Use of Reference Materials in Accelerated Durability Tests," *VAMAS Technical Report No. 30*, available from NIST, Gaithersburg, MD.

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7.2.2 *Cycle B:*

8 h UV with uninsulated black panel temperature controlled at 70 ± 3°C
4 h condensation with uninsulated black panel temperature controlled at 50± 3°C
(Typically used for automotive applications)

7.2.3 *Cycle C:*

8 h UV with uninsulated black panel temperature controlled at 50 ± 3°C
4 h condensation with uninsulated black panel temperature controlled at 50± 3°C
(Typically used for plastic building products)

7.3 Practice G 154 lists several other exposure cycles that are used for fluorescent UV exposures of nonmetallic materials. Obtain mutual agreement between all concerned parties for the specific exposure cycle used.

7.4 In order to minimize any effects from temperature or UV light variation, reposition the specimens as follows. Fig. 1 shows a diagram of the specimen repositioning.

7.4.1 Reposition the specimens horizontally once per week by (*1*) moving the two extreme right-hand holders to the far left of the exposure area, and (*2*) sliding the remaining holders to the right.

7.4.2 Reposition the specimens vertically so that each specimen spends the same amount of exposure time in each vertical position within the specimen holder. For instance, if two specimens are stacked vertically in each holder, then the top and bottom specimens should switch places halfway through the test. If four specimens are stacked vertically, then the specimens should be repositioned vertically three times during the test.

7.5 *Water Purity*—The purity of water used for specimen spray is very important. Follow the purity requirements in Practice G 151 for water sprayed on specimen surfaces. It is recommended that deionized water be used for water used to produce condensation.

7.6 It is recommended that a control material be exposed at the same time as the test specimens for comparison purposes, if performance comparisons are not being made between the test materials themselves. All concerned parties must agree on the control material used.

7.6.1 Identification of any control specimen used shall accompany the report.

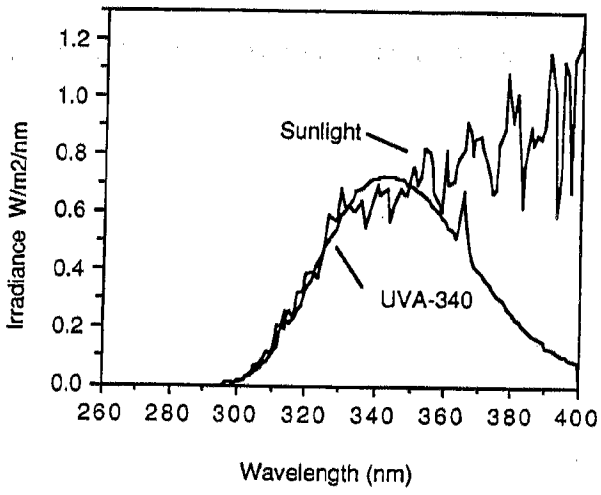


FIG. 1 Representative Spectral Power Distribution of UVA-340 Fluorescent Lamps

8. Periods of Exposure and Evaluation of Test Results

8.1 In most cases, periodic evaluation of test and control materials is necessary to determine the variation in magnitude and direction of property change as a function of exposure time or radiant exposure.

8.2 The time or radiant exposure necessary to produce a defined change in a material property can be used to evaluate or rank the stability of materials. This method is preferred over evaluating materials after an arbitrary exposure time or radiant exposure.

8.2.1 Exposure to an arbitrary time or radiant exposure may be used for the purpose of a specific test if agreed upon between the parties concerned or if required for conformance to a particular specification. When a single exposure period is used, select a time or radiant exposure that will produce the largest performance differences between the test materials or between the test material and the control material.

8.2.2 The minimum exposure time used shall be that necessary to produce a substantial change in the property of interest for the least stable material being evaluated. An exposure time that produces a significant change in one type of material cannot be assumed to be applicable to other types of materials.

8.2.3 The relation between time to failure in an exposure conducted in accordance with this practice and service life in an outdoor environment requires determination of a valid acceleration factor. Do not use arbitrary acceleration factors relating time in an exposure conducted in accordance with this practice and time in an outdoor environment because they can give erroneous information. The acceleration factor is material-dependent and is only valid if it is based on data from a sufficient number of separate exterior and laboratory-accelerated exposures so that results used to relate times to failure in each exposure can be analyzed using statistical methods.

NOTE 6—An example of a statistical analysis using multiple-laboratory and exterior exposures to calculate an acceleration factor is described by Simms.[8] See Practice G 151 for more information and additional cautions about the use of acceleration factors.

8.3 After each exposure increment, evaluate or rate changes in exposed test specimens in accordance with applicable ASTM test methods.

NOTE 7—For some materials, changes may continue after the specimen has been removed from the exposure apparatus. Measurements (visual or instrumental) should be made within a standardized time period or as agreed upon between the interested parties. The standardized time period needs to consider conditioning prior to testing.

8.4 Use of results from exposures conducted in accordance with this practice in specifications:

8.4.1 If a standard or specification for general use requires a definite property level after a specific time or radiant exposure

[8] Simms, J.A., *Journal of Coatings Technology*, Vol 50, 1987, pp. 45–53.

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in an exposure test conducted in accordance with this practice, base the specified property level on results from round-robin experiments run to determine the test reproducibility from the exposure and property measurement procedures. Conduct these round robins in accordance with Practice E 691 or Practice D 3980 and include a statistically representative sample of all laboratories or organizations who would normally conduct the exposure and property measurement.

8.4.2 If a standard or specification for use between two or three parties requires a definite property level after a specific time or radiant exposure in an exposure test conducted in accordance with this practice, base the specified property level on two independent experiments run in each laboratory to determine the reproducibility for the exposure and property measurement process. The reproducibility of the exposure/property measurement process is then used to determine the minimum level of property after the exposure that is mutually agreeable to all parties.

8.4.3 When reproducibility in results from an exposure test conducted in accordance with this practice has not been established through round-robin testing, specify performance requirements for materials in terms of comparison (ranked) to a control material. All specimens shall be exposed simultaneously in the same device. All concerned parties must agree on the specific control material used.

8.4.3.1 Conduct analysis of variance to determine whether any differences between test materials and control materials is statistically significant. Expose replicates of the test specimen and the control specimen so that statistically significant performance differences can be determined

NOTE 8—Fischer illustrates use of rank comparison between test and control materials in specifications.[9]

NOTE 9—The ASTM Committee G-3 on Weathering and Durability is developing a Standard Guide for Application of Basic Statistical Methods to Weathering Tests, which will include examples showing use of analysis of variance to compare materials.

9. Report

9.1 Report the following information:

9.1.1 Type and model of exposure device.

9.1.2 Age of fluorescent lamps used at the start of the exposure, and whether any lamps were changed during the period of exposure.

9.1.3 If required, irradiance in $Wm^{-2} \cdot nm^{-1}$, or radiant exposure in Jm^{-2} at the sample plane, and the wavelength region in which the measurements were made.

9.1.3.1 Do not report irradiance or radiant exposure unless direct measurement of irradiance was made during the exposure.

9.1.4 Elapsed exposure time.

9.1.5 Light- and dark-water condensation or humidity cycle employed.

9.1.6 Operating black panel temperature.

9.1.7 If required, operating relative humidity.

9.1.8 Type of spray nozzle, if used.

9.1.8.1 If used, total solids and silica level of water used for specimen spray (if above limits specified in Practice G 151).

9.1.9 Specimen repositioning procedure, if different from the procedure described in 7.4.

9.1.10 Results of property tests. Calculate retention of characteristic property in accordance with Practice D 5870 when it is reported.

10. Precision and Bias

10.1 *Precision*—The repeatability and reproducibility of results obtained in exposures conducted in accordance with this practice will vary with the materials being tested, the material property being measured, and the specific test conditions and cycles that are used. It is essential to determine reproducibility of the exposure/property measurement process when using the results from exposures conducted in accordance with this practice in product specifications.

10.2 *Bias*—Bias cannot be determined because no acceptable standard weathering reference materials are available.

11. Keywords

11.1 degradation; exposure; fluorescent UV; light exposure; ultraviolet

[9] Fischer, R., Ketola, W., "Impact of Research on Development of ASTM Durability Testing Standards," *Durability Testing of Non-Metallic Materials, ASTM STP 1294*, Robert Herling, ed., American Society for Testing and Materials, Philadelphia, 1995.

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SUMMARY OF CHANGES

This section identifies the location of selected changes to this practice. For the convenience of the user, Committee D–20 has highlighted those changes that may impact the use of this practice. This section may also include descriptions of the changes or reasons for the changes, or both.

D 4329 – 99:

(*1*) Title changed.

(*2*) Referenced new ASTM performance standard for fluorescent UV exposure tests.

(*3*) Added specific procedures for conditioning and handling during the exposure test.

(*4*) Revised section covering evaluation of results.

(*5*) De-emphasized use of a single required exposure time.

The American Society for Testing and Materials takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 100 Barr Harbor Drive, West Conshohocken, PA 19428.

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CERTIFICATE

By Authority Of
THE UNITED STATES OF AMERICA
Legally Binding Document

By the Authority Vested By Part 5 of the United States Code § 552(a) and Part 1 of the Code of Regulations § 51 the attached document has been duly INCORPORATED BY REFERENCE and shall be considered legally binding upon all citizens and residents of the United States of America. *HEED THIS NOTICE*: Criminal penalties may apply for noncompliance.

Document Name: ASTM D4809: Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter (Precision Method)

CFR Section(s): 40 CFR 61.245(e)(3)

Standards Body: American Society for Testing and Materials

APPROVED

Official Incorporator:

THE EXECUTIVE DIRECTOR
OFFICE OF THE FEDERAL REGISTER
WASHINGTON, D.C.

Designation: D 4809 – 95

An American National Standard

Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter (Precision Method)[1]

This standard is issued under the fixed designation D 4809; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of the heat of combustion of hydrocarbon fuels. It is designed specifically for use with aviation turbine fuels when the permissible difference between duplicate determinations is of the order of 0.2 %. It can be used for a wide range of volatile and nonvolatile materials where slightly greater differences in precision can be tolerated.

1.2 In order to attain this precision, strict adherence to all details of the procedure is essential since the error contributed by each individual measurement that affects the precision shall be kept below 0.04 %, insofar as possible.

1.3 Under normal conditions, the method is directly applicable to such fuels as gasolines, kerosines, Nos. 1 and 2 fuel oil, Nos. 1-D and 2-D diesel fuel and Nos. 0-CT, 1-CT, and 2-CT gas turbine fuels.

1.4 Through the improvement of the calorimeter controls and temperature measurements, the precision is improved over that of Test Method D 240.

1.5 The values stated in SI units are to be regarded as the standard.

1.6 *This standard does not purport to address the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see 7.6, 7.8, Notes 3, 4, 5 and 11, 10.6, Note A1.1 and Annex A3.

2. Referenced Documents

2.1 *ASTM Standards:*

D 129 Test Method for Sulfur in Petroleum Products (General Bomb Method)[2]

D 240 Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter[2]

D 1018 Test Method for Hydrogen in Petroleum Fractions[2]

D 1193 Specification for Reagent Water[3]

D 1266 Test Method for Sulfur in Petroleum Products (Lamp Method)[2]

D 2622 Test Method for Sulfur in Petroleum Products by X-Ray Spectrometry[4]

D 3120 Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry[4]

D 3701 Test Method for Hydrogen Content of Aviation Fuels by Low Resolution Nuclear Magnetic Resonance Spectrometry[4]

E 1 Specification for ASTM Thermometers[5]

E 144 Practice for Safe Use of Oxygen Combustion Bombs[6]

E 200 Practice for Preparation, Standardization, and Storage of Standard Solutions for Chemical Analysis[7]

3. Terminology

3.1 *Definitions:*

3.1.1 *gross heat of combustion*—expressed as megajoules per kilogram. The gross heat of combustion at constant volume of a liquid or solid fuel containing only the elements carbon, hydrogen, oxygen, nitrogen, and sulfur is the quantity of heat liberated when a unit mass of the fuel is burned in oxygen in an enclosure of constant volume, the products of combustion being gaseous carbon dioxide, nitrogen, sulfur dioxide, and liquid water, with the initial temperature of the fuel and the oxygen and the final temperature of the products at 25°C. Gross heat of combustion (see Note 1) is represented by the symbol Q_g.

NOTE 1—Users of this test method desiring to calculate $\Delta H°$ for a pure compound should note that corrections must be applied to the value of Q_g for buoyancy of air, heat capacities of reaction components, reduction to a constant-pressure process, and deviations of the reaction from the thermodynamic standard state. In any comparison of measurements on pure compounds with those cited in these compilations, the user of this test method should realize that impurities of various kinds, including water and foreign hydrocarbons may cause significant effects on the values obtained for particular samples of material.

3.1.2 *net heat of combustion*—expressed as megajoules per kilogram. The net heat of combustion at constant

[1] This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.05 on Petroleum, Coke, and Carbon Materials.

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[2] *Annual Book of ASTM Standards*, Vol 05.01.

[3] *Annual Book of ASTM Standards*, Vol 11.01.

[4] *Annual Book of ASTM Standards*, Vol 05.02.

[5] *Annual Book of ASTM Standards*, Vol 14.03.

[6] *Annual Book of ASTM Standards*, Vol 14.02.

[7] *Annual Book of ASTM Standards*, Vol 15.05.

[8] Prosen, E. J., "Experimental Thermochemistry." F. D. Rossini, editor, Interscience Publishers, 1956, pp. 129–148. Reliable values for heats of combustion of pure compounds are given in National Bureau of Standards *Circular C-461*, "Selected Values of Properties of Hydrocarbons" (U.S. Government Printing Office, Washington, DC, 1947) and in F. D. Rossini, et al, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, PA, 1953. These compilations were prepared by F. D. Rossini, et al, as part of American Petroleum Institute Research Project 44.

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pressure of a liquid or a solid fuel containing only the elements carbon, hydrogen, oxygen, nitrogen, and sulfur is the quantity of heat liberated when a unit mass of the fuel is burned in oxygen at a constant pressure of 0.101 MPa (1 atm), the products of combustion being carbon dioxide, nitrogen, sulfur dioxide, and water, all in the gaseous state, with the initial temperature of the fuel and the oxygen and the final temperature of the products of combustion at 25°C. The net heat of combustion[9,10] is represented by the symbol Q_n and is related to the gross heat of combustion by the following equation:

$$Q_n \text{ (net, 25°C)} = Q_g \text{ (gross, 25°C)} - 0.2122 \times H \quad (1)$$

where:

Q_n (net, 25°C) = net heat of combustion at constant pressure, MJ/kg,
Q_g (gross, 25°C) = gross heat of combustion at constant volume, MJ/kg, and
H = mass % of hydrogen in the sample.

3.1.3 *energy equivalent (effective heat capacity or water equivalent)*—the energy equivalent of the calorimeter expressed as joules per degree Celsius, J/°C.

NOTE 2—The energy equivalent may be expressed in any energy unit and any temperature unit so long as the value is used consistently throughout the calculations.

3.2 *Units:*

3.2.1 *Temperatures* are measured in degrees Celsius.

3.2.2 *Time* is expressed in minutes and decimal fractions thereof. It can be measured in minutes or seconds, or both.

3.2.3 *Masses* are measured in grams. No buoyancy corrections are applied except to obtain the mass of benzoic acid.

3.2.4 The energy unit of measurement employed in this test method is the joule with the heat of combustion reported in megajoules per kilogram (Note 3).

$$1 \text{ MJ/kg} = 1000 \text{ J/g} \quad (2)$$

NOTE 3—In SI the unit of heat of combustion has the dimension J/kg, but for practical use a multiple is more convenient. The MJ/kg is customarily used for the representation of heats of combustion of petroleum fuels.

3.2.5 The following relationships may be used for converting to other units;

1 cal (International Table calorie) = 4.1868 J[A]
1 Btu (British thermal unit) = 1055.06 J
1 cal (I.T.)/g = 0.0041868 MJ/kg[A]
1 Btu/lb = 0.002326 MJ/kg[A]

[A] Conversion factor is exact.

4. Summary of Test Method

4.1 The heat of combustion is determined by burning a weighed sample in an oxygen-bomb calorimeter under controlled conditions. The temperature increase is measured by a temperature reading instrument which allows the precision of the method to be met. The heat of combustion is calculated from temperature observations before, during, and after combustion, with proper allowance for thermochemical and heat-transfer corrections. Either isoperibol or adiabatic calorimeters may be used.

5. Significance and Use

5.1 The heat of combustion is a measure of the energy available from a fuel. A knowledge of this value is essential when considering the thermal efficiency of equipment for producing either power or heat.

5.2 The mass heat of combustion, that is, the heat of combustion per unit mass of fuel, is measured by this procedure. Its magnitude is particularly important to weight-limited vehicles such as airplanes, surface effect vehicles, and hydrofoils as the distance such craft can travel on a given weight of fuel is a direct function of the fuel's mass heat of combustion and its density.

5.3 The volumetric heat of combustion, that is, the heat of combustion per unit volume of fuel, can be calculated by multiplying the mass heat of combustion by the density of the fuel (mass per unit volume). The volumetric heat of combustion, rather than the mass heat of combustion, is important to volume-limited craft such as automobiles and ships, as it is directly related to the distance traveled between refuelings.

6. Apparatus

6.1 *Test Room, Bomb, Calorimeter, Jacket, Thermometers, and Accessories*, as described in Annex A1.

6.2 *Semimicro Analytical Balance*, having a sensitivity of 0.01 mg as specified in 10.5.1.

6.3 *Heavy-Duty Analytical Balance*, having a sensitivity of 0.05 g as specified in 10.7.2.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[11] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193, Type IV or better.

7.3 *Benzoic Acid*[12]—The acid must be pelleted before use.

7.4 *Firing Wire*—0.127 mm (No. 36 gage) platinum wire, No. 34 B & S gage iron wire or Chromel C resistance wire, cut in 100-mm lengths.

7.5 *Methyl Red Indicator.*

7.6 *Oxygen*—Commercial oxygen produced from liquid

[9] Derivation of equations has been filed at ASTM Headquarters. Request RR: D02–1346.

[10] See Jessup, R. S., "Precise Measurement of Heat of Combustion with a Bomb Calorimeter," *NBS Monograph 7*, U.S. Government Printing Office.

[11] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

[12] Obtainable from the National Institute of Standards and Technology, Clopper and Quince Orchard Roads, Gaithersburg, MD 20899. as Standard Sample 39i.

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air can be used without purification (**Warning**—See Note 4.) Oxygen prepared by electrolysis of water cannot be used without purification as it can contain some hydrogen. Combustible impurities may be removed by passage over copper oxide at 500°C.

NOTE 4: **Warning**—Oxygen vigorously accelerates combustion. (See Annex A3.1.)

7.7 *Pressure-Sensitive Tape*—Cellophane tape 38 mm (1½ in.) wide, free of chlorine and sulfur.[13]

7.8 *Alkali, Standard Solutions.*

7.8.1 *Sodium Hydroxide Solution* (0.0866 *N*)—Dissolve 3.5 g of sodium hydroxide (NaOH) in water and dilute to 1 L. (**Warning**—See Note 5.) Standardize with potassium acid phthalate and adjust to 0.0866 *N* as described in Practice E 200, or alternative use.

NOTE 5: **Warning**—Corrosive. Can cause severe burns or blindness. Evolution of heat produces a violent reaction or eruption upon too rapid mixture with water. (See Annex A3.2.)

7.8.2 *Sodium Carbonate Solution* (0.0725 *N*)—Dissolve 3.84 g of Na_2CO_3 in water and dilute to 1 L.

7.9 *2,2,4-Trimethylpentane* (*iso*octane), *Standard.*[14]

NOTE 6: **Warning**—Extremely flammable. Harmful if inhaled. Vapors may cause flash fire. (See Annex A3.3.)

8. Preparation of Apparatus

8.1 *Arrangement of Apparatus*—Install the thermometers as recommended by the manufacturer of the calorimeter. Position the mercury-in-glass thermometer so that the bulb is halfway to the bottom of the bucket and locate the thermistor with its sensing element at about the midpoint of the thermometer bulb. Mount these elements so that exactly the same length is immersed each time the calorimeter is used. Install a thermistor in the water jacket with the element immersed to the same depth as in the bucket. It is helpful, but not necessary to have mercury-in-glass calorimetric thermometers in both the bucket and jacket for quick temperature observations. Thermistors can be taped to these thermometers. If the thermistors are taped to the thermometers, it can be done in such a manner that the sensing elements are at the midpoint of the thermometer bulbs. The thermometer bulbs and temperature-sensing elements shall not touch the bomb, bucket, or water jacket.

8.2 *Calorimeter Jacket Controller and Auxiliary Equipment*—Adjust the jacket controller, valves, heater, etc., as recommended by the calorimeter manufacturer.

9. Standardization

9.1 *Energy Equivalent of the Calorimeter*—Benzoic acid shall be used as the primary standard (Note 4). Choose a sample mass so that the temperature rise is approximately equivalent to an energy change of 30 000 J. Initially determine the energy equivalent by averaging six determinations made using benzoic acid over a period of at least 3 days.

9.1.1 A relative standard deviation (RSD) of 0.1 % or less for the six determinations must be achieved. If not, continue to run until six determinations establish a value that has a RSD of 0.1 % or better. If this degree of precision cannot be achieved, review the procedure, critical measurements, mechanical operations and everything that may contribute to scatter in the results. After establishing an energy equivalent value, determine the value at frequent intervals using benzoic acid (every 1 or 2 days of testing) with the average of the last six determinations being used for the energy equivalent as long as the last six determinations have a RSD of 0.1 % or less.

9.1.2 If any part of the equipment is changed or any part of the procedure is altered, redetermine the value. Make each determination in accordance with Section 10. Determine the correction for nitric acid (HNO_3) as described in 11.3 and substitute in the following equation:

$$W = (Q_b \times m + e_1)/\Delta t \quad (3)$$

where:

W = energy equivalent of calorimeter, J/°C,
m = mass of benzoic acid, g, (Note 5),
Δt = corrected temperature rise, as calculated in accordance with 11.1 or 11.2, °C,
e_1 = correction for heat of formation of nitric acid, J, and
Q_b = heat of combustion of benzoic acid, J/g calculated from the certified value in kilojoules per gram mass given for NBS Standard 39i. Multiply kilojoules per gram mass by 1000 to obtain joules per gram (Note 8).

NOTE 7—2,2,4-trimethyl pentane may be used for checking the energy equivalent of the system for use with volatile fuels.

NOTE 8—Multiply the heat evolved by combustion of the standard sample by the following factor.[15]

$$1 + 10^{-6}[197\,(P - 3.04) + 42((m/V) - 3) + 30((M_w/V) - 3) - 45(t - 25)] \quad (5)$$

where:

P = initial absolute pressure of oxygen, MPa (1 atm = 0.101325 MPa) at temperature t,
m = mass of benzoic acid, g,
M_w = mass of water placed in bomb before combustion, g,
V = internal volume of bomb, L, and
t = temperature to which the combustion reaction is referred, °C (final temperature of the calorimeter).

9.2 *Heat of Combustion of Pressure-Sensitive Tape*—Determine the heat of combustion of the pressure-sensitive tape in accordance with Section 10 using about 1.2 g of tape and omitting the sample. Make at least three determinations and calculate the heat of combustion as follows:

$$Q_{pst} = (\Delta t \times W - e_1)/a \quad (6)$$

where:

Q_{pst} = heat of combustion of the pressure-sensitive tape, J/g
Δt = corrected temperature rise, as calculated in accordance with 11.1 or 11.2, °C,
W = energy equivalent of the calorimeter, J/°C,
e_1 = correction for the heat of formation of HNO_3, J, and
a = mass of the pressure-sensitive tape, g.

9.2.1 Average the determinations, and redetermine the heat of combustion of the tape whenever a new roll is started.

[13] Cellophane tape Scotch Brand No. 610, available from 3M Co., meets the specification requirements.

[14] Obtainable from the National Institute of Standards and Technology, Clopper and Quince Roads, Gaithersburg, MD 20899, as Standard Sample No. 217b.

[15] See *NBS Monograph 7*, p. 12.

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10. Procedure

10.1 Turn on the apparatus. Make all electrical connections and open the water lines.

10.2 Before beginning, be sure that the bomb and its fittings are completely dry, inside and out.

10.3 Measure a piece of firing wire 100 mm long and attach the wire to the bomb electrodes forming a U-shaped loop.

10.4 Pipet 1.0 cm^3 of water into the bomb and cover with a watch glass.

10.5 *Mass of Sample:*

10.5.1 Weigh the sample cup to 0.01 mg on a semimicro analytical balance. Place a piece of pressure-sensitive type (Note 9) across the top of the cup, trim around the edge with a razor blade, and seal tightly. Place a 3 by 12-mm strip of tape creased in the middle and sealed by one edge in the center of the tape disk to give a flap arrangement. Weigh the cup and tape. Remove from the balance with forceps. Fill a hypodermic syringe with the sample. The volume of sample necessary to produce a temperature rise equivalent to approximately 30 000 J can be estimated as follows:

$$V = (W \times 0.0032)/(Q \times D) \quad (7)$$

where:

V = volume of sample to be used, cm^3,
W = energy equivalent of the calorimeter, J/°C,
Q = approximate heat of combustion of the sample, MJ/kg, and
D = density, g/cm^3, of the sample.

or

$$V = (W \times 1.3)/(Q \times D) \quad (8)$$

where:

Q = approximate heat of combustion of the sample, Btu/lb.

NOTE 9—For relatively high-boiling samples, such as non-volatile (i.e. IBP above 180°C) kerosine-type jet fuels, it is not necessary to use tape.

10.5.2 Add the sample to the cup by inserting the tip of the needle through the tape disk at a point so that the flap of tape will cover the puncture upon removal of the needle. Seal down the flap by pressing lightly with a metal spatula. Reweigh the cup with the tape and sample. Take care throughout the weighing and filling operation to avoid contacting the tape or cup with bare fingers. Place the cup in the curved electrode and arrange the fuse wire so that the central portion of the loop presses down on the center of the tape disk.

10.6 *Bomb Assembly*—Assemble the bomb and tighten the cover securely. Connect the bomb to the oxygen cylinder and slowly admit oxygen until a pressure of 3.0 MPa (30 atm) is attained. Do not purge the bomb to remove entrapped air. Disconnect the bomb from the oxygen cylinder and replace the valve cover. (**Warning**—See Note 10.) Be careful not to overcharge the bomb. If by accident, the oxygen introduced into the bomb does exceed 4.0 MPa (40 atm) *DO NOT* proceed with the combustion. A violent explosion, capable of rupturing the bomb, might occur. Detach the filling connection and exhaust the bomb in the usual manner. Discard the sample.

NOTE 10—**Warning**—A violent explosion may occur.

NOTE 11—Pressures within the range of from 2.5 to 3.55 MPa (25 to 35 atm) may be used, provided the same pressure is used for all tests, including standardization.

10.7 *Calorimeter Water:*

10.7.1 Adjust the temperature of the calorimeter water. The choice of the temperature to which the water is adjusted before weighing depends on a number of factors, including room temperature, the desired initial temperature of the experiment, and the relative heat capacities of the calorimeter bucket, water, and bomb. No definite rule can be given, but the operator will learn by experience how to select the proper temperature under the conditions of his particular laboratory and apparatus. The following can be used as a guide:

Isothermal method	3.0 to 3.5°C below jacket temperature
Adiabatic method	1.5 to 1.8°C below room temperature

10.7.1.1 *Isoperibol Method*—Adjust the temperature such that after assembly of the calorimeter bomb and bucket its temperature will be a few tenths of a degree below the desired initial temperature.

10.7.1.2 *Adiabatic Method*—Adjust the temperature so that the initial temperature of the determination will be as close to some fixed values as possible. Control the mean temperature of all determinations within more than ±0.5°C and the temperature rise for all determinations within ±0.3°C.

10.7.2 Weigh the calorimeter bucket to ±0.05 g on a heavy-duty analytical balance. After once establishing the dry bucket weight, it need only be checked occasionally. Fill with the desired quantity of water (2000 to 2100 g) and reweigh to 0.05 g (Note 9). The exact quantity of water is not important as long as it is enough to cover the bomb and its fittings and is the same in each determination.

NOTE 12—The change in the mass of the water in the calorimeter bucket due to evaporation after weighings will affect the energy equivalent. The effect of this loss is small and cancels if the procedure of placing the bomb in its bucket and completing the assembly of the system is carried out in the same manner and in the same length of time in the calibration experiments as in the measurement of the heat of combustion.

10.7.3 Immediately after weighing, place the bucket in position in the calorimeter jacket, carefully place the bomb in the bucket, and complete the firing circuit. Close the calorimeter cover and lower thermometers and thermistors.

NOTE 13—The bomb should be lowered into the calorimeter withouttouching the water with the fingers. This can be done by using a hook on which the bomb can be hung and which can be removed after the bomb is in place in the calorimeter bucket. A hook made of a piece of brass rod about 1.6 mm (1/16 in.) in diameter has been found satisfactory. The hooked ends of the rod are inserted into holes on opposite sides of the screw top of the bomb and are easily removed after the bomb is in place. It is very important that all operations in the experimental procedure be carried out in an identical manner throughout for the energy equivalent and heat of combustion measurements.

10.8 *Procedure for Isoperibol Method:*

10.8.1 Start the stirrer motor and the controller on the jacket heater to bring the temperature of the water in the jacket to 28°C. Take time and temperature readings over a 25-min period. During this period there are three definite time intervals:

10.8.1.1 An initial period of about 6 to 9 min during

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which the temperature change results solely from thermal leakage and heat of stirring.

10.8.1.2 A middle period of about 12 min, at the beginning of which the charge in the bomb is fired, and during which the temperature change is due primarily to the heat liberated by the combustion reaction in the bomb and partly to thermal leakage and heat of stirring, and

10.8.1.3 A final period of 9 to 11 min during which the temperature change is again due solely to thermal leakage and heat of stirring.

10.8.2 Allow the temperature of the calorimeter water to drift up to the starting temperature and then make and record readings of the time and temperature of the initial period. During this initial period when the rate of temperature rise is constant, make observations of temperature at 1-min intervals. The starting temperature always has the same value as determined from the calibration runs.

10.8.3 When the firing temperature is reached, fire the sample by closing the firing circuit through the fuse wire in the bomb by depressing the button on the ignition unit. The pilot light should glow momentarily and the temperature should start increasing in about 15 s. If the circuit does not close, or if it remains closed, or if the temperature does not start rising, the experiment has misfired and must be discontinued. After the combustion of the sample and during the middle period when the temperature is rising rapidly, take temperature measurements at 30 s intervals. After about 3 min, the rate of temperature rise will decrease so that temperature readings may be taken with more accuracy. These readings shall be continued until the rate of temperature change has been constant for at least 10 min. The readings made after the rate of temperature change has become constant constitute the final period.

NOTE 14—During the initial and final periods the thermometer should be read with the highest possible care, since the overall precision of the determination depends directly upon these temperature measurements. During the middle period, because of the very rapid rate of temperature rise, it is not possible to make readings as carefully as during the initial and final periods. This is not important because the readings of the middle period are used only for calculating the relatively small correction for thermal leakage and heat of stirring.

10.9 *Procedure for Adiabatic Method:*

10.9.1 Start the stirrer motor and turn on the calorimeter controller. Use the manual control switch of the controller to bring the jacket temperature in close agreement with the bucket temperature. Allow the controller to automatically control the temperature and wait 15 min for equilibrium to be attained. At this point, and at the end point also, control the temperature of the jacket to the same temperature as the bucket, or slightly (0.005°C at most) below. Make readings at 1-min intervals until three consecutive readings show no change. Fire the sample by depressing the button of the ignition unit. The pilot light should glow momentarily and the temperature should start increasing in about 15 s. (If the temperature does not start rising, the experiment has misfired and must be discontinued.) Read and record the initial resistance, estimating the value to the nearest 0.00005°C.

10.9.2 After 6 min from firing, begin reading temperature every minute. Continue until three consecutive readings show no change, or the readings decrease. Read and record the final temperature reading estimating the value to the nearest 0.0005°C.

10.10 *Analysis of Bomb Contents:*

10.10.1 Turn off the controller and stirrer and remove the bomb from the calorimeter. Open the needle valve and allow the gas to escape at a uniform rate such as to reduce the pressure to atmospheric in not less than 1 min. Open the bomb and examine the interior for unburned carbon. If any trace of unburned carbon is found, the experiment should be rejected. Wash the interior of the bomb including the electrodes and the sample cup with a fine jet of water and quantitatively collect the washings in a 500-cm^3 Erlenmeyer flask. Use a minimum amount of wash water, preferably less than 300 cm^3. Titrate the washings with standard alkali solution using methyl red indicator.

10.10.2 Determine the sulfur content of the sample to the nearest 0.02 % sulfur as described in Test Method D 129, D 1266-IP 107, D 2622, or D 3120, depending upon the volatility of the sample.

10.10.3 When iron or Chromel C wire is used, remove and measure the combined pieces of unburned firing wire, and subtract from the original length. Record the difference as *wire consumed.*

11. Calculation

11.1 *Temperature Rise Isoperibol Method*—Using data obtained in Section 10, plot a graph of readings of temperature versus time and calculate the corrected temperature rise, Δt, in °C as follows:

$$\Delta t = t_f - t_i - r_1(b - a) - r_2(c - b) \quad (9)$$

where:

Δt = corrected temperature rise, °C,
a = time of firing,
b = time (to nearest 0.1 min) when the temperature rise reaches 63 % of total (obtained graphically or numerically),
c = time at beginning of final period in which the rate of temperature change with time has become constant,
t_i = temperature at time of firing, °C,
t_f = temperature at time c, °C,
r_1 = rate at which the temperature was rising during the initial period before firing, °C, and
r_2 = rate at which the temperature as rising during the final period, °C.

11.2 *Temperature Rise, Adiabatic Method*—Using data obtained in Section 10, calculate the temperature rise, Δt, in °C, as follows:

$$\Delta t = t_f - t_i \quad (10)$$

where:

Δt = corrected temperature rise, °C,
t_f = final equilibrium temperature, °C, and
t_i = temperature at time of firing, °C.

11.3 *Thermochemical Correction* (Annex A2)—Calculate the following corrections for each test:

e_1 = correction for the heat of formation of the HNO_3, J = cm^3 of standard (0.0866 N) NaOH solution used in titration × 5,
e_2 = correction for the heat of formation of sulfuric acid (H_2SO_4), J = 58.6 × percentage of sulfur in sample × mass of sample, g.

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e_3 = correction for the heat of combustion of pressure-sensitive tape, J = mass of tape, g × heat of combustion of tape J/g.

e_4 = correction for heat of combustion of firing wire, MJ
= 1.13 × millimetres of iron wire consumed/10^6
= 0.96 × millimetres of Chromel C wire consumed/10^6

11.4 *Gross Heat of Combustion*—Calculate the gross heat of combustion by substituting in the following equations:

$$Q_g \text{ (gross } t°C) = (\Delta t \times W - e_1 - e_2 - e_3 - e_4)/1000\, M\, Q_g$$
$$\text{(gross, 25°C)} = Q_g \text{ (gross, } t°C) + A(t - 25) \quad (11)$$

where:

Q_g (gross, t°C) = gross heat of combustion at constant volume and final temperature of the experiment, expressed as MJ/kg,

Q_g (gross, 25°C) = gross heat of combustion at constant volume expressed as MJ/kg,

Δt = corrected temperature rise, °C,

W = energy equivalent of calorimeter, J/°C

M = mass of sample, g,

t = final temperature of combustion, °C,

e_1, e_2, e_3, e_4 = corrections as described in 11.3, and

A = correction factor, MJ/kg °C to correct from final temperature of combustion to 25°C[15] where values of factor A are given in Table 1.

NOTE 15—The gross heat of combustion at constant pressure may be calculated as follows:

$$Q_{gp} = Q_g + 0.006145H$$

where:

Q_{gp} = gross heat of combustion at constant pressure, $\frac{\text{MJ}}{\text{kg}}$, and

H = hydrogen content, mass %

$Q_{btu/lb}$ = (Q, MJ/kg)/0.002326

$Q_{cal/g}$ = (Q, MJ/kg)/0.0041868

11.5 *Net Heat of Combustion*—Calculate the net heat of combustion[16] as follows:

$$Q_n\text{(net, 25°C)} = Q_g\text{(gross, 25°C)} - 0.2122 \times H \quad (12)$$

where:

Q_n(net, 25°C) = net heat of combustion at constant pressure, MJ/kg,

Q_g(gross, 25°C) = gross heat of combustion at constant volume, MJ/kg, and

H = mass percent of hydrogen in the sample.

When the percentage of hydrogen in the sample is not known, determine the hydrogen in accordance with Test Methods D 1018 or D 3701.

12. Report

12.1 Net heat of combustion is the quantity required in practical applications. Both gross and net heat are reported to the nearest 0.002 MJ/kg.

12.1.1 To obtain the gross or net heat of combustion in cal (I.T.)/g or Btu/lb divide by the appropriate factor given in 3.2.2 reporting to the nearest 0.5 cal/g or 1 Btu/lb.

TABLE 1 Values of Factor A

Q_g (Gross, t°C)	A	Q_g (Gross, t°C)	A
MJ/kg	MJ/kg·°C	MJ/kg	MJ/kg·°C
43.00	0.00157	45.75	0.00271
43.25	0.00167	46.00	0.00282
43.50	0.00178	46.25	0.00292
43.75	0.00188	46.50	0.00302
44.00	0.00199	46.75	0.00313
44.25	0.00209	47.00	0.00323
44.50	0.00219	47.25	0.00333
44.75	0.00230	47.50	0.00344
45.00	0.00240	47.75	0.00354
45.25	0.00250	48.00	0.00365
45.50	0.00261		

13. Precision and Bias[17]

13.1 *Precision*—The precision of this test method as determined by the statistical examination of interlaboratory test results is as follows.

13.1.1 *Repeatability*—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty.

	Repeatability, MJ/kg	
	Gross	Net
Method		
1. All fuels	0.097	0.096
2. Nonvolatile	0.096	0.099
3. Volatile	0.100	0.091

13.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, exceed the following values only in one case in twenty.

	Reproducibility, MJ/kg	
	Gross	Net
Method		
1. All fuels	0.228	0.324
2. Nonvolatile	0.239	0.234
3. Volatile	0.207	0.450

13.2 *Bias*—The bias of the procedure in this test method as determined by the statistical examination of interlaboratory test results is as follows:

Bias, MJ/kg	
Gross	Net
0.001	0.089

[16] See *NBS Monograph 7*, p. 16.

[17] The precision and bias values in this statement were determined in a cooperative laboratory program that follows RR: D02 – 1007. Supporting data have been filed at ASTM Headquarters and may be obtained by requesting RR: D02 – 1229.

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ANNEXES

(Mandatory Information)

A1. APPARATUS FOR HEAT OF COMBUSTION TEST

A1.1 Test Room

A1.1.1 The room in which the calorimeter is operated must be free from drafts and not subject to sudden temperature changes. The exact temperature is not important as long as it is in the range from 23 to 26°C (74 to 78°F) and is held constant. The temperature must be constant, not only throughout the day, but from one time of the year to another. The direct rays of the sun shall not strike the calorimeter jacket, bridge, and galvanometer. Adequate facilities for lighting, heating, and ventilation should be provided. Thermostatic control of room temperature and controlled humidity are desirable.

A1.2 Oxygen Bomb

A1.2.1 The oxygen bomb shall meet the requirements specified in Practice E 144 and have an internal volume of 350 ± 50 mL. All parts shall be constructed of materials that are not affected by the combustion process or products sufficient to introduce measurable heat input or alteration of end products. If the bomb is lined with platinum or gold, all openings shall be sealed to prevent combustion products from reaching the base metal. The bomb must be designed so that all liquid combustion products can be completely recovered by washing the inner surfaces. There must be no gas leakage during a test. The bomb must be capable of withstanding a hydrostatic pressure test to a gage pressure of 20.7 MPa (3000 psi) at room temperature without stressing any part beyond its elastic limit.[18] If necessary, modify the bomb such that the feet are 12 mm high to allow for better water circulation under the bomb.

A1.3 Calorimeter Bucket

A1.3.1 The calorimeter bucket shall be made of metal (preferably copper or brass) with a tarnish-resistant coating, and with all outer surfaces highly polished. Its size shall be such that the bomb will be completely immersed in water when the calorimeter is assembled. It shall have a device for stirring the water thoroughly and at a uniform rate but with minimum heat input. Continuous stirring for 10 min shall not raise the temperature more than 0.01°C starting with identical temperatures in the calorimeter, room, and jacket. The immersed portion of the stirrer shall be coupled to the outside through a material of a low-heat conductivity.

A1.4 Jacket

A1.4.1 The calorimeter bomb, bucket, and water shall be completely enclosed within a stirred water jacket and supported so that its sides, top, and bottom are approximately 1 cm from the jacket walls. The jacket may be arranged so as to remain at a constant temperature, or with provisions for automatically adjusting the jacket temperature to equal that of the calorimeter bomb, bucket, and water for adiabatic operation. It must be constructed so that any water evaporating from the jacket will not condense on the calorimeter bucket.[19]

A1.5 Thermometers

A1.5.1 Temperatures in the jacket and the calorimeter, respectively, shall be measured with the following thermometers:

A1.5.1.1 Etched stem, mercury-in-glass, ASTM Bomb Calorimeter Thermometers, having a range from 66 to 95°F, 19 to 35°C, 18.9 to 25.1°C, or 23.9 to 30.1°C as specified, and conforming to the requirements for Thermometer 56F, 56C, 116C, or 117C, respectively, as prescribed in Specification E 1. Each of these thermometers shall have been tested for accuracy at intervals no larger than 2.5°F or 1.5°C over the entire graduated scale. Corrections shall be calculated to 0.005°F or 0.002°C, respectively, for each test point.

A1.5.2 Temperature in the calorimeter shall be measured with the following thermometers:

A1.5.2.1 Platinum resistance, thermistor, or other temperature measuring devices which when used with its associated instrumentation will measure the temperature rise repeatably with a recorded resolution of 0.0001°C and a repeatability such that the precision requirements for the energy equivalent are met. Further, that these specifications are limited to the requirements that the mean temperature of all determinations not deviate by more than 0.05°C and that the temperature rise for all experiments be within ±0.3°C.

A1.6 Automatic Calorimeter Microprocessor Controller

A1.6.1 In place of manually recording temperatures and calculating the energy equivalent, an automatic controller may be used. It shall be capable of storing calorimeter temperature readings taken at accurate intervals, firing the bomb and ending the experiment. The stored information along with the sample mass, nitric acid correction and sulfur content, when entered into the instrument, shall be used to calculate the desired energy equivalent or heat of combustion.

A1.7 Firing Circuit

A1.7.1 A 6 to 16-V alternating or direct current is required for ignition purposes with an ammeter or pilot light in the circuit to indicate when current is flowing. A step-down transformer connected to a 115 V, 50/60-Hz lighting

[18] The oxygen bomb, Parr No. 1108 or equivalent, available from Parr Instrument Co., 211 Fifty-third St., Moline, IL 61265.

[19] The Calorimeter Jacket, Parr No. 1261 or equivalent, available from Parr Instrument Co., meets the specification requirements.

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circuit or storage battery may be used.[20]

NOTE A1.1: **Caution**—The ignition circuit switch shall be of themomentary contact type, normally open, except when held closed by the operator.

A1.8 Timing Device

A1.8.1 A watch or other timing device capable of measuring time to 1 s is required for use with the isoperibol method.

A1.9 Sample Cup

A1.9.1 A low-form platinum cup, 26 mm in diameter and 11 mm deep with a spun rim.[21] Base metal alloy crucibles are acceptable if after a few preliminary firings the weight does not change significantly between tests.

[20] Ignition Unit, Parr No. 2901, available from Parr Instrument Co., meets the specification requirements.

[21] Sample Cup, Parr No. 43A6, available from Parr Instrument Co., has been found satisfactory.

A2. CORRECTIONS

A2.1 Thermometer Corrections

A2.1.1 It is not necessary to apply stem corrections to the thermometers.

A2.2 Thermochemical Corrections

A2.2.1 *Heat of Formation of Nitric Acid*—A correction of 5 J is applied for each cubic centimetre of standard (0.0866 *N*) NaOH solution used in the acid titration. This is based on the assumption that (1) all of the acid titrated is HNO_3 and (2) the heat of formation of 0.1 *N* HNO_3 under the test conditions is 57.8 kJ/mole. When H_2SO_4 is also present, part of the correction for H_2SO_4 is contained in the e_1 correction, and the remainder in the e_2 correction.

A2.2.2 *Heat of Formation of Sulfuric Acid*—A correction of 5.86 kJ is applied to each gram of sulfur in the sample. This is based upon the heat of formation of 0.17 *N* H_2SO_4, which is +301.4 kJ/mole. But, a correction equal to 2×57.8 kJ/mole of sulfur was applied for H_2SO_4 in the e_1 correction. Thus, the additional correction necessary is $301.4 - (2 \times 57.8) = 185.8$ kJ/mole or 5.86 kJ/g of sulfur.

A2.2.2.1 The value of 5.86 kJ/g of sulfur is based on a fuel oil containing a relatively large amount of sulfur since as the percentage of sulfur decreases, the correction decreases and consequently a larger error can be tolerated. For this calculation 0.8 % S, 99.2 % CH_2 was taken as the empirical composition of fuel oil. If a 0.6-g sample of such a fuel oil is burned in a bomb containing 1 cm^3 of water, the H_2SO_4 formed will be approximately 0.17 *N*.

A2.2.2.2 Using data from National Bureau of Standards *Circular No. 500*, the heat of reaction SO_2 (g) + ½ O_2 (g) + 651 H_2O (1) − $H_2SO_4 \cdot 650$ H_2O (1) at constant volume and 3 MPa is −301.4 kg/mole.

A2.2.3 *Heat of Combustion of Fuse Wire*—When using platinum wire no correction need be applied for the heat of combustion of the wire. The electrical energy required can be neglected if the same length of wire is used in both the energy equivalent and unknown experiments. When using iron or Chromel C wire, the following heats of combustion are accepted:

Iron wire, No. 34 B & S gage	=	1.13 J/mm
Chromel C wire	=	0.96 J/mm

A2.2.4 *Heat of Combustion of Pressure-Sensitive Tape*—The correction for the heat of combustion of the tape (as determined in accordance with 9.2) assumes complete combustion of the tape.

A3. PRECAUTIONARY STATEMENTS

A3.1 Oxygen

Do not exceed the sample size limits.

Following manufacturer's commendations for filling the bomb.

Do not use oil or grease on regulators, gages, or control equipment.

Use only with equipment conditioned for oxygen service by carefully cleaning to remove oil, grease, and other combustibles.

Keep combustibles away from oxygen and eliminate ignition sources.

Keep surfaces clean to prevent ignition or explosion, or both, on contact with oxygen.

Always use a pressure regulator. Release regulator tension before opening cylinder valve.

All equipment and containers used must be suitable and recommended for oxygen service.

Never attempt to transfer oxygen from cylinder in which it is received to any other cylinder.

Do not mix gases in cylinders.

Do not drop cylinder. Make sure cylinder is secured at all times.

Keep cylinder valve closed when not in use.

Stand away from outlet when opening cylinder valve.

Keep cylinder out of sun and away from heat.

Keep cylinder from corrosive environment.

Do not use cylinder without label.

Do not use dented or damaged cylinders.

For technical use only. Do not use for inhalation purposes.

Use only in well-ventilated area.

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See compressed gas association booklets G-4 and G-4.1 for details of safe practice in the use of oxygen.

A3.2 Sodium Hydroxide

Before using, secure information on procedures and protective measures for safe handling.

Do not get in eyes, on skin, on clothing.

Avoid breathing dusts or mists.

Do not take internally.

When handling, use chemical safety goggles or face shield, protective gloves, boots and clothing.

When mixing with water, add slowly to surface of solution to avoid violent spattering. In the preparation of solutions do not use hot water, limit temperature rise, with agitation, to 10°C/min or limit solution temperature to a maximum of 90°C. No single addition should cause a concentration increase greater than 5 %.

A3.3 2,2,4-Trimethylpentane

Keep away from heat, sparks, and open flame.

Keep container closed.

Use with adequate ventilation.

Avoid buildup of vapors and eliminate all sources of ignition, especially nonexplosion-proof electrical apparatus and heaters.

Avoid prolonged breathing of vapor or spray mist.

Avoid prolonged or repeated skin contact.

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Designation: D 4891 – 89 (Reapproved 1994)ε1

Standard Test Method for Heating Value of Gases in Natural Gas Range by Stoichiometric Combustion[1]

This standard is issued under the fixed designation D 4891; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

ε1 NOTE—Section 11 was added editorially in July 1994.

1. Scope

1.1 This test method covers the determination of the heating value of natural gases and similar gaseous mixtures within the range of composition shown in Table 1.

1.2 *This standard involves combustible gases. It is not the purpose of this standard to address the safety concerns, if any, associated with their use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1826 Test Method for Calorific Value of Gases in Natural Gas Range by Continuous Recording Calorimeter[2]

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[3]

3. Terminology

3.1 All of the terms defined in Test Method D 1826 are included by reference.

3.2 *Descriptions of Terms:*

3.2.1 *combustion ratio*—the ratio of combustion air to gaseous fuel.

3.2.2 *stoichiometric ratio*—the combustion ratio when the quantity of combustion air is just sufficient to convert all of the combustibles in the fuel to water and carbon dioxide.

3.2.3 *burned gas parameter*—a property of the burned gas after combustion which is a function of the combustion ratio.

3.2.4 *critical combustion ratio—for a specific burned gas parameter*, the combustion ratio at which a plot of burned gas parameter versus combustion ratio has either maximum value or maximum slope.

4. Summary of Test Method

4.1 Air is mixed with the gaseous fuel to be tested. The mixture is burned and the air-fuel ratio is adjusted so that essentially a stoichiometric proportion of air is present. More exactly, the adjustment is made so that the air-fuel ratio is in a constant proportion to the stoichiometric ratio which is a relative measure of the heating value. To set this ratio, a characteristic property of the burned gas is measured, such as temperature or oxygen concentration.

5. Significance and Use

5.1 This test method provides an accurate and reliable procedure to measure the total heating value of a fuel gas, on a continuous basis, which is used for regulatory compliance, custody transfer, and process control.

5.2 Some instruments which conform to the requirements set forth in this test method can have response times on the order of 1 min or less and can be used for on-line measurement and control.

5.3 The method is sensitive to the presence of oxygen and nonparaffin fuels. For components not listed and composition ranges that fall outside those in Table 1, modifications in the method may be required to obtain correct results.

6. Apparatus

6.1 A suitable apparatus for carrying out the stoichiometric combustion method will have at least the following four components: flow meter or regulator, or both; combustion chamber; burned gas sensor; and electronics. The requirement for each of these components is discussed below. The detailed design of each of these components can vary. Two different apparatus are shown in Figs. 1 and 2. In each figure the equivalent of the four necessary components are enclosed in dashed lines.

6.2 *Overview*—Air and fuel enter the apparatus and the flow of each is measured. Alternatively, only one gas flow need be measured if the flow of the other is kept the same

TABLE 1 Natural Gas Components and Range of Composition Covered

Compound	Concentration Range, mole, %
Helium	0.01 to 5
Nitrogen	0.01 to 20
Carbon dioxide	0.01 to 10
Methane	50 to 100
Ethane	0.01 to 20
Propane	0.01 to 20
n-butane	0.01 to 10
isobutane	0.01 to 10
n-pentane	0.01 to 2
Isopentane	0.01 to 2
Hexanes and heavier	0.01 to 2

[1] This test method is under the jurisdiction of ASTM Committee D-3 on Gaseous Fuels and is the direct responsibility of Subcommittee D03.03 on Determination of Heating Value and Relative Density of Gaseous Fuels.

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[2] *Annual Book of ASTM Standards*, Vol 05.05.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

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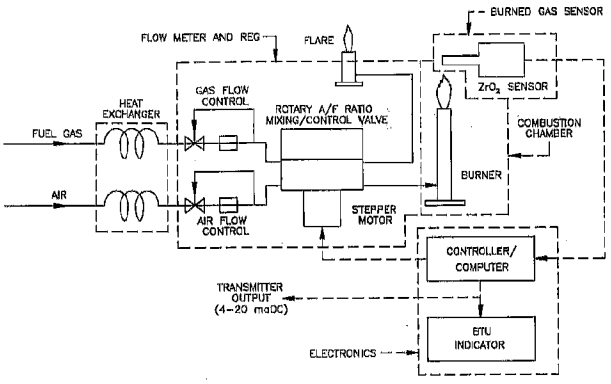


FIG. 1 Gas Btu Transmitter (Functional Overview)

during measurement and calibration. This is illustrated in Fig. 2. Next there is a combustion chamber in which the air and fuel are mixed and burned. This can be as simple as a bunsen or meeker burner, but precautions should be taken that subsequent measurements of burned gas characteristics are not influenced by ambient conditions. Finally, there is a sensor in the burned gas which measures a property of this gas that is sensitive to the combustion ratio and has a unique feature at the stoichiometric ratio. Two such properties are temperature and oxygen concentrations, and either can be measured.

6.3 *Flow Meter and/or Regulator*—The flow measurement part of the apparatus should have an accuracy and precision of the order of 0.1 %. Likewise, if the flow is to be kept constant, the flow regulator should maintain this constant value within 0.1 %. The meter or regulator for natural gas must maintain this precision and accuracy over the density and viscosity ranges consistent with the composition range in Table 1.

6.4 *Combustion Chamber:*

6.4.1 There are two different types of combustion chambers that may be used. In the first type the air and fuel are mixed and burned in a single burner. The apparatus shown in Fig. 1 has this type of combustion chamber.

6.4.2 In the second type of combustion chamber, the air and fuel are each divided into two streams, and combustion takes place simultaneously in two burners. The division of air flow must be such that the proportion of air going to each burner always remains the same. Likewise the division of fuel flow must always remain the same even through fuel composition changes. Another requirement is that the flow divisions be such that one burner has a mixture with a slightly higher combustion ratio than the other. The apparatus shown in Fig. 2 has this type of combustion chamber.

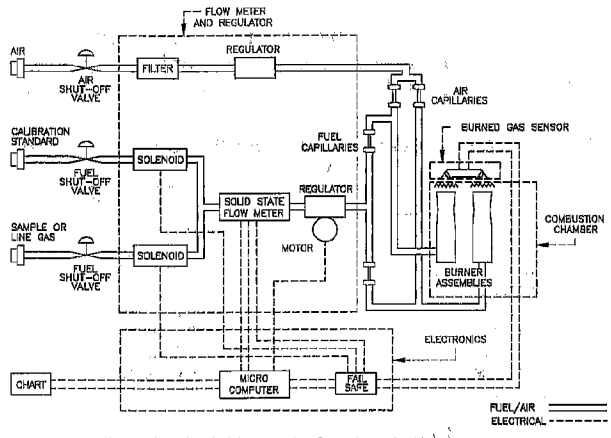


FIG. 2 Stoichiometric Combustion Apparatus

6.5 *Burned Gas Sensor:*

6.5.1 The burned gas sensor must measure a characteristic of the burned gas which is a function of the combustion ratio and for which there is a critical combustion ratio related to the stoichiometric ratio. A combustion chamber of the first type (Fig. 1) would have one sensor in the burned gas and its output signal would constitute the desired measurement. In a combustion chamber of the second type (Fig. 2) there would be a sensor in the burned gas from each burner. The difference between the two output signals would constitute the desired measurement.

6.5.2 There are several properties of the burned gas which are related uniquely to the combustion ratio. A burned gas sensor may be selected which provides a measure of any one of these, for example, either temperature or oxygen partial pressure.

6.6 *Electronics*—Electronics are used to receive the signals from the components described above to control the flow of gases into the combustion chamber in response to the signal from the burned gas sensor and to provide a digital or analog output signal, or both, which is proportional to the heating value of the gaseous fuel.

6.7 *Temperature Stability and Operating Environment*—The method is capable of operating over a range of temperatures limited only by the specific apparatus used to realize the method. It is desirable to equilibrate the air and fuel temperatures before the gases are measured. The electronics should also be stabilized against temperature changes and the burned gas sensor should be insensitive to changes in the ambient conditions.

7. Reagents and Materials

7.1 *Physical Contamination*—The air and gas must be free of dust, liquid, water, liquid hydrocarbons, and other entrained solids. Foreign materials should be removed by a sample line filter. To avoid any problems in the line from any liquid accumulation, pitch the line to a low point and provide a drip leg.

7.2 *Chemical Contamination*—The air must be free of combustible compounds. The oxygen content and the absolute humidity of the air should be the same during measurement as during calibration.

8. Procedure

8.1 Measure the burned gas parameter at different combustion ratios and determine that combustion ratio for which the parameter has a specified characteristic such as a maximum, minimum, or maximum rate of change.

8.1.1 Use an apparatus such as in Figs. 1 or 2 where the components of the apparatus meet the requirements of Section 6. If the apparatus has two flow meters, the combustion ratio is the ratio of the output of the air flow meter

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divided by the output of the fuel flow meter. If the apparatus has only one flow meter, then the combustion ratio is set numerically equal to either the output of the air flow meter or the reciprocal of the output of the fuel flow meter. The burned gas parameter is a function of the combustion ratio and is measured at different combustion ratios. The critical combustion ratio, R, is taken as that point where this function has a maximum value, minimum value, or maximum rate of change. The heating value, C, is calculated from the equation

$$C = F \cdot R + B,$$

where the constants B and F are determined as described in 9.1 and 9.2.

8.1.2 This procedure may be automated, for example, by using a microprocessor in the electronics.

8.2 For making laboratory measurements of highest precision, use the following procedure:

8.2.1 First calibrate the instrument as described in 9.2. Then, before measuring the test gases, measure two other standard gases of known heating value. After the test gas measurements, measure the two standard gases again. The known heating values of these standard gases, CAL.VAL. LOW and CAL.VAL.HIGH, should bracket that of the unknown gas. Combine the measured values of the standard gases and the test gases to obtain a best estimate of the heating value of the test gas. Do this using the following calculation procedure.

8.2.1.1 *Step 1*—There are four measured values for the calibration gases, two for the high calorific gas and two for the low calorific gas. Average these four measurements together. The result is represented by the symbol, AV.STD.GASES.

8.2.1.2 *Step 2*—Average the two known heating values of the standard gases together. The result is represented by the symbol, AV.CAL.VAL. Thus, AV.CAL.VAL = [(CAL.VAL. HIGH) + (CAL.VAL.LOW)]/2.

8.2.1.3 *Step 3*—Calculate a correction to the test gas measurements. This correction is represented by the symbol, CORR. The calculation is as follows: CORR = (AV.STD.GASES) − (AV.CAL.VAL).

8.2.1.4 *Step 4*—Subtract the quantity, CORR, that is calculated in Step 3 from each of the test gas measurements to give the corrected value.

8.2.2 *Example 1*—Standard gas low has CAL.VAL.LOW = 1000 Btu/standard cubic foot and measured values after calibration are 1002.0 and 1002.8. (All heating values in Example 1 and Example 2 have units of Btu per standard cubic foot.) Standard gas high has CAL.VAL.HIGH = 1200 and measured values of 1202.0 and 1203.2.

AV.STD.GASES = (1002.0 + 1002.8 + 1202.0 + 1203.2)/4 = 1102.5.
AV.CAL.VAL = (1000.0 + 1200.0)/2 = 1100.0
CORR = 1102.5 − 1100 = 2.5
TEST GAS MEASUREMENT = 1080.6
CORRECTED VALUE = (1080.6 − 2.5) = 1078.1

8.2.3 *Example 2:*

CAL.VAL.LOW = 1000 Btu/standard cubic foot.
Measured values are 998.0 and 998.2.
CAL.VAL.HIGH = 1200
Measured values are 1199.0 and 1199.2
AV.STD.VAL = (998.0 + 998.2 + 1199.0 + 1199.2)/4 = 1098.6
AV.CAL.VAL = 1100
CORR = (1098.6 − 1100) = 1.4
TEST GAS MEASUREMENT = 1076.7
CORRECTED VALUE = [1076.7 − (−1.4)] = 1078.1

9. Calibration and Standardization

9.1 The calibration factor, F, and the constant, B, in the equation, $C = F \cdot R + B$, are determined through an initial calibration, in which the critical combustion ratios of at least two standard gases of known but different heating values are measured using the procedure described in 8.1.

9.2 The calibration factor, F, is routinely redetermined at regular intervals under field conditions using a calibration gas of known heating value. The constant, B, is not adjusted in the routine calibrations. The interval between routine calibrations must be determined under the specific operating conditions, and is usually of the order of 24 h. Determination of F establishes the amount of net oxygen per standard volume of combustion air. Variations in net oxygen constant can be caused by several factors, such as changes in absolute humidity or the presence of contaminants in the air supply.

10. Precision and Bias

10.1 To determine precision and bias, an interlaboratory study was carried out using two types of commercial instruments that implement the stoichiometric method. For each type of instrument six different laboratories each measured five different reference gases. Cylinders containing these reference gases were transported from laboratory to laboratory. Each laboratory used its own instrument and personnel to measure the heating values of the gases in these cylinders. The same calibration gas was used to calibrate each instrument.

10.2 The heating values of the reference gases were determined prior to the study by the Institute of Gas Technology. These values were established by averaging three recording calorimeter measurements. The values were unknown to the participants in the interlaboratory test program. At the end of the study, the heating values were remeasured at the Institute of Gas Technology to establish that the gas compositions did not change. The statistical analysis of the results was in accordance with the procedures in Practice E 691.

10.2.1 *Repeatability*—The root mean square estimate of the within laboratory component of standard deviation was 0.76 Btu/standard cubic foot. The corresponding 95 % confidence repeatability interval was 2.1 Btu/standard cubic foot.

10.2.2 *Reproducibility*—The root mean square estimate of the between laboratory component of standard deviation was 1.67 Btu/standard cubic foot. The corresponding 95 % confidence reproducibility interval was 5.1 Btu/standard cubic foot.

10.2.3 *Bias*—The average of all measurements agreed with the average reference value within 0.1 %.

11. Keywords

11.1 natural gas range by stoichiometric conversion

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Standard Test Method for Horizontal Burning Characteristics of Cellular Polymeric Materials[1]

This standard is issued under the fixed designation D 4986; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This fire-test-response test method describes a small-scale horizontally oriented burning test procedure for comparing the relative rate of burning and the extent and time of burning of cellular polymeric materials having a density less than 250 kg/m^3.

1.2 The classification system described in the Appendix X1 is intended for quality assurance and the preselection of component materials for products.

1.3 *This standard measures and describes the response of materials, products, or assemblies to heat and flame under controlled conditions, but does not by itself incorporate all factors required for fire hazard or fire risk assessment of the materials, products, or assemblies under actual fire conditions.*

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For a specific hazard statement, see Note 2.

NOTE 1—This test method and ISO 9772 are equivalent.

2. Referenced Documents

2.1 *ASTM Standards:*

D 4483 Practice for Determining Precision for Test Method Standards in the Rubber and Carbon Black Industries[2]

D 5025 Specification for Laboratory Burner Used for Small-Scale Burning Tests on Plastic Materials[3]

E 176 Terminology to Fire Standards[4]

E 437 Specification for Industrial Wire Cloth and Screens (Square Opening Series)[5]

2.2 *ISO Standard:*

ISO 9772 Cellular Plastics—Determination of Horizontal Burning Characteristics of Small Specimens Subjected to a Small Flame[6]

3. Terminology

3.1 *Definitions*—For definitions of fire-related terms used in this test method, refer to Terminology E 176.

3.2 *afterflame time, n*—the length of time for which a material continues to flame, under specified conditions, after the ignition source has been removed.

3.3 *afterglow time, n*—the length of time for which a material continues to glow under specified test conditions, after the ignition source has been removed or cessation of flaming, or both.

3.4 *flame, vb*—to undergo combustion in the gaseous phase with emission of light.

3.5 *glow, n*—visible light, other than from flaming, emitted by a solid undergoing combustion.

4. Summary of Test Method

4.1 This test method for measuring the burning characteristics of cellular polymeric materials employs a small standard test specimen 50 by 150 mm. The specimen is supported horizontally. One end is exposed to a specified gas flame for 60 s and the extent of burning is measured.

5. Significance and Use

5.1 This test method provides a means of measuring the time and extent of burning for cellular polymeric materials. It also provides a means of measuring burning rates for materials that continue to burn past the specified gage marks.

5.2 This test method provides a means of comparing the burning characteristics of materials of like thickness density, cell size, and skin irregularities, including the effect of falling particles of cellular polymeric materials. It may be used for quality control, specification acceptance, and for research and development. Such materials may be filled or reinforced, rigid or flexible, cut or formed.

5.3 In this test method, the specimens are subjected to one or more specific sets of laboratory fire test exposure conditions. If different test conditions are substituted or if the anticipated end-use conditions are changed, it may not be

[1] This test method is under the jurisdiction of ASTM Committee D-20 on Plastics and is the direct responsibility of Subcommittee D20.30 on Thermal Properties.

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[2] *Annual Book of ASTM Standards*, Vol 09.01.

[3] *Annual Book of ASTM Standards*, Vol 08.03.

[4] *Annual Book of ASTM Standards*, Vol 04.07.

[5] *Annual Book of ASTM Standards*, Vol 14.02.

[6] Available from American National Standards Institute, 11 W. 42nd Street, 13th Floor, New York, NY 10036.

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possible from this test method to predict changes in the performance characteristics measured. Therefore, the results are strictly valid only for the fire test exposure conditions described in this procedure.

5.4 This test method is not intended to be a criterion for fire hazard. The fire hazard created by materials depends upon the form and end use of the material. Assessment of fire hazard includes, but is not limited to, many factors such as flame spread, burning rate, ease of ignition, fuel contribution, heat evolution, products of combustion, and others.

6. Apparatus

6.1 *Test Chamber*—A laboratory hood free of induced or forced draft during test. The hood shall be totally enclosed, with a heat-resistant transparent window for observing the test. Alternatively, the test may be conducted in a cabinet placed inside the hood. The cabinet should be constructed of noncombustible materials and should have a transparent window for observing the test. The cabinet must provide adequate ventilation for characteristic burning, but must not allow drafts across the burning specimen; therefore, a suitable damper may be necessary.

6.2 *Laboratory Burner*—Burner shall be constructed in accordance with Specification D 5025.

6.3 *Wing Top*—Wing top, having an opening 48 ± 1 mm in length by 1.3 ± 0.05 mm in width fitted to the burner. (See Fig. 1.)

6.4 *Gas Supply*—Methane gas, technical grade or natural gas having a heat content of 37 ± 1 MJ/m^3 with suitable regulator and meter for uniform gas flow.

6.5 *Wire Cloth*—Low-carbon, plain, steel wire, 6.4-mm mesh of 0.90 ± 0.05-mm wire diameter. The cloth mesh and wire diameter shall be determined in accordance with Specification E 437, Appendix X3. The wire cloth shall be cut to approximately 215 by 75 mm and shall be formed to provide a 90° bend at one end, 13 mm high. (See Fig. 1.)

6.6 *Support Fixture*—Any fixture that will support the wire cloth horizontally, 13 ± 1 mm above the burner wing top and 175 ± 25 mm above the base of the test chamber. Figure 2 shows one acceptable arrangement.

6.7 *Timing Device(s)*—Accurate to ±1 s.

6.8 *Linear Measuring Device*—Graduated in millimeters.

6.9 *Cotton*—A supply of dry, absorbent 100 % cotton.

6.10 *Desiccator*—Containing a suitable drying agent, capable of maintaining a relative humidity not exceeding 20 % at 23 ± 2°C.

6.11 *Conditioning Room or Chamber*—Capable of being maintained at 23 ± 2°C and a relative humidity of 50 ± 5 %.

6.12 *Conditioning Oven*—A full-draft circulating air oven capable of being maintained at 70 ± 2°C.

6.13 *Dial Gage Micrometer*—For measuring thicknesses with a 650-mm^2 pressure ft exerting a pressure of 0.175 ± 0.035 kPa.

7. Test Specimens

7.1 The standard test specimen shall be 150 ± 10 by 50 ± 1 mm, in the thickness appropriate to the objectives of the determination. Specimens tested in accordance with this test method are limited to a maximum thickness of 13 mm. Materials supplied in thicknesses over 13 mm, shall be cut to 13 ± 1 mm thickness with the skin on one side.

7.2 The surfaces of the specimen must be smooth and unbroken. Any loose particles shall be removed. The corner radius must not exceed 1.3 mm. Specimens with skin shall be tested skin side down.

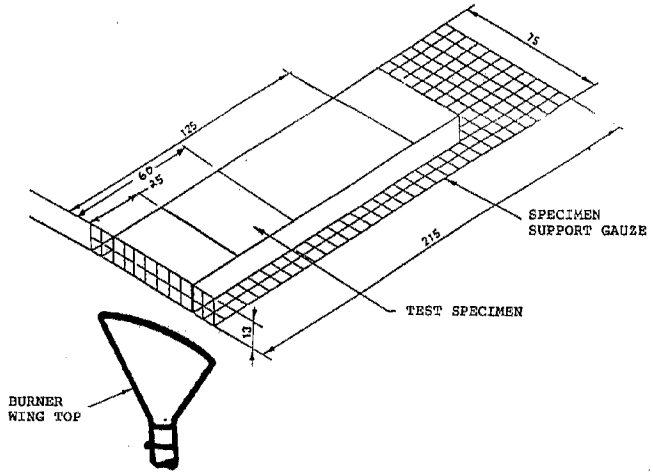
7.3 Five specimens per type of conditioning are to be tested, ten specimens in all.

8. Conditioning

8.1 Condition specimens as follows:

8.1.1 Condition one set of five specimens for at least 48 h at a temperature of 23 ± 2°C and a relative humidity of 50 ± 5 % prior to testing.

8.1.2 Condition a second set of five specimens in a circulating air oven for 168 ± 2 h at 70 ± 2°C, and then cool in a desiccator for at least 4 h at room temperature prior to testing.



NOTE—Dimensions in millimetres.

FIG. 1 Test Specimen and Specimen Support Gauze

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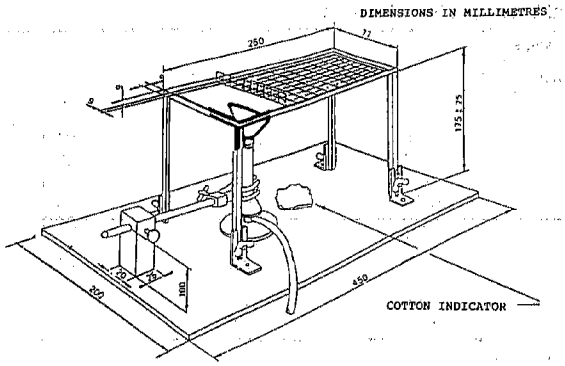


FIG. 2 Support Gauze Holder

8.2 All specimens shall be tested in a laboratory atmosphere of 15 to 35°C and 45 to 75 % relative humidity.

9. Procedure

NOTE 2: **Warning**—Conduct the burning test in an enclosed laboratory hood or cabinet free of induced or forced draft. An exhaust fan is required for removing the products of combustion which may be toxic, immediately after the test.

NOTE 3—To maintain a draft-free environment during the test, it may be necessary to install a damper in the exhaust duct which can be closed during the test.

9.1 Position the formed wire cloth in the support fixture so that the major section is horizontal and the upturned edge is nearest the burner. The bottom of the cloth shall be 13 ± 1 mm above the burner wing top and 175 mm above the base of the test chamber. Place 0.05 to 0.08 g of cotton thinned to an area approximately 75 × 75 mm and a maximum thickness of 6 mm. on the base of the test chamber under the front portion of the wire cloth having the upturned ends.

9.2 Mark the test specimen across its width with lines at 25 mm, 60 mm, and 125 mm from one end. Place the test specimen flat on the wire cloth with the 150 by 50-mm surface horizontal. The end of the specimen closer to the 60-mm mark is to be placed in contact with the upturned end of the wire cloth. (See Fig. 1.)

9.3 Place the burner, with wing top, remote from the specimen, ignite, and adjust it to produce a blue flame 38 mm high. Adjust the gas supply and the air ports of the burner until a yellow-tipped blue flame is produced, and then increase the air supply until the yellow tip just disappears. Measure the height of the flame, and, if necessary, readjust to obtain a flame 38 ± 2 mm high.

9.4 Place the burner under the upturned end of the wire cloth so that one edge of the flame is in line with the upturned end and the other edge of the flame extends into the front end of the specimen. (See Fig. 3.) The center of the wing top is to be in line with the longitudinal axis of the specimen.

9.5 Start the timing device(s) when the test flame is applied. Remove the flame after 60 s. Record the times when the flame reaches the 25-mm, 60-mm, or 125-mm mark, when the specimen extinguishes.

9.6 If the specimen burns past the 125-mm mark, the time for the specimen to burn from the 25-mm mark to the 125-mm mark is to be determined. Record the time, in seconds, as the burning time, *t*. Calculate the burning rate as 600/*t* cm/min.

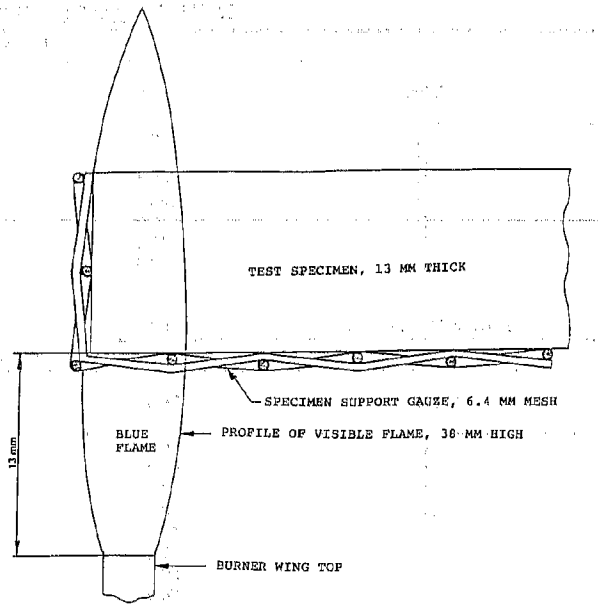


FIG. 3 Details of Flame and Relative Positions of Burner Wing Top, Test Specimen, and Specimen Support Gauze

9.7 If the specimen ceases to burn, the duration of the total afterflame plus afterglow time after removal of the test flame is to be recorded. The furthest distance affected by burning (flaming plus glowing) is to be measured and recorded. Also, it is to be noted whether or not the cotton placed 175 mm below the test specimen was ignited by flaming particles.

9.8 If the specimen does not burn after removal of the test flame, record the duration of afterflame time as zero. The furthest distance affected by burning is to be measured and recorded. Note whether or not the cotton was ignited.

9.9 Repeat the procedure in 9.1 through 9.8 on the four remaining specimens for each set. If a new wire cloth is not used for each test, any material remaining on the wire cloth from previous tests is to be burned off and the wire cloth allowed to cool to room temperature before conducting the test.

NOTE 4—When the test chamber is in continuous use, heating of the chamber may affect test results.

10. Report

10.1 The complete report shall include the following:

10.1.1 *Material Identification*—The generic description, manufacturer, commercial designation, lot number, color, conditioning, density, thickness, and the presence or absence of skin.

10.1.2 The burning rate of each specimen that has burned to the 125-mm mark.

10.1.3 The duration of afterflame and afterglow time and the distance affected for each specimen.

10.1.4 Whether or not any of the specimens drip flaming particles that ignite cotton.

10.1.5 Note any unusual burning phenomena, such as warpage, shrinkage, melting, or other atypical responses.

10.1.6 The statement: These data describe the response of materials to heat and flame under controlled laboratory conditions and should not be used for the appraisal or regulation of

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TABLE 1 Type 1 (Test) Horizontal Burning Characteristics

Part 1 Burn Times, s					
Material	Mean	Within Laboratories		Between Laboratories	
		Sr	*r*	*SR*	*R*
A	60.8	8.0	22.6	22.7	64.3
B	77.1	12.5	35.4	15.4	43.5
C	109.4	23.3	66.0	30.2	85.3
D	185.9	62.5	177.0	86.6	245.2
E	6.5	6.7	18.8	8.8	24.8
F	10.3	12.4	35.1	18.8	53.1
G	2.3	5.7	16.3	7.4	21.0
H	4.1	2.1	6.0	8.5	24.1
I	0.6	0.7	1.9	1.8	5.1
Average Pooled Values	50.8	23.4	66.1	32.9	93.0
Part 2 Burn Lengths, mm					
Material	Mean	Within Laboratories		Between Laboratories	
		Sr	*r*	*SR*	*R*
A	99.4	5.3	14.9	5.3	14.9
B	100.0	0.0	0.0	0.0	0.0
C	98.9	10.5	29.6	10.5	29.6
D	80.2	19.3	54.7	24.6	69.9
E	18.9	3.3	9.3	8.3	23.5
F	52.3	18.5	35.2	23.8	67.3
G	26.7	9.4	90.5	14.5	41.1
H	24.6	8.7	19.1	11.0	31.0
I	6.0	2.1	16.6	8.4	23.9
Average Pooled Values	56.3	10.7	30.3	14.1	39.8

Sr = Within-laboratory standard deviation.
r = Repeatability.
SR = Between-laboratory standard deviation.
R = Reproducibility.

the fire hazards associated with them under actual fire conditions.

10.1.7 If the material will be classified, indicate the category designation from the classification system in Appendix X1.

11. Precision and Bias

11.1 An interlaboratory test program was conducted to obtain precision data for this test method. Both precision and bias sections were prepared in accordance with Practice D 4483.

11.2 *Test Method:*

11.2.1 The interlaboratory program was a Type 1 precision conducted in 1990. Both repeatability and reproducibility were short term. A test result is the average value obtained from five determinations. A single test result was obtained for two fire test responses for all materials on each of two separate days.

11.2.2 Nine different materials were used in this study and nine laboratories participated in the interlaboratory program.

11.2.2.1 The precision results in this precision and bias section give an estimate of the precision of this test method with the materials used in this particular interlaboratory program. These precision parameters should not be used for acceptance or rejection testing of any group of materials without documentation that they are applicable.

11.2.3 All materials were prescreened for properties by one laboratory and then forwarded to a second laboratory. The second laboratory prepared all samples for testing and distributed them to the other participating laboratories. The test specimens only had to be conditioned in accordance with this test method prior to actual testing.

11.2.4 Material testing order was randomized.

11.2.5 The results of the precision calculations for repeatability and reproducibility are given in Table 1.

11.2.6 *Repeatability*—The repeatability, *r*, of this test method has been established in Table 1. Two single test results obtained within one laboratory that differ by more than this tabulated *r* (for any given material) must be considered to have come from different or nonidentical sample populations.

11.2.7 *Reproducibility*—The reproducibility, *R*, of this test method has been established in Table 1. Two single test results obtained in different laboratories that differ by more than this tabulated *R* (for any given material) must be considered to have come from different or nonidentical sample populations.

11.2.8 *Bias*—In test method terminology, bias is the difference between an average test value and the reference (true) test property value. Reference values do not exist for this test method since the value or level of the test property is exclusively defined by this test method. Bias, therefore, cannot exist.

12. Keywords

12.1 burning characteristics; burning rate; cellular materials; horizontal

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APPENDIX

(Nonmandatory Information)

X1. CLASSIFICATION SYSTEM FOR DETERMINING THE COMPARATIVE HORIZONTAL BURNING CHARACTERISTICS OF CELLULAR POLYMERIC MATERIALS

X1.1 This appendix describes a classification system that can be used to characterize the burning behavior of cellular materials, supported in a horizontal position, in response to a small flame ignition source. The use of a category designation code is optional and is determined by examining the test results of materials tested by this test method. Each category code represents a preferred range of performance levels that simplifies description in material designations or specifications and may assist certification bodies to determine compliance with applicable requirements.

X1.2 *Materials Classified HBF*—Materials classified HBF shall perform as follows:

X1.2.1 HBF materials shall not have any specimens with a burning rate exceeding 40 mm/min over a 100 mm span, or

X1.2.2 HBF materials shall have each specimen cease to burn before flaming or glowing reaches the 125 mm gage mark.

X1.3 If only one specimen from a set of five specimens does not comply with the requirements in X1.2, another set of five specimens, subjected to the same conditioning, shall be tested. All specimens from this second set of specimens shall comply with the requirements in X1.2 for the material in that thickness and density to be classed HBF.

X1.4 *Materials Classified HF1 and HF2*—Materials classified HF1 and HF2 shall be in compliance with Table X1.1.

TABLE X1 Material Classifications

Criteria Conditions	HF1	HF2
Afterflame time	4/5 is ≤2 s[A] 1/5 is ≤10 s[B]	4/5 is ≤2 s[A] 1/5 is ≤10 s[B]
Afterglow time for each individual specimen	≤30 s	≤30 s
Cotton indicator ignited by flaming particles or drops	No	Yes
Damaged length for each individual specimen	<60 mm	<60 mm

[A] 4/5—Four out of a set of five specimens.
[B] 1/5—One out of a set of five specimens.

X1.5 If a set of five specimens does not comply with the requirements in X1.4, because of one of the following situations, another set of five specimens subjected to the same conditioning shall be tested as follows:

X1.5.1 A single specimen flames for more than 10 s; or,

X1.5.2 Two specimens flame for more than 2 s but less than 10 s; or,

X1.5.3 One specimen flames for more than 2 s but less than 10 s, and a second specimen flames for more than 10 s; or,

X1.5.4 One specimen does not comply with the additional criteria in X1.4.

X1.6 All specimens from this second set shall comply with the requirements in X1.4 in order for the foamed plastic material in that thickness and density to be classed HF1 or HF2.

SUMMARY OF CHANGES

This section identifies the location of selected changes to this test method. For the convenience of the user, Committee D-20 has highlighted those changes that may impact the use of this test method. This section may also include descriptions of the changes or reasons for the changes, or both.

D 4986 – 98:

(*1*) Specified the density of a cellular material covered by this test method (1.1).

(*2*) Added an ISO equivalency statement (Note 1).

(*3*) Added an option to use a classification system to categorize materials (1.2, 10.1.7 and Appendix X1).

(*4*) Added a reference to ISO 9772 and removed the reference to ISO 3582 (2.2).

(*5*) Provided terminology for *afterflame time* and *afterglow time* (3.2 and 3.3).

(*6*) Deleted reference to joint task group with D 11.17 (5.4).

(*7*) Removed references to inch-pound units and added tolerances to critical dimensions for harmonization with ISO 9772.

(*8*) Added a Dial Gage Micrometer with a pressure foot to the Apparatus Section (6.13).

(*9*) Added requirements for the amount of cotton to be used (9.1).

(*10*) Added a marker line on the specimen at 60 mm from the upturned end of the wire cloth so that the material can be classified HF1 or HF2 (9.2, 9.5 and Appendix X1).

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CERTIFICATE

By Authority Of
THE UNITED STATES OF AMERICA
Legally Binding Document

By the Authority Vested By Part 5 of the United States Code § 552(a) and Part 1 of the Code of Regulations § 51 the attached document has been duly INCORPORATED BY REFERENCE and shall be considered legally binding upon all citizens and residents of the United States of America. *HEED THIS NOTICE*: Criminal penalties may apply for noncompliance.

Document Name: ASTM D512: Standard Test Methods for Chloride Ion In Water

CFR Section(s): 40 CFR 136.3(a)

Standards Body: American Society for Testing and Materials

APPROVED

Official Incorporator:
THE EXECUTIVE DIRECTOR
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WASHINGTON, D.C.

Designation: D 512 – 89 (Reapproved 1999)

Standard Test Methods for Chloride Ion In Water[1]

This standard is issued under the fixed designation D 512; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope *

1.1 These test methods cover the determination of chloride ion in water, wastewater (Test Method C only), and brines. The following three test methods are included:

	Sections
Test Method A (Mercurimetric Titration)	7 to14
Test Method B (Silver Nitrate Titration)	15 to 21
Test Method C (Ion-Selective Electrode Method)	22 to 29

1.2 Test Methods A, B, and C were validated under Practice D2777 – 77, and only Test Method B conforms also to Practice D 2777 – 86. Refer to Sections 14, 21, and 29 for further information.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For a specific hazard statement, see 26.1.1.

1.4 A former colorimetric test method was discontinued. Refer to Appendix X1 for historical information.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1066 Practice for Sampling Steam[2]

D 1129 Terminology Relating to Water[2]

D 1193 Specification for Reagent Water[2]

D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water[2]

D 3370 Practices for Sampling Water from Closed Conduits[2]

D 4127 Terminology Used with Ion-Selective Electrodes[2]

3. Terminology

3.1 *Definitions*—For definitions of terms used in these test methods, refer to Terminologies D 1129 and D 4127.

4. Significance and Use

4.1 Chloride ion is under regulation in water, and must, therefore, be measured accurately. It is highly detrimental to high-pressure boiler systems and to stainless steel, so monitoring is essential for prevention of damage. Chloride analysis is widely used as a tool for estimating the cycles of concentration, such as in cooling tower applications. Processing waters and pickling solutions used in the food processing industries also require dependable methods of analysis for chloride.

5. Purity of Reagents

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[3] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 *Purity of Water*— Unless otherwise indicated, all references to water shall be understood to mean Type II reagent water conforming to Specification D 1193.

6. Sampling

6.1 Collect the sample in accordance with Practice D 1066 and Practices D 3370, as applicable.

TEST METHOD A—MERCURIMETRIC TITRATION[4]

7. Scope

7.1 This test method can be used to determine chloride ion in water, provided interferences are absent (see Section 9).

7.2 Though not specified in the research report, the precision statement is presumed to have been obtained using Type II reagent water. It is the responsibility of the analyst to assure the validity of this test method for untested matrices.

7.3 This test method was validated for the concentration

[1] These test methods are under the jurisdiction of ASTM Committee D-19 on Water and are the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

[4] For information of interest in connection with this test method, and supporting data, refer to Clark, F. E., "Determination of Chloride in Water," *Analytical Chemistry*, Vol 22, April 1950, pp. 553–555, and Vol 22, November 1950, p. 1458.

***A Summary of Changes section appears at the end of this standard.**

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range 8.0 to 250 mg/L Cl^-.

8. Summary of Test Method

8.1 Dilute mercuric nitrate solution is added to an acidified sample in the presence of mixed diphenylcarbazone-bromophenol blue indicator. The end point of the titration is the formation of the blue-violet mercury diphenylcarbazone complex.

9. Interferences

9.1 The anions and cations generally found in water offer no interference. Zinc, lead, nickel, and ferrous and chromous ions affect solution and end-point colors, but do not reduce the accuracy of the titration when present in concentrations up to 100 mg/L. Copper is tolerable up to 50 mg/L. Titration in the presence of chromate ion requires indicator with extra background color (alphazurine) and prior reduction for concentrations above 100 mg/L. Ferric ion above 10 mg/L must be reduced before titration, and sulfite ion must be oxidized. Bromide and fluoride will be partially titrated with the chloride. Quaternary ammonium salts also interfere if present in significant amounts (1 to 2 mg/L). Deep color may also interfere.

10. Apparatus

10.1 *Microburet*, 1 or 5-mL, with 0.01-mL graduation intervals.

11. Reagents and Materials

11.1 *Hydrogen Peroxide* (30 % H_2O_2).

11.2 *Hydroquinone Solution* (10 g/L)—Dissolve 1 g of purified hydroquinone in water and dilute to 100 mL.

11.3 *Mercuric Nitrate Solution, Standard (0.025N)*—Dissolve 4.2830 g of mercuric nitrate ($Hg(NO_3)_2 \cdot H_2O$) in 50 mL of water acidified with 0.5 mL of concentrated nitric acid (HNO_3, sp gr 1.42). Dilute the acidified $Hg(NO_3)_2$ solution with water to 1 L. Filter if necessary, and standardize against the standard sodium chloride (NaCl) solution, using the procedure described in Section 12 (see Note 1).

NOTE 1—*Sharpness of End Point*—The end point, while sharp, can be improved somewhat for certain types of water by adding several drops of a 0.05-g/L solution of xylene cyanole FF or alphazurine blue-green dye (color index 714) to the titration sample.

11.4 *Mixed Indicator Solution* [5]—Dissolve 0.5 g of crystalline diphenylcarbazone and 0.05 g of bromophenol blue powder in 75 mL of ethyl alcohol (95 %), and dilute to 100 mL with the alcohol (Note 2). Store in a brown bottle and discard after 6 months (Note 3).

NOTE 2—Methanol, isopropanol, or ethanol denatured with either methanol or isopropanol (Formula 3A) may be used if pure ethyl alcohol is not available. Other denatured ethanol formulae are not suitable.

NOTE 3—Liquid indicator generally deteriorates to the point that it yields no end-point color after 12 to 18 months of storage. High temperature (above 37.8°C (100°F)) and exposure to bright light may shorten storage life. A dry powder mixture of the two indicator ingredients is stable for much longer periods. Both the powder mixture (capsule form) and the liquid indicator are available commercially.

11.5 *Nitric Acid (3 + 997)*—Mix 3 volumes of concentrated nitric acid (HNO_3, sp gr 1.42) with 997 volumes of water.

11.6 *pH Indicating Paper*, long-range type, covering a pH range 1 to 11.

11.7 *Sodium Chloride Solution, Standard* (0.025*N*)—Dry several grams of sodium chloride (NaCl) for 1 h at 600°C. Dissolve 1.4613 g of the dry salt in water, and dilute to 1 L at 25°C in a volumetric flask.

11.8 *Sodium Hydroxide Solution* (10 g/L)—Dissolve 10 g of sodium hydroxide (NaOH) in water and dilute to 1 L.

12. Procedure

12.1 Use a volume of sample such that it will contain not more than 20 mg of chloride ion, diluting the sample with water to approximately 50-mL volume if necessary. Determine an indicator blank on 50 mL of chloride-free water, applying the same procedure followed for the sample.

12.2 Add 5 to 10 drops of mixed indicator solution, and shake or swirl the flask. If a blue-violet or red color develops, add HNO_3 (3 + 997) dropwise until the color changes to yellow. Add 1 mL of excess acid. If a yellow or orange color forms immediately on addition of the mixed indicator, add NaOH solution (10 g/L) dropwise until the color changes to blue-violet; then add HNO_3 (3 + 997) dropwise until the color changes to yellow and further add 1 mL excess of acid (Note 4).

NOTE 4—The prescribed acidification provides a satisfactory pH range from 3.0 to 3.5. Acidified samples on which electrometric pH measurements have been made shall not be used for chloride determinations, because the use of the calomel reference electrode may introduce error due to chloride contamination. For precise pH adjustment of samples having a low-chloride concentration, instrumental measurements may be made on one sample aliquot to determine treatment needed for another to be used for the chloride test.

12.3 Titrate the solution and a blank with 0.025 *N* $Hg(NO_3)_2$ solution until a blue-violet color, as viewed by transmitted light, persists throughout the solution (Note 5). Record the millilitres of $Hg(NO_3)_2$ solution added in each case.

NOTE 5—The use of indicator modifications and the presence of heavy metal ions can change solution colors without affecting accuracy of the determination. For example, solutions containing alphazurine may be bright blue when neutral, grayish purple when basic, blue-green when acidic, and blue-violet at the chloride end point. Solutions containing about 100 mg/L nickel ion and normal mixed indicator are purple when neutral, green when acid, and gray at the chloride end point. When applying this test method to samples that contain colored ions or that require modified indicator, it is recommended that the operator be familiar with the specific color changes involved by experimenting with solutions prepared as standards for comparison of color effects.

12.4 If chromate ion is present in the absence of iron and in concentration less than 100 mg/L, use the alphazurine modified mixed indicator (Note 1) and acidify the sample as described in 12.2 but to pH 3 as indicated by pH indicating paper. Titrate the solution as described in 12.3, but to an olive-purple end point.

12.5 If chromate ion is present in the absence of iron and in concentration greater than 100 mg/L, add 2 mL of fresh

[5] This diphenylcarbazone 1-bromophenol blue indicator is covered by U.S. Patent No. 2,784,064.

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hydroquinone solution and proceed as described in 12.2 and 12.3.

12.6 If ferric ion is present in the absence or presence of chromate ions, use a sample of such volume as to contain no more than 2.5 mg of ferric ion or of ferric ion plus chromate ion. Add 2 mL of fresh hydroquinone solution, and proceed as described in 12.2 and 12.3.

12.7 If sulfite ion is present, add 0.5 mL of H_2O_2 to 50 mL of the sample in the Erlenmeyer flask and mix for 1 min. Then proceed as described in 12.2 and 12.3.

13. Calculation

13.1 Calculate the chloride ion concentration, in milligrams per litre, in the original sample as follows:

$$\text{Chloride, mg/L} = [(V_1 - V_2) \times N \times 35\,453]/S$$

where:

V_1 = standard $Hg(NO_3)_2$ solution required for titration of the sample, mL,
V_2 = standard $Hg(NO_3)_2$ solution required for titration of the blank, mL,
N = normality of the $Hg(NO_3)_2$ solution, and
S = sample used in 12.1, mL.

14. Precision and Bias [6]

14.1 *Precision Statement*—The precision of this test method may be expressed as follows:

$$S_T = 0.023X + 0.43$$
$$S_O = 0.002X + 0.46$$

where:

S_T = overall precision, mg/L,
S_O = single-operator precision, mg/L, and
X = concentration of chloride ion determined.

14.2 *Bias Statement*— Recoveries of known amounts of chloride were as follows:

Amount Added, mg/L	Amount Found, mg/L	± % Bias	Statistically Significant (95 % Confidence Level)
250	248	−0.80	no
80.0	79.3	−0.88	no
8.00	7.51	−6.13	yes

14.3 The information presented in 14.1 and 14.2 is derived from round-robin testing in which five laboratories, including seven operators, participated. Though not clearly specified in the test report, the matrix is presumed to be Type II reagent water. Of seven data sets ranked as described in Practice D 2777, none was rejected, nor were any data points determined to be "outliers." Three sample levels were run on at least three days. The method of "least squares" was used to determine the precision statement, with correlation of 0.7394 for S_O and 0.9993 for S_T.

14.4 It is the responsibility of the analyst to assure the validity of this test method for untested matrices.

14.5 Precision and bias for this test method conforms to Practice D 2777 – 77, which was in place at the time of collaborative testing. Under the allowances made in 1.5 of Practice D 2777 – 86, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D–19 test methods.

[6] Supporting data are available from ASTM Headquarters. Request RR: D19-1076.

TEST METHOD B—SILVER NITRATE TITRATION

15. Scope

15.1 This test method[7] is intended primarily for water where the chloride content is 5 mg/L or more, and where interferences such as color or high concentrations of heavy metal ions render Test Method A impracticable.

15.2 Though not specified in the research report, the precision and bias statement is presumed to have been obtained using Type II reagent water. It is the responsibility of the analyst to assure the validity of this test method for untested matrices.

15.3 This test method was validated for the concentration range 8.0 to 250 mg/L Cl^-.

16. Summary of Test Method

16.1 Water adjusted to approximately pH 8.3 is titrated with silver nitrate solution in the presence of potassium chromate indicator. The end point is indicated by persistence of the brick-red silver chromate color.

17. Interferences

17.1 Bromide, iodide, and sulfide are titrated along with the chloride. Orthophosphate and polyphosphate interfere if present in concentrations greater than 250 and 25 mg/L, respectively. Sulfite and objectionable color or turbidity must be eliminated. Compounds which precipitate at pH 8.3 (certain hydroxides) may cause error by occlusion.

18. Reagents

18.1 *Hydrogen Peroxide* (30 %) (H_2O_2).

18.2 *Phenolphthalein Indicator Solution* (10 g/L)—Prepare as directed in Methods E 200.

18.3 *Potassium Chromate Indicator Solution*—Dissolve 50 g of potassium chromate (K_2CrO_4) in 100 mL of water, and add silver nitrate ($AgNO_3$) until a slight red precipitate is produced. Allow the solution to stand, protected from light, for at least 24 h after the addition of $AgNO_3$. Then filter the solution to remove the precipitate, and dilute to 1 L with water.

18.4 *Standard Solution, Silver Nitrate (0.025 N)*—Crush approximately 5 g of silver nitrate ($AgNO_3$) crystals and dry to constant weight at 40°C. Dissolve 4.2473 g of the crushed, dried crystals in water and dilute to 1 L. Standardize against the standard NaCl solution, using the procedure given in Section 19.

18.5 *Standard Solution, Sodium Chloride* (0.025 *N*)— Prepare as described in 11.7.

18.6 *Sodium Hydroxide Solution* (10 g/L)—Prepare as described in 11.8.

18.7 *Sulfuric Acid* (1 + 19)—Carefully add 1 volume of concentrated sulfuric acid (H_2SO_4, sp gr 1.84) to 19 volumes of water, while mixing.

[7] Mohr, F., *ANN.*, 97, 335 (1856).

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19. Procedure

19.1 Pour 50 mL, or less, of the sample, containing not more than 20 nor less than 0.25 mg of chloride ion, into a white porcelain container (see Note 6). If sulfite ions are present, add 0.5 mL of hydrogen peroxide (H_2O_2) to the sample, mix, and let stand for 1 min. Dilute to approximately 50 mL with water, if necessary. Adjust the pH to the phenolphthalein end point (pH 8.3), using H_2SO_4, (1 + 19) or NaOH solution (10 g/L).

NOTE 6—An 80 mL white porcelain dish, a 1-in stirrer bar, and a magnetic stirrer have been found useful for this purpose.

19.2 Add approximately 1.0 mL of K_2CrO_4 indicator solution and mix. Add standard $AgNO_3$ solution dropwise from a 25-mL buret until the brick-red (or pink) color persists throughout the sample when illuminated with a yellow light or viewed with yellow goggles.

19.3 Repeat the procedure described in 19.1 and 19.2, using exactly one half as much original sample, diluted to 50 mL with water.

19.4 If the volume of titrant used in 19.3 is one-half of that used in titrating the aliquot in 19.1, proceed to the calculation section. If not, significant interferences are present and compensation must be made; alternatively, another method must be used.

20. Calculation

20.1 Calculate the chloride ion concentration in the original sample, in milligrams per litre as follows:

$$\text{Chloride, mg/L} = [(V_1 - V_2) \times N \times 70\ 906]/S$$

where:

V_1 = standard solution $AgNO_3$ added in titrating the sample prepared in 19.1, mL,
V_2 = standard solution, $AgNO_3$ added in titrating the sample prepared in 19.3, mL,
N = normality of standard $AgNO_3$ solution, and
S = original sample in the 50-mL test specimen prepared in 19.1, mL.

21. Precision and Bias [6]

21.1 *Precision*—The precision of this test method may be expressed as follows:

$$S_T = 0.013X + 0.70$$
$$S_O = 0.007X + 0.53$$

where:

S_T = overall precision, mg/L,
S_O = single-operator precision, mg/L, and
X = concentration of chloride ion determined.

21.2 *Bias*—Recoveries of known amounts of chloride were as follows:

Amount Added, mg/L	Amount Found, mg/L	± % Bias	Statistically Significant (95 % Confidence Level)
250	248	−0.80	yes
80.00	79.1	−1.13	yes
8.00	7.77	−2.88	yes

21.3 The information in 21.2 is derived from round-robin testing in which six laboratories, including ten operators, participated. Though not clearly specified in the test report, the matrix is presumed to be Type II reagent water. Of ten data sets ranked as described in Practice D 2777, none was rejected, but one data point was determined to be an "outlier." Three sample levels were run on at least three days.

The method of least squares was used to determine the precision statement, with correlation of 0.9959 for S_O and 0.9940 for S_T.

21.4 It is the responsibility of the analyst to assure the validity of this test method for untested matrices.

TEST METHOD C—ION-SELECTIVE ELECTRODE

22. Scope

22.1 This test method is applicable to the measurement of chloride ion in natural waters, drinking water, and waste waters.

22.2 Samples containing 2 to 1000 mg/L of chloride may be analyzed by this test method. The concentration range may be extended by dilution of an appropriate aliquot before the addition of the ionic strength adjustor.

22.3 The precision and bias statements were obtained using reagent water and a water matrix of choice that included natural and waste waters. It is the responsibility of the analyst to determine the acceptability of this test method for the matrix being analyzed.

23. Summary of Test Method

23.1 Chloride ion is measured potentiometrically using a chloride ion-selective electrode in conjunction with a double junction, sleeve-type reference electrode. Potentials are read using a pH meter having an expanded millivolt scale, or a selective-ion meter having a direct concentration scale for chloride.

23.2 The electrodes are calibrated in known chloride solutions, and the concentrations of unknowns are determined in solutions with the same background. Samples and standards should be at the same temperature.

23.3 Standards and samples are diluted with an ionic strength adjustor that also minimizes possible interferences such as ammonia, bromide, iodide, cyanide, or sulfide.

24. Interferences

24.1 There is no interference from up to 500 mg/L of sulfide, 1000 mg/L of bromide or iodide, a hundredfold excess of cyanide over chloride, or from 1000 mg/L of ammonia.

25. Apparatus

25.1 *pH Meter*, with expanded millivolt scale. This test method can be adapted for use with a *selective-ion meter.*

25.2 *Chloride Ion-Selective Electrode*, having a light-desensitized silver chloride (AgCl) membrane. Not all chloride ion-selective electrodes are suitable for this test method, since the ionic strength adjustor is incompatible with some membranes. In particular, silver chloride/silver sulfide membranes are inappropriate, since the sulfide can be oxidized by the ionic strength adjustor.

25.3 *Sleeve-Type Double Junction Reference Electrode*, using solution prepared in 26.4 as the outer sleeve filling solution.

NOTE 7—Other types of double junction reference electrodes may be

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suitable, but supporting data included in this test method reflect only the recommended type.

25.4 *Mixer*, magnetic, with a TFE-fluorocarbon-coated stirring bar.

26. Reagents

26.1 *Chloride Ionic Strength Adjustor (CISA)*—Dissolve 15.1 g of sodium bromate in 800 mL of water. Add 75 mL of concentrated nitric acid (HNO_3, sp. gr 1.42) (Note 8). Stir well. Dilute with water to 1 L. Store CISA in a polyethylene or glass container.

NOTE 8—For low-level chloride measurement (less than 5 mg/L) the nitric acid used must not contain more than 0.005 % chloride and the sodium bromate must not contain more than 0.003 % chloride. A test for reagent purity is included in this test method.

26.1.1 **Caution**—Sodium bromate is a strong oxidant and should be handled appropriately. Also note that preparation and dilutions of CISA should be made in a well-ventilated area, preferably a hood.

26.2 *Chloride Solution, Stock* (1000 mg/L)—Dissolve 1.648 g of sodium chloride (dried for 1 h at 600°C), in water in a volumetric flask and dilute to 1 L.

26.3 *Chloride Solutions, Standard* (100, 10, and 1 mg/L)—Using volumetric pipets, transfer 100, 10, and 1.0 mL of the chloride stock solution into separate 1-L volumetric flasks and dilute each to 1 L with water.

26.4 *Double-Junction Reference Electrode Outer Filling Solution*—Dilute 1 volume of CISA (26.1) with 1 volume of water.

27. Calibration

27.1 Mix equal volumes of the 1000 mg/L of chloride standard solution, and CISA reagent. Do the same for each of the other three standards.

27.2 Mix equal volumes of water and CISA reagent.

27.3 Place the electrodes in the solution from 27.2, stir well, wait 3 to 5 min, and record the millivolt reading. This solution contains no added chloride, and the potential reading will not be very stable.

27.4 Rinse the electrodes thoroughly, place them in the 1 mg Cl^-/L-CISA mixture and stir well. Wait 1 to 2 min and record the result.

27.4.1 If the difference in readings between 27.3 and 27.4 is less than 15 mV, there is chloride contamination of the reagent that will affect low-level readings, and purer reagents must be obtained.

27.5 Rinse the electrodes, place them in the 10 mg Cl -/LCISA mixture and stir well. Wait 1 min and record the results.

27.6 Repeat 27.5 with 100 and 1000 mg Cl^-/L-CISA mixtures.

27.7 Prepare a calibration curve by plotting, on semilogarithmic graph paper, the potential observed (on the linear scale) versus the concentration of each of the standards used (on the logarithmic scale). Note that volume corrections are incorporated into the calibration, so that samples analyzed in accordance with Section 28 can be read directly.

28. Procedure

28.1 Mix the sample with an equal volume of CISA reagent, and stir thoroughly for 1 to 2 min.

28.2 Insert the electrodes, wait 1 to 2 min, and record the reading.

28.3 Read chloride concentration of the sample in milligrams per litre directly from the calibration curve.

29. Precision and Bias [6]

29.1 *Precision*—The overall and single-operator precision of this test method, within its designated range, varies with the quantity tested, as shown in Fig. 1, for reagent water, and in Fig. 2, for selected water matrices. These matrices included natural and waste waters.

29.2 *Bias*—Recoveries of known amounts of chloride from reagent water and selected water matrices are as shown in Table 1.

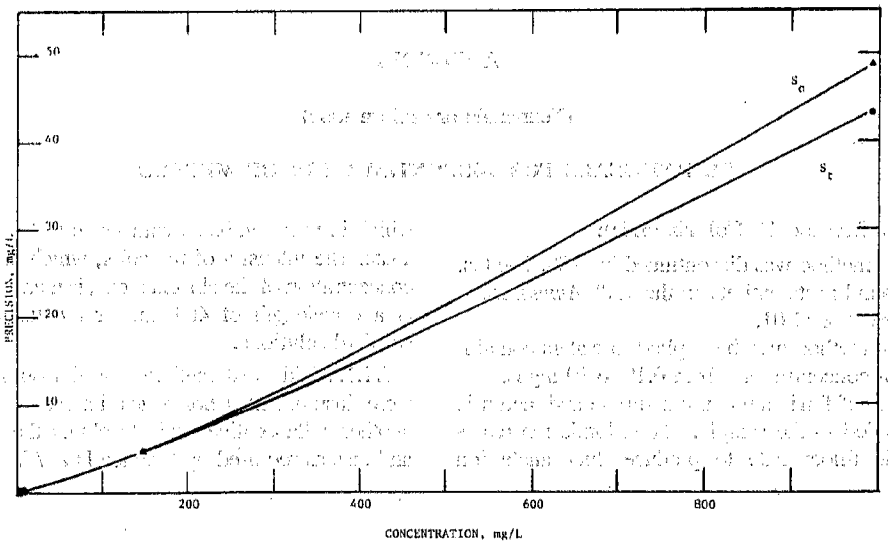


FIG. 1 Interlaboratory Precision for Chloride Found in Reagent Water (Ion Selective Electrode)

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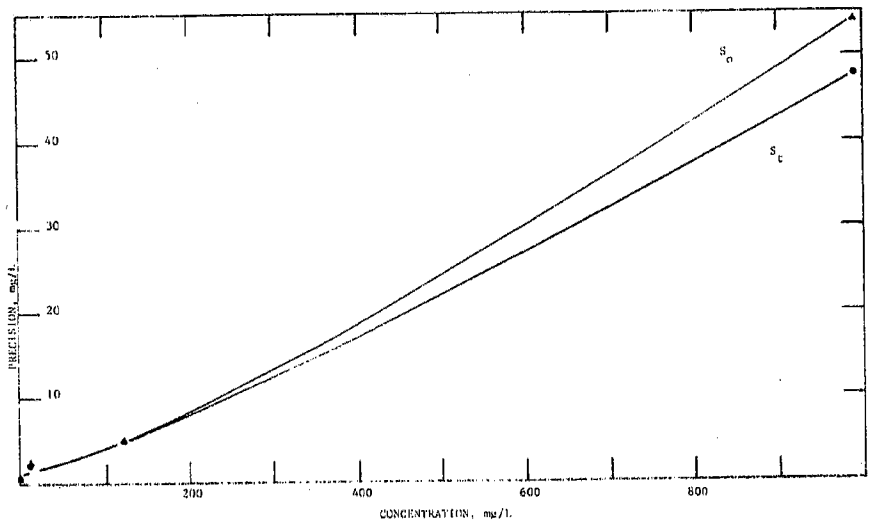


FIG. 2 Interlaboratory Precision for Chloride Found in Selected Water Matrices (Ion Selective Electrode)

TABLE 1 Determination of Bias (Ion Selective Electrode)

	Amount Added, mg/L	Amount Found, mg/L	Bias, ± %	Statistically Significant (95 % Confidence Level)
Reagent water	1.1	1.03	−6.4	no
	10.0	9.94	−0.6	no
	150	148.8	−0.8	no
	1000	992	−0.8	no
Water matrices	1.1	1.04	−5.5	no
	10.0	10.24	+2.4	no
	150	146.0	−2.7	no
	1000	991	−0.9	no

29.3 The information in Table 1 is derived from round-robin testing in which five laboratories, including seven operators, participated. Of seven data sets ranked as described in Practice D 2777, none was rejected in the case of reagent water and one was rejected in the case of selected water matrices. Eight "outlier" data points within the sets were also rejected. Four sample levels were run on three days, and blanks were obtained for the water used.

29.4 It is the responsibility of the analyst to assure the validity of this test method for untested matrices.

29.5 Precision and bias for this test method conforms to Practice D 2777 – 77, which was in place at the time of collaborative testing. Under the allowances made in 1.5 of Practice D 2777 – 86, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D–19 test methods.

30. Keywords

30.1 analysis; chloride; electrode; titrametric; water

APPENDIX

(Nonmandatory Information)

X1. RATIONALE FOR DISCONTINUATION OF METHOD

X1.1 Former Test Method C (Colorimetric):

X1.1.1 This test method was discontinued in 1988. The test method may be found in its entirety in the 1988 *Annual Book of ASTM Standards*, Vol 11.01.

X1.1.2 This test method may be applied to waters containing chloride ion in concentrations from 0.10 to 10 mg/L.

X1.1.3 Solutions of ferric ammonium sulfate and mercuric thiocyanate are added to the sample. The chloride ion reacts with the mercuric thiocyanate to produce thiocyanate ion which in turn combines with ferric to form red ferric thiocyanate. The intensity of the color, which is proportional to the concentration of the chloride ions, is measured photometrically at a wavelength of 463 nm, or by visual comparison with standard solutions.

X1.1.4 This test method was discontinued because there were insufficient laboratories interested in participating in another collaborative study to obtain the necessary precision and bias as required by Practice D 2777.

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SUMMARY OF CHANGES

This section identifies the location of selected changes to these test methods that have been incorporated since the last issue. For the convenience of the user, Committee D–19 has highlighted those changes that may impact the use of these test methods. This section may also include descriptions of the changes or reasons for the changes, or both.

(1) Subsequent to round robin testing, waters tested and ranges used were revised.

(2) The equation in 20.1 was revised from a previously rounded value.

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