EXHIBIT 152
PART 3

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Standard Test Method for Analysis of Natural Gas by Gas Chromatography[1]

This standard is issued under the fixed designation D 1945; 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 chemical composition of natural gases and similar gaseous mixtures within the range of composition shown in Table 1. This test method may be abbreviated for the analysis of lean natural gases containing negligible amounts of hexanes and higher hydrocarbons, or for the determination of one or more components, as required.

1.2 The values stated in SI units are to be regarded as the 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.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 2597 Test Method for Analysis of Demethanized Hydrocarbon Liquid Mixtures Containing Nitrogen and Carbon Dioxide by Gas Chromatography[2]

D 3588 Practice for Calculating Heat Value, Compressibility Factor, and Relative Density (Specific Gravity) of Gaseous Fuels[3]

E 260 Practice for Packed Column Gas Chromatography[4]

3. Summary of Test Method

3.1 Components in a representative sample are physically separated by gas chromatography (GC) and compared to calibration data obtained under identical operating conditions from a reference standard mixture of known composition. The numerous heavy-end components of a sample can be grouped into irregular peaks by reversing the direction of the carrier gas through the column at such time as to group the heavy ends either as C_5 and heavier, C_6 and heavier, or C_7 and heavier. The composition of the sample is calculated by comparing either the peak heights, or the peak areas, or both, with the corresponding values obtained with the reference standard.

4. Significance and Use

4.1 This test method is of significance for providing data for calculating physical properties of the sample, such as heating value and relative density, or for monitoring the concentrations of one or more of the components in a mixture.

5. Apparatus

5.1 *Detector*—The detector shall be a thermal-conductivity type, or its equivalent in sensitivity and stability. The thermal conductivity detector must be sufficiently sensitive to produce a signal of at least 0.5 mV for 1 mol % *n*-butane in a 0.25-mL sample.

5.2 *Recording Instruments*—Either strip-chart recorders or electronic integrators, or both, are used to display the separated components. Although a strip-chart recorder is not required when using electronic integration, it is highly desirable for evaluation of instrument performance.

5.2.1 The recorder shall be a strip-chart recorder with a full-range scale of 5 mV or less (1 mV preferred). The width of the chart shall be not less than 150 mm. A maximum pen response time of 2 s (1 s preferred) and a minimum chart speed of 10 mm/min shall be required. Faster speeds up to 100 mm/min are desirable if the chromatogram is to be interpreted using manual methods to obtain areas.

5.2.2 *Electronic or Computing Integrators*—Proof of separation and response equivalent to that for a recorder is required for displays other than by chart recorder. Baseline tracking with tangent skim peak detection is recommended.

5.3 *Attenuator*—If the chromatogram is to be interpreted using manual methods, an attenuator must be used with the detector output signal to maintain maximum peaks within the recorder chart range. The attenuator must be accurate to within 0.5 % between the attenuator range steps.

5.4 *Sample Inlet System:*

5.4.1 The sample inlet system shall be constructed of materials that are inert and nonadsorptive with respect to the components in the sample. The preferred material of construction is stainless steel. Copper, brass, and other copper-bearing alloys are unacceptable. The sample inlet system from the cylinder valve to the GC column inlet must be maintained at a temperature constant to ±1°C.

5.4.2 Provision must be made to introduce into the carrier gas ahead of the analyzing column a gas-phase sample that has been entrapped in a fixed volume loop or tubular section. The fixed loop or section shall be so constructed that the total volume, including dead space, shall not normally exceed 0.5 mL at 1 atm. If increased accuracy of the hexanes and heavier portions of the analysis is required, a larger sample size may be used (see Test Method D 2597). The sample volume must be reproducible such that successive runs agree within 1 % on each component. A flowing sample inlet system is acceptable as long as viscosity effects are

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[1] This test method is under the jurisdiction of ASTM Committee D-3 on Gaseous Fuels and is the direct responsibility of Subcommittee D 03.07 on Analysis of Chemical Composition of Gaseous Fuels.

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

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

[4] *Annual Book of ASTM Standards*, Vol 14.02.

TABLE 1 Natural Gas Components and Range of Composition Covered

Component	Mol %
Helium	0.01 to 10
Hydrogen	0.01 to 10
Oxygen	0.01 to 20
Nitrogen	0.01 to 100
Carbon dioxide	0.01 to 20
Methane	0.01 to 100
Ethane	0.01 to 100
Hydrogen sulfide	0.3 to 30
Propane	0.01 to 100
isobutane	0.01 to 10
n-Butane	0.01 to 10
neoPentane	0.01 to 2
isoPentane	0.01 to 2
n-Pentane	0.01 to 2
Hexane isomers	0.01 to 2
Heptanes plus	0.01 to 1

accounted for.

NOTE 1—The sample size limitation of 0.5 mL or smaller is selected relative to linearity of detector response, and efficiency of column separation. Larger samples may be used to determine low-quantity components in order to increase measurement accuracy.

5.4.3 An optional manifold arrangement for entering vacuum samples is shown in Fig. 1.

5.5 *Column Temperature Control:*

5.5.1 *Isothermal*—When isothermal operation is utilized, maintain the analyzer columns at a temperature constant to 0.3°C during the course of the sample run and corresponding reference run.

5.5.2 *Temperature Programming*—Temperature programming may be used, as feasible. The oven temperature shall not exceed the recommended temperature limit for the materials in the column.

5.6 *Detector Temperature Control*—Maintain the detector temperature at a temperature constant to 0.3°C during the course of the sample run and the corresponding reference run. The detector temperature shall be equal to or greater than the maximum column temperature.

5.7 *Carrier Gas Controls*—The instrument shall be equipped with suitable facilities to provide a flow of carrier gas through the analyzer and detector at a flow rate that is constant to 1 % throughout the analysis of the sample and the reference standard. The purity of the carrier gas may be improved by flowing the carrier gas through selective filters prior to its entry into the chromatograph.

5.8 *Columns:*

5.8.1 The columns shall be constructed of materials that are inert and nonadsorptive with respect to the components in the sample. The preferred material of construction is stainless steel. Copper and copper-bearing alloys are unacceptable.

5.8.2 An adsorption-type column and a partition-type column may be used to make the analysis.

NOTE 2—See Practice E 260.

5.8.2.1 *Adsorption Column*—This column must completely separate oxygen, nitrogen, and methane. A 13X molecular sieve 80/100 mesh is recommended for direct injection. A 5A column can be used if a pre-cut column is present to remove interfering hydrocarbons. If a recorder is used, the recorder pen must return to the baseline between each successive peak. The resolution (R) must be 1.5 or greater as calculated in the following equation:

$$R(1,2) = \frac{x_2 - x_1}{y_2 + y_1} \times 2, \qquad (1)$$

where x_1, x_2 are the retention times and y_1, y_2 are the peak widths. Figure 2 illustrates the calculation for resolution. Figure 3 is a chromatogram obtained with an adsorption column.

5.8.2.2 *Partition Column*—This column must separate ethane through pentanes, and carbon dioxide. If a recorder is used, the recorder pen must return to the base line between each peak for propane and succeeding peaks, and to base line within 2 % of full-scale deflection for components eluted ahead of propane, with measurements being at the attenuation of the peak. Separation of carbon dioxide must be sufficient so that a 0.25-mL sample containing 0.1-mol % carbon dioxide will produce a clearly measurable response. The resolution (R) must be 1.5 or greater as calculated in the above equation. The separation should be completed within 40 min, including reversal of flow after *n*-pentane to yield a group response for hexanes and heavier components. Figures

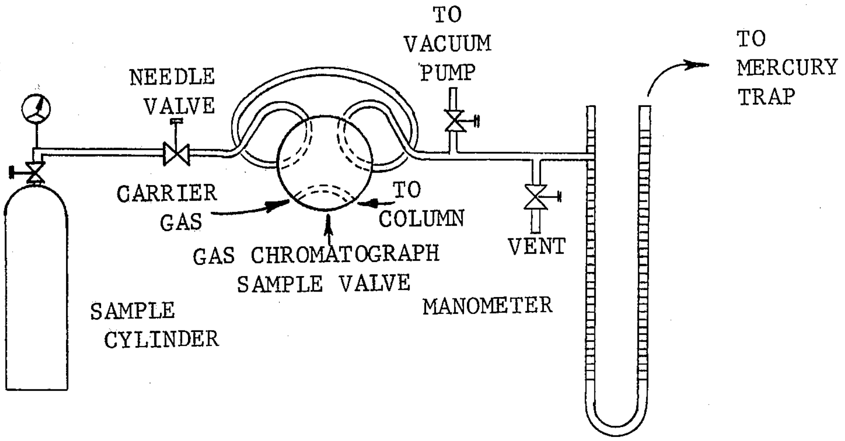


FIG. 1 Suggested Manifold Arrangement for Entering Vacuum Samples

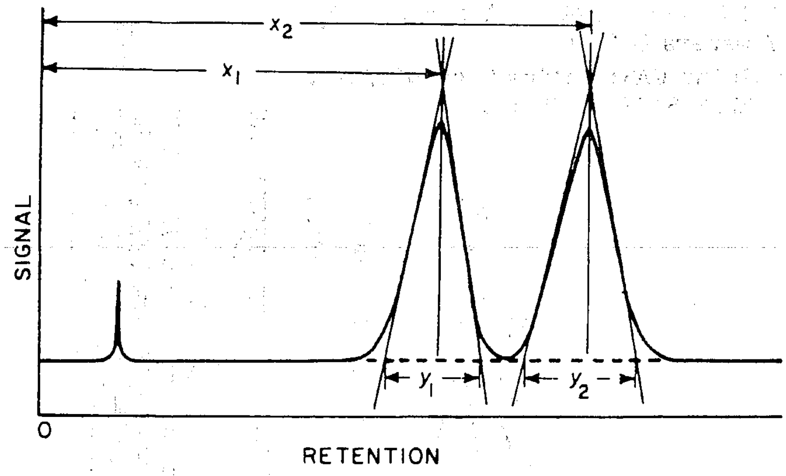


FIG. 2 Calculation for Resolution

4, 5, and 6 are examples of chromatograms obtained on some of the suitable partition columns.

5.8.3 *General*—Other column packing materials that provide satisfactory separation of components of interest may be utilized (see Fig. 7). In multi-column applications, it is preferred to use front-end backflush of the heavy ends.

NOTE 3—The chromatograms in Figs. 3 through 8 are only illustrations of typical separations. The operating conditions, including columns, are also typical and are subject to optimization by competent personnel.

5.9 *Drier*—Unless water is known not to interfere in the analysis, a drier must be provided in the sample entering system, ahead of the sample valve. The drier must remove moisture without removing selective components to be determined in the analysis.

NOTE 4—See Annex A2.2 for preparation of a suitable drier.

5.10 *Valves*—Valves or sample splitters, or both, are required to permit switching, backflushing, or for simultaneous analysis.

5.11 *Manometer*—May be either U-tube type or well type equipped with an accurately graduated and easily read scale covering the range 0 to 900 mm (36 in.) of mercury or larger. The U-tube type is useful, since it permits filling the sample loop with up to two atmospheres of sample pressure, thus extending the range of all components. The well type inherently offers better precision and is preferred when calibrating with pure components. Samples with up to one

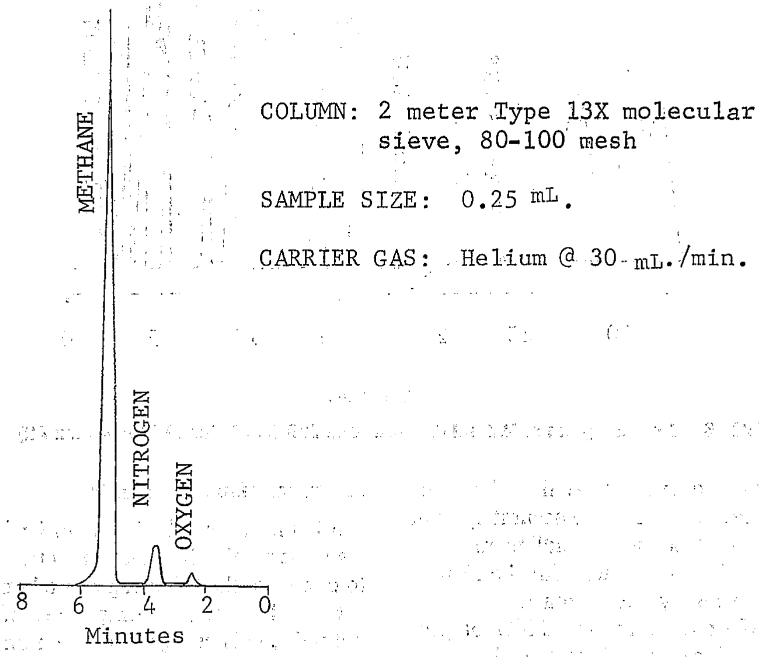
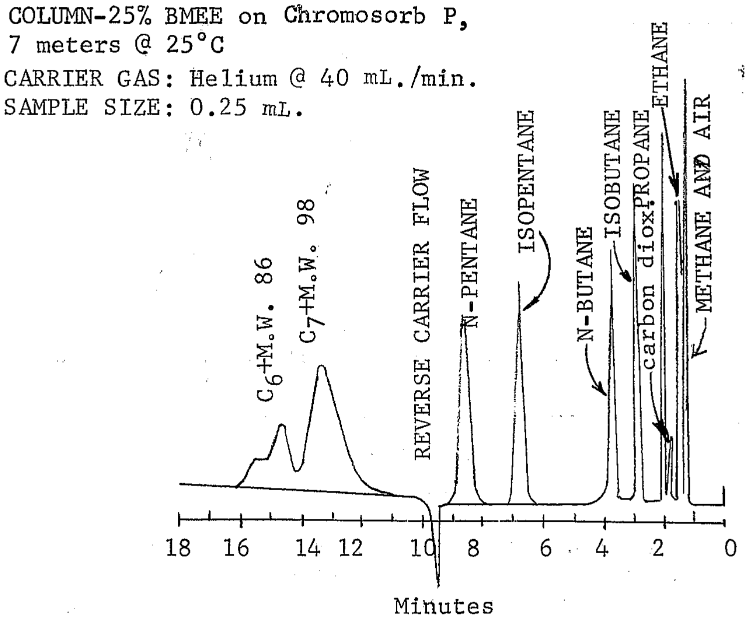


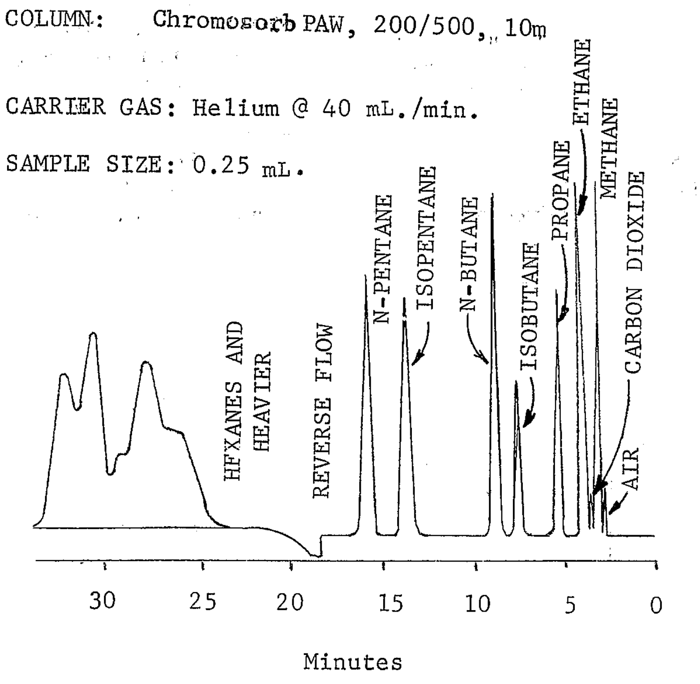
FIG. 3 Separation Column for Oxygen, Nitrogen, and Methane (See Annex A2)


COLUMN-25% BMEE on Chromosorb P, 7 meters @ 25°C

CARRIER GAS: Helium @ 40 mL./min.

SAMPLE SIZE: 0.25 mL.

FIG. 4 Chromatogram of Natural Gas (BMEE Column) (See Annex A2)


COLUMN: Chromosorb PAW, 200/500, 10m

CARRIER GAS: Helium @ 40 mL./min.

SAMPLE SIZE: 0.25 mL.

FIG. 5 Chromatogram of Natural Gas (Silicone 200/500 Column) (See Annex A2)

atmosphere of pressure can be entered. With either type manometer the mm scale can be read more accurately than the inch scale. Caution should be used handling mercury because of its toxic nature. Avoid contact with the skin as much as possible. Wash thoroughly after contact.

5.12 *Vacuum Pump*—Must have the capability of producing a vacuum of 1 mm of mercury absolute or less.

6. Preparation of Apparatus

6.1 *Linearity Check*—In order to establish linearity of response for the thermal conductivity detector, it is necessary to complete the following procedure:

6.1.1 The major component of interest (methane for natural gas) is charged to the chromatograph by way of the fixed-size sample loop at partial pressure increments of 13

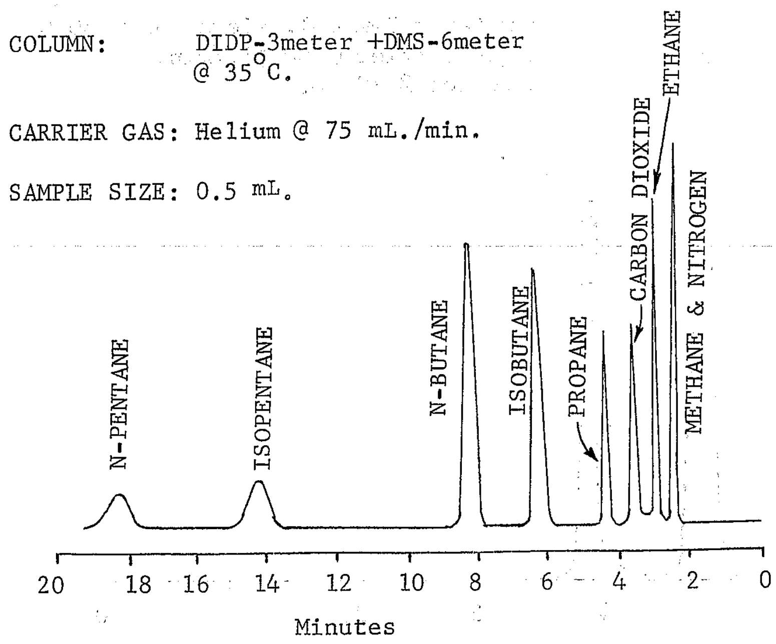


FIG. 6 Chromatogram of Natural Gas (See Annex A2)

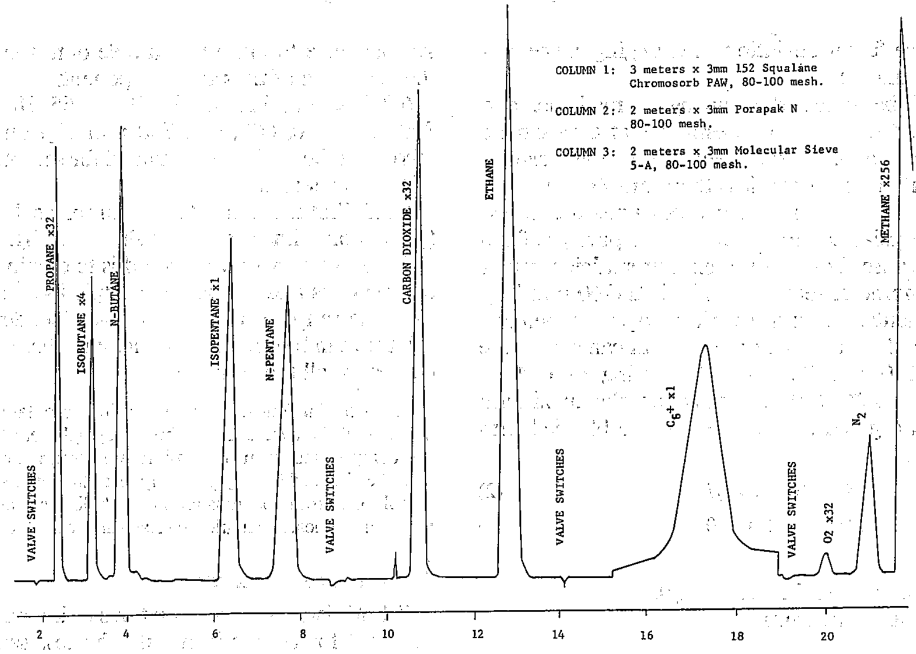


FIG. 7 Chromatogram of Natural Gas (Multi-Column Application) (See Annex A2)

kPa (100 mm Hg) from 13 to 100 kPa (100 to 760 mm Hg) or the prevailing atmospheric pressure.

6.1.2 The integrated peak responses for the area generated at each of the pressure increments are plotted versus their partial pressure (see Fig. 9).

6.1.3 The plotted results should yield a straight line. A perfectly linear response would display a straight line at a 45° angle using the logarithmic values.

6.1.4 Any curved line indicates the fixed volume sample loop is too large. A smaller loop size should replace the fixed volume loop and 6.1.1 through 6.1.4 should be repeated (see Fig. 9).

6.1.5 The linearity over the range of interest must be known for each component. It is useful to construct a table

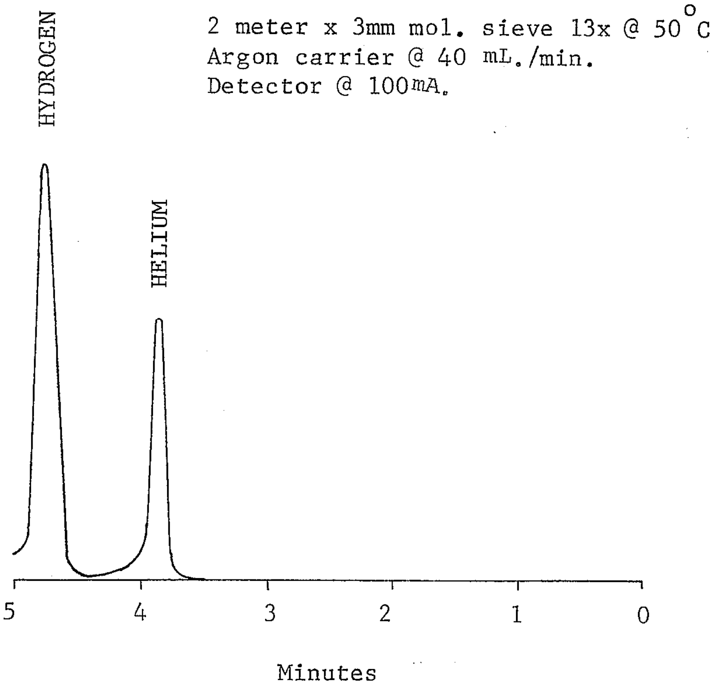


FIG. 8 Separation of Helium and Hydrogen

noting the response factor deviation in changing concentration. (See Table 2 and 3).

6.1.6 It should be noted that nitrogen, methane, and ethane exhibit less than 1 % compressibility at atmospheric pressure. Other natural gas components do exhibit a significant compressibility at pressures less than atmospheric.

6.1.7 Most components that have vapor pressures of less than 100 kPa (15 psia) cannot be used as a pure gas for a linearity study because they will not exhibit sufficient vapor pressure for a manometer reading to 100 kPa (760 mm Hg). For these components, a mixture with nitrogen or methane can be used to establish a partial pressure that can extend the total pressure to 100 kPa (760 mm Hg). Using Table 4 for vapor pressures at 38°C (100°F), calculate the maximum pressure to which a given component can be blended with nitrogen as follows:

$$B = (100 \times V)/i \quad (2)$$

$$P = (i \times M)/100 \quad (3)$$

where:

B = blend pressure, max, kPa (mm Hg),
V = vapor pressure, kPa (mm Hg),
i = mol %
P = partial pressure, kPa (mm Hg), and
M = manometer pressure, kPa (mm Hg).

6.2. *Procedure for Linearity Check:*

6.2.1 Connect the pure-component source to the sample-entry system. Evacuate the sample-entry system and observe the manometer for leaks. (See Fig. 1 for a suggested manifold arrangement.) The sample-entry system must be vacuum tight.

6.2.2 Carefully open the needle valve to admit the pure component up to 13 kPa (100 mm Hg) of partial pressure.

6.2.3 Record the exact partial pressure and actuate the sample valve to place the sample onto the column. Record the peak area of the pure component.

6.2.4 Repeat 6.2.3 for 26, 39, 52, 65, 78, and 91 kPa (200, 300, 400, 500, 600, and 700 mm Hg) on the manometer, recording the peak area obtained for sample analysis at each of these pressures.

6.2.5 Plot the area data (x axis) versus the partial pressures (y axis) on a linear graph as shown in Fig. 9.

6.2.6 An alternative method is to obtain a blend of all the components and charge the sample loop at partial pressure over the range of interest. If a gas blender is available the mixture can be diluted with methane thereby giving response curves for all the components.

NOTE 5: **Caution**—If it is not possible to obtain information on the linearity of the available gas chromatograph detector for all of the test gas components, then as a minimum requirement the linearity data must be obtained for any gas component that exceeds a concentration of 5 mol %. Chromatographs are not truly linear over wide concentration ranges and linearity should be established over the range of interest.

7. Reference Standards

7.1 Moisture-free gas mixtures of known composition are required for comparison with the test sample. They must contain known percents of the components, except oxygen (Note 6), that are to be determined in the unknown sample. All components in the reference standard must be homogenous in the vapor state at the time of use. The concentration of a component in the reference standard gas should not be less than one half nor more than twice the concentration of the corresponding component in the test gas.

NOTE 6—Unless the reference standard is stored in a container that has been tested and proved for inertness to oxygen, it is preferable to calibrate for oxygen by an alternative method.

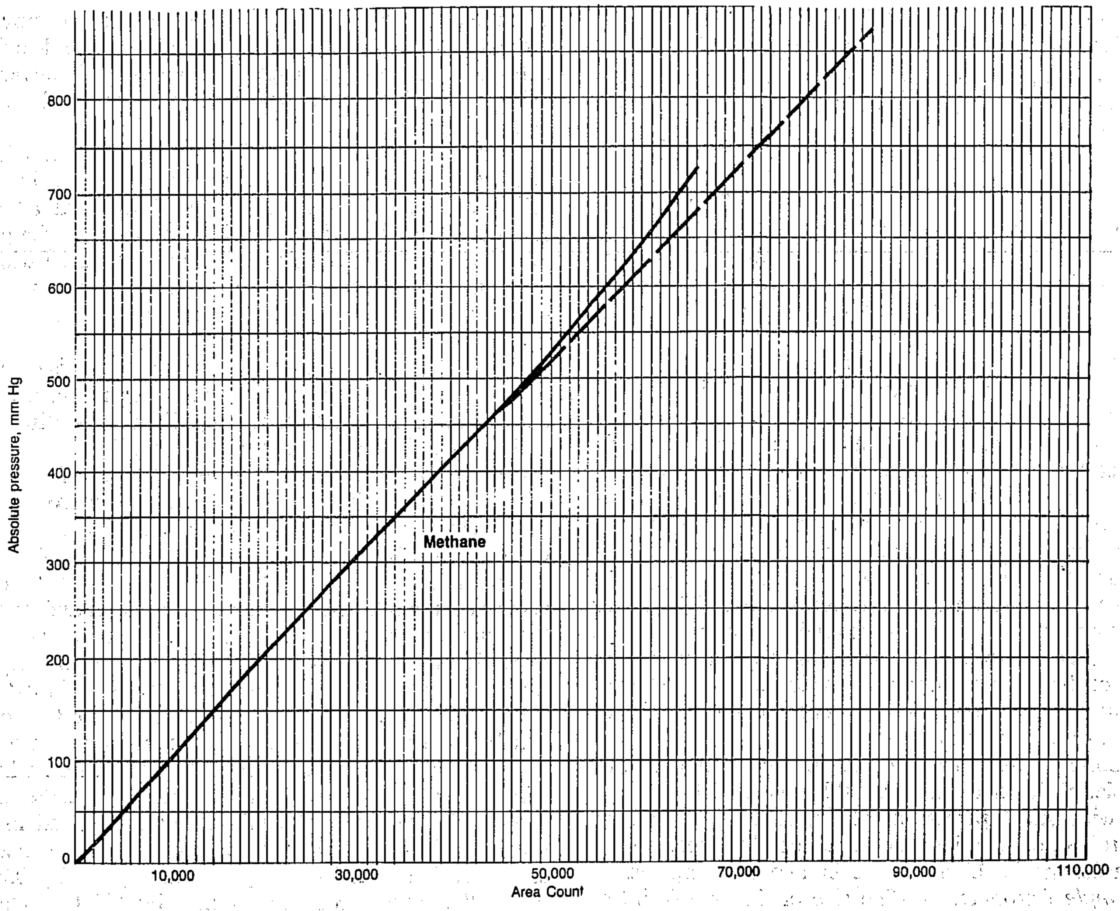


FIG. 9 Linearity of Detector Response

TABLE 2 Linearity Evaluation of Methane

S/B diff = (low mole % − high mole %)/low mole % × 100

B area	S mole %	S/B mole %/area	S/B diff., % on low value
223119392	51	2.2858e-07	
242610272	56	2.3082e-07	−0.98
261785320	61	2.3302e-07	−0.95
280494912	66	2.3530e-07	−0.98
299145504	71	2.3734e-07	−0.87
317987328	76	2.3900e-07	−0.70
336489056	81	2.4072e-07	−0.72
351120721	85	2.4208e-07	−0.57

TABLE 3 Linearity Evaluation for Nitrogen

S/B diff = (low mole % − high mole %)/low mole % × 100

B area	S mole %	S/B mole %/area	S/B diff., % on low value
5879836	1	1.7007e-07	
29137066	5	1.7160e-07	−0.89
57452364	10	1.7046e-07	−1.43
84953192	15	1.7657e-07	−1.44
111491232	20	1.7939e-07	−1.60
137268784	25	1.8212e-07	−1.53
162852288	30	1.8422e-07	−1.15
187232496	35	1.8693e-07	−1.48

TABLE 4 Vapor Pressure at 38°C (100°F)[A]

Component	kPa absolute	psia
Nitrogen	>34 500	>5 000
Methane	>34 500	>5 000
Carbon dioxide	>5 520	>800
Ethane	>5 520	>800
Hydrogen sulfide	2 720	395
Propane	1 300	189
Isobutane	501	72.6
n-Butane	356	51.7
Isopentane	141	20.5
n-Pentane	108	15.6
n-Hexane	34.2	4.96
n-Heptane	11.2	1.62

[A] The most recent data for the vapor pressures listed are available from the Thermodynamics Research Center, Texas A&M University System, College Station, TX 77843.

7.2 *Preparation*—A reference standard may be prepared by blending pure components. Diluted dry air is a suitable standard for oxygen and nitrogen (see 8.5.1).[5,6]

8. Procedure

8.1 *Instrument Preparation*—Place the proper column(s) in operation as needed for the desired run (as described in either 8.4, 8.5, or 8.6). Adjust the operating conditions and

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[5] A suitable reference standard is available from Phillips Petroleum Co., Borger, TX 79007.

[6] A ten-component reference standard traceable to the National Institute of Standards and Technology (NIST) is available from Institute of Gas Technology (IGT), 3424 S. State St., Chicago, IL 60616.

allow the chromatograph to stabilize.

8.1.1 For hexanes and higher, heat the sample loop.

NOTE 7—Most modern chromatographs have valve ovens that can be temperature controlled. It is strongly recommended in the absence of valve ovens to mount the gas sampling valve in the chromatograph oven and operate at the column temperature.

8.1.2 After the instrument has apparently stabilized, make check runs on the reference standard to establish instrument repeatability. Two consecutive checks must agree within 1 % of the amount present of each component. Either the average of the two consecutive checks, or the latest check agreeing within 1 % of the previous check on each component may be used as the reference standard for all subsequent runs until there is a change in instrument operating conditions. Daily calibrations are recommended.

8.2 *Sample Preparation*—If desired, hydrogen sulfide may be removed by at least two methods (see Annex A2.3).

8.2.1 *Preparation and Introduction of Sample*—Samples must be equilibrated in the laboratory at 20–50°F above the source temperature of the field sampling. The higher the temperature the shorter the equilibration time (approximately two hours for small sample containers of 300 mL or less). This analysis method assumes field sampling methods have removed entrained liquids. If the hydrocarbon dewpoint of the sample is known to be lower than the lowest temperature to which the sample has been exposed, it is not necessary to heat the sample.

8.2.2 Connections from the sample container to the sample inlet of the instrument should be made with stainless steel or with short pieces of TFE-fluorocarbon. Copper, vinyl, or rubber connections are not acceptable. Heated lines may be necessary for high hydrocarbon content samples.

8.3 *Sample Introduction*—The size of the sample introduced to the chromatographic columns shall not exceed 0.5 mL. (This small sample size is necessary to obtain a linear detector response for methane.) Sufficient accuracy can be obtained for the determination of all but the minor constituents by the use of this sample size. When increased response is required for the determination of components present in concentrations not exceeding 5 mol %, it is permissible to use sample and reference standard volumes not exceeding 5 mL. (Avoid introduction of liquids into the sample system.)

8.3.1 *Purging Method*—Open the outlet valve of the sample cylinder and purge the sample through the inlet system and sample loop or tube. The amount of purging required must be established and verified for each instrument. The sample loop pressure should be near atmospheric. Close the cylinder valve and allow the pressure of the sample in the loop or tube to stabilize. Then immediately inject the contents of the loop or tube into the chromatographic column to avoid infiltration of contaminants.

8.3.2 *Water Displacement*—If the sample was obtained by water displacement, then water displacement may be used to purge and fill the sample loop or tube.

NOTE 8: **Caution**—Some components, such as carbon dioxide, hydrogen sulfide, and hexanes and higher hydrocarbons, may be partially or completely removed by the water.

8.3.3 *Evacuation Method*—Evacuate the charging system, including the sample loop, and the sample line back to the valve on the sample cylinder, to less than 0.1 kPa (1 mm Hg) absolute pressure. Close the valve to the vacuum source and carefully meter the fuel-gas sample from the sample cylinder until the sample loop is filled to the desired pressure, as indicated on the manometer (see Fig. 1). Inject the sample into the chromatograph.

8.4 *Partition Column Run for Ethane and Heavier Hydrocarbons and Carbon Dioxide* —This run is made using either helium or hydrogen as the carrier gas; if other than a thermal conductivity detector is used, select a suitable carrier gas for that detector. Select a sample size in accordance with 8.1. Enter the sample, and backflush heavy components when appropriate. Obtain a corresponding response on the reference standard.

8.4.1 Methane may also be determined on this column if the column will separate the methane from nitrogen and oxygen (such as with silicone 200/500 as shown in Fig. 5), and the sample size does not exceed 0.5 mL.

8.5 *Adsorption Column Run for Oxygen, Nitrogen, and Methane*—Make this run using helium or hydrogen as the carrier gas. The sample size must not exceed 0.5 mL for the determination of methane. Enter the sample and obtain a response through methane (Note 6). Likewise, obtain a response on the reference standard for nitrogen and methane. Obtain a response on dry air for nitrogen and oxygen, if desired. The air must be either entered at an accurately measured reduced pressure, or from a helium-diluted mixture.

8.5.1 A mixture containing approximately 1 % of oxygen can be prepared by pressurizing a container of dry air at atmospheric pressure to 2 MPa (20 atm) with pure helium. This pressure need not be measured precisely, as the concentration of nitrogen in the mixture thus prepared must be determined by comparison to nitrogen in the reference standard. The percent nitrogen is multiplied by 0.268 to obtain the mole percent of oxygen, or by 0.280 to obtain the mole percent total of oxygen and argon. Do not rely on oxygen standards that have been prepared for more than a few days. It is permissible to use a response factor for oxygen that is relative to a stable constituent.

8.6 *Adsorption Column Run for Helium and Hydrogen*—Make this run using either nitrogen or argon as the carrier gas. Enter a 1 to 5-mL sample and record the response for helium, followed by hydrogen, which will be just ahead of oxygen (Note 6). Obtain a corresponding response on a reference standard containing suitable concentrations of helium and hydrogen (see Fig. 8).

9. Calculation

9.1 The number of significant digits retained for the quantitative value of each component shall be such that accuracy is neither sacrificed or exaggerated. The expressed numerical value of any component in the sample should not be presumed to be more accurate than the corresponding certified value of that component in the calibration standard.

9.2 *External Standard Method:*

9.2.1 *Pentanes and Lighter Components*—Measure the height of each component peak for pentanes and lighter, convert to the same attenuation for corresponding components in the sample and reference standard, and calculate the concentration of each component in the sample as follows:

$$C = S \times (A/B) \tag{4}$$

where:

C = component concentration in the sample, mol %,
A = peak height of component in the sample, mm,
B = peak height of component in the standard, mm, and
S = component concentration in the reference standard, mol %.

9.2.1.1 If air has been run at reduced pressure for oxygen or nitrogen calibration, or both, correct the equation for pressure as follows:

$$C = S \times (A/B) \times (P_a/P_b) \qquad (5)$$

where:

P_a = pressure at which air is run, and
P_b = true barometric pressure during the run, with both pressures being expressed in the same units.

9.2.1.2 Use composition values of 78.1 % nitrogen and 21.9 % oxygen for dry air, because argon elutes with oxygen on a molecular sieves column under the normal conditions of this test method.

9.2.2 *Hexanes and Heavier Components*—Measure the areas of the hexanes portion and the heptanes and heavier portion of the reverse-flow peak (see Annex A1, Fig. A1.1, and Appendix X3.6). Also measure the areas of both pentane peaks on the sample chromatogram, and adjust all measured areas to the same attenuation basis.

9.2.3 Calculate corrected areas of the reverse flow peaks as follows:

$$\text{Corrected } C_6 \text{ area} = 72/86 \times \text{measured } C_6 \text{ area} \qquad (6)$$

$$\text{Corrected } C_7 \text{ and heavier area} = 72/A \times \text{measured } C_7 \text{ and heavier area} \qquad (7)$$

where A = average molecular weight of the C_7 and heavier fraction.

NOTE 9—The value of 98 is usually sufficiently accurate for use as the C_7 and heavier fraction average molecular weight; the small amount of C_8 and heavier present is usually offset by the lighter methyl cyclopentane and cyclohexane that occur in this fraction. A more accurate value for the molecular weight of C_7 and heavier can be obtained as described in Annex A1.3.

9.2.4 Calculate the concentration of the two fractions in the sample as follows:

$$\text{Mol \% } C_6 = (\text{corrected } C_6 \text{ area}) \times (\text{mol \% } iC_5 + nC_5)/(iC_5 + nC_5 \text{ area}). \qquad (8)$$

$$\text{Mol \% } C_7{+} = (\text{corrected } C_7 \text{ area}) \times (\text{mol \% } iC_5 + nC_5)/(iC_5 + nC_5 \text{ area}). \qquad (9)$$

9.2.4.1 If the mole percent of iC_5 + nC_5 has been determined by a separate run with a smaller sized sample, this value need not be redetermined.

9.2.5 The entire reverse flow area may be calculated in this manner as C_6 and heavier, or as C_5 and heavier should the carrier gas reversal be made after *n*-butane. The measured area should be corrected by using the average molecular weights of the entire reverse-flow components for the value of A. The mole percent and area of the iC_5 and nC_5 reverse flow peak of an identically sized sample of reference standard (free of C_6 and heavier) shall then be used for calculating the final mole percent value.

9.2.6 Normalize the mole percent values by multiplying each value by 100 and dividing by the sum of the original values. The sum of the original values should not differ from 100.0 % by more than 1.0 %.

9.2.7 See sample calculations in Appendix X2.

10. Precision

10.1 *Precision*—The precision of this test method, as determined by the statistical examination of the interlaboratory test results, for gas samples of pipeline quality 38 MJ/m^3 (1000 Btu/SCF) is as follows:

10.1.1 *Repeatability*—The difference between two successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials should be considered suspect if they differ by more than the following amounts:

Component, mol %	Repeatability
0 to 0.1	0.01
0.1 to 1.0	0.04
1.0 to 5.0	0.07
5.0 to 10	0.08
Over 10	0.10

10.1.2 *Reproducibility*—The difference between two results obtained by different operators in different laboratories on identical test materials should be considered suspect if they differ by more than the following amounts:

Component, mol %	Reproducibility
0 to 0.1	0.02
0.1 to 1.0	0.07
1.0 to 5.0	0.10
5.0 to 10	0.12
Over 10	0.15

11. Keywords

11.1 gas analysis; gas chromatography; natural gas composition

ANNEXES

(Mandatory Information)

A1. SUPPLEMENTARY PROCEDURES

A1.1 Analysis for only Propane and Heavier Components

A1.1.1 This determination can be made in 10 to 15-min run time by using column conditions to separate propane, isobutane, *n*-butane, isopentane, *n*-pentane, hexanes and heptanes, and heavier, but disregarding separation on ethane and lighter.

A1.1.2 Use a 5-m bis-(2(2-methoxyethoxy) ethyl)ether (BMEE) column at about 30°C, or a suitable length of another partition column that will separate propane through *n*-pentane in about 5 min. Enter a 1 to 5-mL sample into the column and reverse the carrier gas flow after *n*-pentane is separated. Obtain a corresponding chromatogram on the reference standard, which can be accomplished in about 5-min run time, as there is no need to reverse the flow on the reference standard. Make calculations in the same manner as for the complete analysis method.

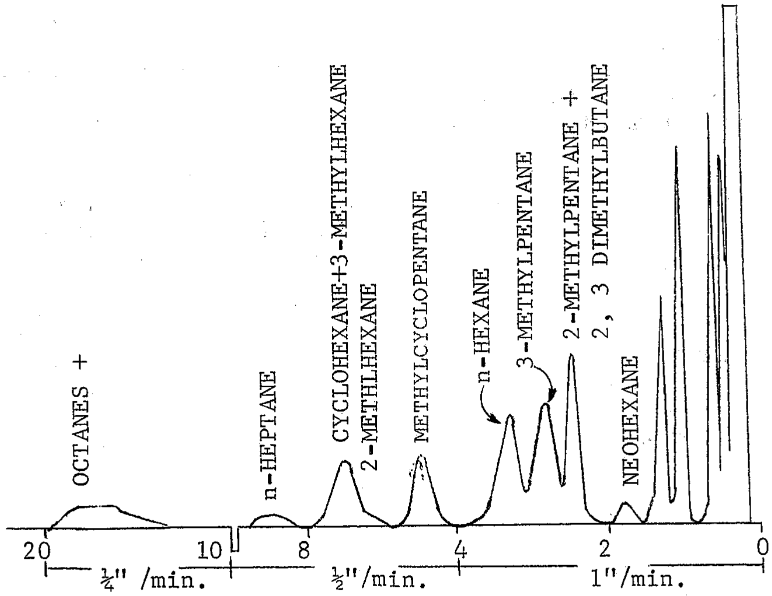

FIG. A1.1 Composition of Hexanes and Heavier Fraction

A1.1.3 A determination of propane, isobutane, *n*-butane, and pentanes and heavier can be made in about 5-min run time by reversing the carrier-gas flow after *n*-butane. However, it is necessary to know the average molecular weight of the pentanes and heavier components.

A1.2 Single-run Analysis for Ethane and Heavier Components

A1.2.1 In many cases, a single partition run using a sample size in the order of 1 to 5 mL will be adequate for determining all components except methane, which cannot be determined accurately using this size sample with peak height measurements, because of its high concentration.

A1.2.2 Enter a 1 to 5-mL sample into the partition column and reverse the carrier gas flow after *n*-pentane is separated. Obtain a corresponding chromatogram of the reference standard. Measure the peak heights of ethane through *n*-pentane and the areas of the pentane peaks of the standard. Make calculations on ethane and heavier components in the same manner as for the complete analysis method. Methane and lighter may be expressed as the difference between 100 and the sum of the determined components.

A1.3 Special Analysis to Determine Hexanes and Heavier Components

A1.3.1 A short partition column can be used advantageously to separate heavy-end components and obtain a more detailed breakdown on composition of the reverse-flow fractions. This information provides quality data, and a basis for calculating physical properties such as molecular weight on these fractions.

A1.3.2 Figure A1.1 is a chromatogram that shows components that are separated by a 2-m BMEE column in 20 min. To make this determination, enter a 5-mL sample into the short column and reverse the carrier gas after the separation of *n*-heptane. Measure areas of all peaks eluted after *n*-pentane. Correct each peak area to the mol basis by dividing each peak area by the molecular weight of the component. A value of 120 may be used for the molecular weight of the octanes and heavier reverse-flow peak. Calculate the mole percent of the hexanes and heavier components by adding the corrected areas and dividing to make the total 100 %.

A2. PREPARATION OF COLUMNS AND DRIER

A2.1 *Preparation of Columns*—See Practice E 260.

A2.2 *Preparation of Drier*—Fill a 10-mm diameter by 100-mm length glass tube with granular phosphorus pentoxide or magnesium perchlorate, observing all proper safety precautions. Mount as required to dry the sample. Replace the drying agent after about one half of the material has become spent.

A2.3 *Removal of Hydrogen Sulfide:*

A2.3.1 For samples containing more than about 300 ppm by mass hydrogen sulfide, remove the hydrogen sulfide by connecting a tube of sodium hydrate absorbent (Ascarite) ahead of the sample container during sampling, or ahead of the drying tube when entering the sample into the chromatograph. This procedure also removes carbon dioxide, and the results obtained will be on the acid-gas free basis.

A2.3.2 Hydrogen sulfide may also be removed by connecting a tube of pumice that has been impregnated with cupric sulfate in the line upstream of both the chromatograph and drying tube. This procedure will remove small amounts of hydrogen sulfide while having but minimal effect on the carbon dioxide in the sample.

A2.4 *Column Arrangement*—For analyses in which

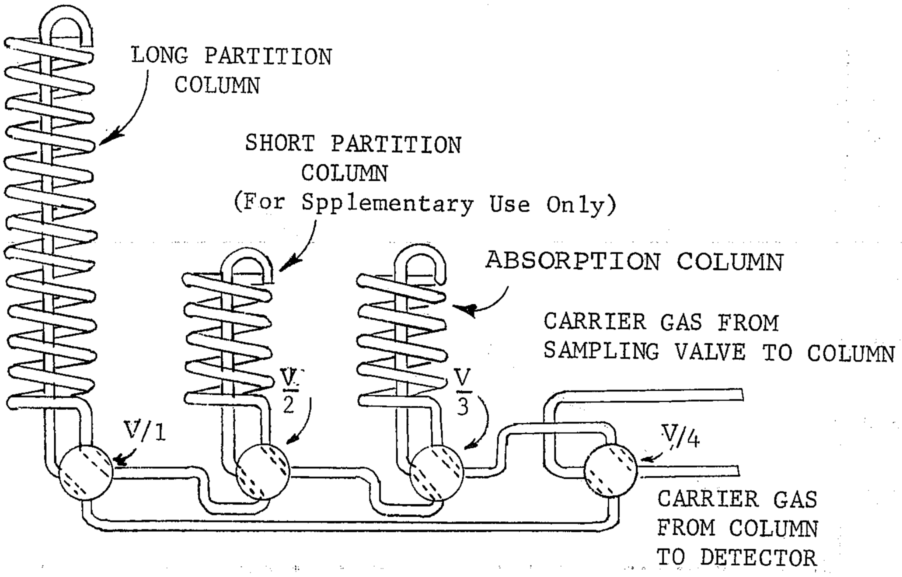

FIG. A2.1 Column Arrangement

hexanes and heavier components are to be determined, Fig. A2.1 shows an arrangement whereby columns can be quickly and easily changed by the turn of a selector valve. Two columns are necessary to determine all of the components covered in this test method. However, short and long partition columns provide the flexibility of three partition column lengths, by using them either singly or in series. The connection between V_1 and V_2 in Fig. A2.1 should be as short as possible (20 mm is practical) to minimize dead space between the columns when used in series. If all columns are chosen to operate at the same temperature, then stabilization time between changing columns will be minimized.

APPENDIXES

(Nonmandatory Information)

X1. REFERENCE STANDARD MIXTURE

X1.1 Preparation

X1.1.1 Gas mixtures of the following typical compositions will suffice for use as reference standards for most analytical requirements (Note X1.1):

Component	Lean gas, mol %	Rich gas, mol %
Helium	1.0	0.5
Hydrogen	3.0	0.5
Nitrogen	4.0	0.5
Methane (maximum)	85	74
Ethane	6.0	10
Carbon dioxide	1.0	1.0
Propane	4.0	7.0
Isobutane	2.0	3.0
n-Butane	2.0	3.0
*neo*pentane	0.5	1.0
Isopentane	0.5	1.0
n-pentane	0.5	1.0
Hexanes +	0.1	0.2

NOTE X1.1—If the mixture is stored under pressure, take care to ensure that the partial pressure of any component does not exceed its vapor pressure at the temperature and pressure at which the sample is stored and used. The Lean mixture has a cricondentherm at 60°F and the Rich mixture has a cricondentherm at 100°F.

X1.1.2 A useful method for preparation of a reference standard by weight is as follows:[5]

X1.1.2.1 Obtain the following equipment and material:

Cylinder, 20-L

Pressure Cylinders, two 100-mL (*A* and *B*)

Balance, 2000-g capacity, sensitivity of 10 mg.

Pure Components, methane through *n*-pentane, and carbon dioxide. The pure components should be 99+ % pure. Methane should be in a 1-L cylinder at 10 MPa (100-atm) pressure. Run a chromatogram of each component to check on its given composition.

X1.1.2.2 Evacuate the 20-L cylinder for several hours. Evacuate 100-mL Cylinder *A*, and obtain its true weight. Connect Cylinder *A* to a cylinder of pure *n*-pentane with a metal connection of calculated length to contain approximately the amount of *n*-pentane to be added. Flush the connection with the *n*-pentane by loosening the fitting at the valve on Cylinder *A*. Tighten the fitting. Close the *n*-pentane cylinder valve and open Cylinder *A* valve to admit the *n*-pentane from the connection and then close the valve on Cylinder *A*. Disconnect and weigh Cylinder *A* to obtain the weight of *n*-pentane added.

X1.1.2.3 Similarly, add isopentane, *n*-butane, isobutane, propane, ethane, and carbon dioxide, in that order, as desired, in the reference standard. Weigh Cylinder *A* after each addition to obtain the weight of the component added. Connect Cylinder *A* to the evacuated 20-L cylinder with as

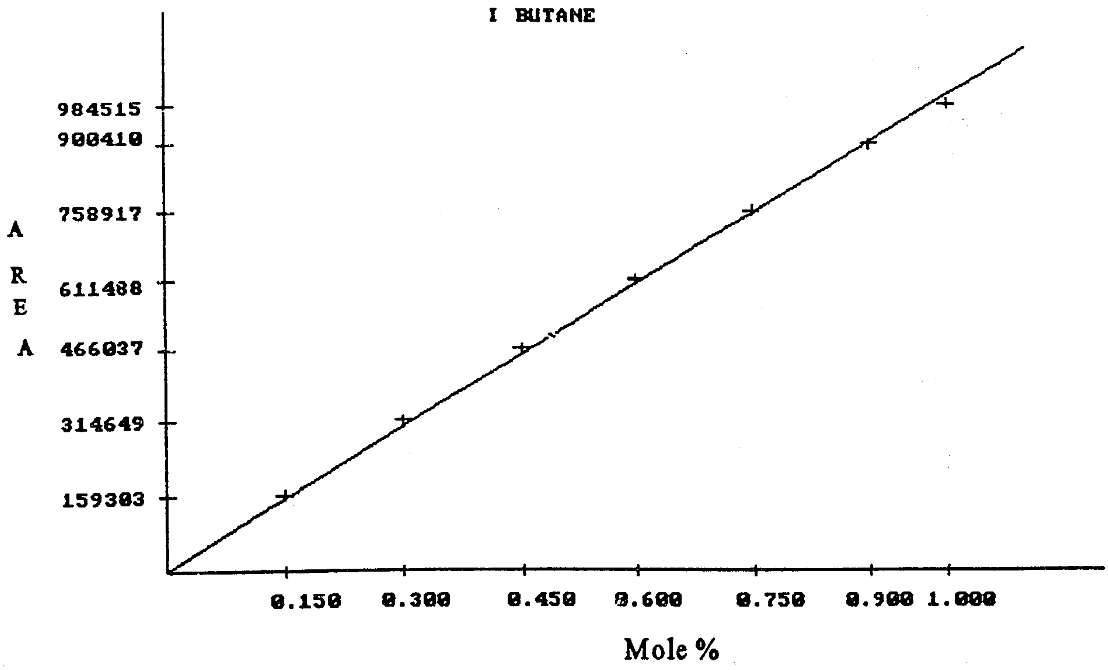

FIG. X1.1 Example of Deriving a Relative Molar Response Factor

TABLE X1.1 Least Square Calculation for Slope of iso-Butane

	area Y	mole % X	XY	Y²
	984515	1	984515	9.693e+11
	900410	0.9	810369	8.107e+11
	758917	0.75	569187.75	5.670e+11
	611488	0.6	366892.8	3.739e+11
	466037	0.45	209716.65	2.172e+11
	314649	0.3	94394.7	9.900e+10
	159303	0.15	23895.45	2.538e+10
sum =	4195319	4.15	3058971.35	3.071452e+12
	slope =	ΣXY/ΣY²	9.9594e-07	

short a clean, small-diameter connector as possible. Open the valve on the 20-L cylinder, then open the valve on Cylinder *A*. This will result in the transfer of nearly all of the contents of Cylinder *A* into the 20-L cylinder. Close the cylinder valves, disconnect, and weigh Cylinder *A* to determine the weight of mixture that was not transferred to the 20-L cylinder.

X1.1.2.4 Evacuate and weigh 100-mL Cylinder *B*. Then fill Cylinder *B* with helium and hydrogen respectively to the pressures required to provide the desired concentrations of these components in the final blend. (Helium and hydrogen are prepared and measured separately from the other components to prevent their pressures, while in the 100-mL cylinder, from causing condensation of the higher hydrocarbons.) Weigh Cylinder *B* after each addition to obtain the weight of the component added. Connect Cylinder *B* to the 20-L cylinder with as short a clean, small-diameter connector as possible. Open the valve on the 20-L cylinder, then open the valve on Cylinder *B*, which will result in the transfer of nearly all of the contents of Cylinder *B* into the 20-L cylinder. Close the cylinder valves, disconnect, and weigh Cylinder *B* to obtain the weight of the mixture that was not transferred to the 20-L cylinder.

X1.1.2.5 Weigh a 1-L cylinder containing pure methane at about 10-MPa (100-atm) pressure. Transfer the methane to the 20-L cylinder until the pressure equalizes. Weigh the 1-L cylinder to determine the weight of methane transferred.

X1.1.2.6 Thoroughly mix the contents of the 20-L cylinder by heating at the bottom by a convenient means such as hot water or a heat lamp, and leaving the cylinder in a vertical position for at least 6 h.

X1.1.2.7 Use the weights and purities of all components added to calculate the weight composition of the mixture. Convert the weight percent to mole percent.

X1.2 Calibration with Pure Components

X1.2.1 Use helium carrier gas to admit a sample volume of 0.25 to 0.5 mL into the adsorption column, providing methane at 50 kPa (375 mm Hg) and nitrogen at 10 kPa (75 mm Hg) absolute pressure. Run a sample of the standard mixture at 70 kPa (525 mm Hg) pressure, and obtain peaks for methane and nitrogen.

NOTE X1.2—Each run made throughout this procedure should be repeated to ensure that peak heights are reproducible after correction for pressure differences to within 1 mm or 1 % of the mean value. All peaks should be recorded at an instrument attenuation that gives the maximum measurable peak height.

X1.2.2 Change the carrier gas to argon or nitrogen and, after the base line has stabilized, enter a sample of pure helium at 7 kPa (50 mm Hg) absolute pressure, recording the peak at an attenuation that allows maximum peak height. Run a sample of the mixture at 70 kPa (525 mm Hg) absolute pressure, and obtain the helium peak.

X1.2.3 Switch to the partition column with helium carrier gas, and run the gas mixture at 70 kPa (525 mm Hg) absolute

TABLE X1.2 Calculation of Response Factors Using Relative Molar Response Values

Comp.	Mole % in Reference Standard S	Response of Reference Standard B	Response Factor From Reference Standard S/B,K	Relative Molar[A] Response from Slope$_i$/K$_i$ RMR$_i$	Response Factor of Referenced Components (RMR$_i$)x(K$_i$)
Nitrogen	5.08	2685885	1.8914E-6		
Methane	82.15	36642384	2.2419E-6		
Ethane	8.75	6328524	1.3826E-6		
Propane	4.02	3552767	1.1315E-6		
Carbon Dioxide				1.11607$_{c2}$	1.5429E-6
iso-Butane				0.72958$_{c3}$	9.9594E-7
n-Butane				0.69310$_{c3}$	9.1142E-7
neopentane				0.68271$_{c3}$	8.9776E-7
iso-Pentane				0.63874$_{c3}$	8.3994E-7
n-Pentane				0.60041$_{c3}$	7.8953E-7
Hexanes +				0.54762$_{c3}$	7.2012E-7

[A] The Relative Molar Response is a constant that is calculated by dividing the slope of the referenced component by the component that is present in the reference standard. For example:

$$RMR_{ic_4} = (\text{slope}ic_4)/(Kc_3) = 9.9594E\text{-}7\ 1.1315E\text{-}6 = 0.72958$$

pressure. Then admit samples of pure ethane and propane at 10 kPa (75 mm Hg) absolute pressure, and butanes, pentanes, and carbon dioxide at 5 kPa (38 mm Hg) absolute pressure.

X1.2.4 Run the gas mixture at 70 kPa (525 mm Hg) absolute pressure.

X1.2.5 Calculate the composition of the prepared gas mixture as follows:

X1.2.5.1 Correct peak heights of all pure components and the respective components in the blend to the same attenuation (Note X1.2).

X1.2.5.2 Calculate the concentration of each component as follows:

$$C = (100V_f)(A/B)(P_b/P_a)$$

where:

C = component concentration, mol %,
A = peak height of component in blend,
B = peak height of pure component,
P_a = pressure at which blend is run, kPa (mm Hg),
P_b = pressure at which component is run, kPa (mm Hg), and
V_f = volume fraction of pure component.

NOTE X1.3—V_f = 1.000 if the calibration component is free of impurities.

X1.2.5.3 Normalize values to 100.0 %.

X1.3 Calibration using Relative Molar Response Values

X1.3.1 Relative response ratios can be derived from linearity data and used for calculating response factors. This eliminates the need for a multi-component standard for daily calibration. The test method can be used on any gas chromatograph using a thermal conductivity or thermistor detector.

X1.3.2 Obtain a blend that brackets the expected concentration the instrument will be analyzing. The major component (methane) is used as the balance gas and may fall below the expected concentration. This component is present in the daily calibration standard and linearity is assured from previous tests.

X1.3.3 Inject the sample at reduced pressures using the apparatus in Fig. 1 or using a mechanical gas blender. Obtain repeatable peak areas or height at 90 %, 75 %, 60 %, 45 %, 30 %, and 15 % of absolute pressure. For 100 kPa (760 mm Hg) the pressures used are 90 kPa (684 mm Hg), 75 kPa (570 mm Hg), 60 kPa (456 mm Hg), 45 Kpa (342 mm Hg), 30 kPa (228 mm Hg), 15 kPa (114 mm Hg).

X1.3.4 Plot the area or height (attenuated at the same height as the reference component) versus concentration and calculate the slope of the line by the least squares method. Given the equation of the line as $Y = a_0 + a_1X$ where Y represents the area or height points and X the concentration points. The line is assumed to intersect through the origin and $a_0 = 0$. The slope a_1 can be calculated by:

$$a_1 = \frac{\Sigma XY}{(\Sigma Y)^2} \qquad (X1.1)$$

X1.3.5 Ratio the slopes of the referenced components (i) to the slopes of the reference components (r) present in the daily calibration standard. This gives the Relative Molar Response factor (RMR_i) for component (i). The reference component must be present in the same instrumental sequence (except Hexanes +) as the referenced components. For instance, propane can be the reference component for the butanes and pentanes if propane is separated on the same column in the same sequence as the butanes and pentanes. Ethane can be the reference component for carbon dioxide if it elutes in the same sequence as carbon dioxide. The hexanes + peak can be referenced to propane or calculated as mentioned in the body of the standard.

X1.3.6 For daily calibration a four component standard is used containing nitrogen, methane, ethane, and propane. The fewer components eliminates dew point problems, reactivity, is more accurate and can be blended at a higher pressure. The referenced components' response factors are calculated from the current reference factor and the Relative Molar Response factor. Following is a description of the basic calculations, an example of deriving a Relative Molar Response factor (Fig. X1.1), and a table showing how response factors are calculated (Table X1.2).

$$\text{Response Factor } (R) = \frac{\text{Mole \%}}{\text{Area}}, \qquad (X1.2)$$

$$\text{Relative Molar Response } (RMR_i) = \frac{\text{Mole \%}(i)/\text{Area}(i)}{\text{Mole \%}(r)/\text{Area}(r)} \qquad (X1.3)$$

$$R_{iC_4} = RMR_{ic_4} \times R_{C_3} \qquad (X1.4)$$

X1.3.7 Periodic checks of the RMR relationship is recommended. The relationship is independent of temperature, sample size, and carrier gas flow rate. If changes occur in these operating conditions, all of the components will be affected equally and the calculated response factors will shift accordingly. See Table X1.1 and Figs. X1.1 and X1.2.

X2. SAMPLE CALCULATIONS (SEE SECTION 9)

TABLE X2.1 Sample Calculations

Component	Mol % in Reference Standard, *S*	Response of Reference Standard, *B*	Response Factor, *S/B*	Response for Sample,[A] *A*	Percent $C = (S \times A)/B$	Normalized, %
Helium	0.50	41.1	0.0122	12.6	0.154	0.15
Hydrogen	0.74	90.2	0.0082	1.5	0.012	0.01
Oxygen	0.27	35.5	0.0076	2.1	0.016	0.02
Nitrogen	4.89	77.8	0.0629	75.6	4.755	4.75
Methane	70.27	76.4	0.9198	90.4	83.150	83.07
Ethane	9.07	96.5	0.0940	79.0	7.426	7.42
Carbon dioxide	0.98	57.5	0.0170	21.2	0.360	0.36
Propane	6.65	55.2	0.1205	20.6	2.482	2.48
*Iso*butane	2.88	73.2	0.0393	11.0	0.432	0.43
n-Butane	2.87	60.3	0.0476	15.0	0.714	0.71
*neo*pentane	0.59	10.4	0.0567	0.1	0.006	0.01
Isopentane	0.87	96.0	0.0091	24.0	0.218	0.22
n-Pentane	0.86	86.8	0.0099	20.5	0.203	0.20
Hexanes +[D]				72.1[B]	0.166[C]	0.17
					100.094 %	100.00 %

[A] The response for a constituent in the sample has been corrected to the same attenuation as for that constituent in the reference standard.

[B] Corrected C_6 response = (original response of 92.1) × (72/92) = 72.1.

[C] Mol % C_6+ = (0.218 + 0.203) × (72.1)/(96.0 + 86.8) = 0.166.
% iC_5 % nC_5 Areas $iC + nC_5$

[D] Average molecular weight of C_6+ = 92.

X3. PRECAUTIONS FOR AVOIDING COMMON CAUSES OF ERRORS

X3.1 Hexane and Heavier Content Change

X3.1.1 The amounts of heavy-end components in natural gas are easily changed during handling and entering of samples to give seriously erroneous low or high values. Concentration of these components has been observed to occur in a number of cases because of collection of heavier components in the sample loop during purging of the system. The surface effect of small diameter tubing acts as a separating column and must not be used in the sampling and entering system when components heavier than pentanes are to be determined. An accumulation of oily film in the sampling system greatly aggravates this problem. Also, the richer the gas, the worse the problem. Periodically, check C_6 and heavier repeatability of the apparatus by making several check runs on the same sample. It is helpful to retain a sample containing some hexanes and heavier for periodic checking. When enlargement of the heavy end peaks is noted, thoroughly clean the sampling valve and loop with acetone. This trouble has been experienced with some inlet systems even when clean and with the specified sample loop size. This contamination can be minimized by such techniques as purging with inert gas, heating the sample loop, using a vacuum system, or other such effective means.

X3.2 Acid Gas Content Change

X3.2.1 The carbon dioxide and hydrogen sulfide contents of gas are easily altered during sampling and handling. If samples containing carbon dioxide or hydrogen sulfide, or both, are to be taken, use completely dry sample cylinders, connections, and lines, as moisture will selectively absorb appreciable amounts of the acid gases. If hydrogen is present, use aluminum, stainless steel, or other materials inert to hydrogen sulfide for the cylinder, valves, lines, and connections.

X3.3 Sample Dew Point

X3.3.1 Nonrepresentative samples frequently occur because of condensation of liquid. Maintain all samples above the hydrocarbon dew point. If cooled below this, heat 10°C or more above the dew point for several hours before using. If the dew point is unknown, heat above the sampling temperature.

X3.4 Sample Inlet System

X3.4.1 Do not use rubber or plastic that may preferentially adsorb sample components. Keep the system short and the drier small to minimize the purging required.

X3.5 Sample Size Repeatability

X3.5.1 Varying back pressures on the sample loop may impair sample size repeatability.

X3.5.2 Make it a practice to make all reverse flow determinations in the same carrier gas flow direction. All single-peak determinations and corresponding reference runs will then be made in the same carrier gas flow direction.

X3.5.3 Be sure that the inlet drier is in good condition.

Moisture on the column will enlarge the reverse flow peak.

X3.5.4 Be sure the column is clean by occasionally giving it several hours sweep of carrier gas in reverse flow direction. A level base line should be quickly attained in either flow direction if the column is clean.

X3.5.5 When the reverse flow valve is turned there is a reversal of pressure conditions at the column ends that upsets the carrier gas flow. This flow should quickly return to the same flow rate and the base line level out. If it does not, the cause may be a leak in the carrier gas system, faulty flow regulator, or an unbalanced condition of the column or plumbing.

X3.6 Reference Standard

X3.6.1 Maintain the reference standard at +15 °C or a temperature that is above the hydrocarbon dew point. If the reference standard should be exposed to lower temperatures, heat at the bottom for several hours before removing a sample. If in doubt about the composition, check the *n*-pentane and isopentane values with pure components by the procedure prescribed in Annex A2.

X3.7 Measurements

X3.7.1 The base line and tops of peaks should be plainly visible for making peak height measurements. Do not use a fixed zero line as the base line, but use the actual observed base line. On high sensitivity, this base line may drift slightly without harm and it need not frequently be moved back to zero. A strip chart recorder with an offset zero is desirable. The area of reverse flow peak may be measured by planimeter or geometric construction. The reverse flow area, and the pentanes peaks used for comparison should be measured by the same method. That is, use either geometric construction or planimeter, but do not intermix. When a planimeter is used, carefully make several tracings and use the average. Check this average by a second group of tracings.

X3.8 Miscellaneous

X3.8.1 Moisture in the carrier gas that would cause trouble on the reverse flow may be safeguarded against by installing a cartridge of molecular sieves ahead of the instrument. Usually 1 m of 6-mm tubing packed with 30 to 60-mesh molecular sieves is adequate, if changed with each cylinder of carrier gas.

X3.8.2 Check the carrier gas flow system periodically for leaks with soap or leak detector solution.

X3.8.3 Use electrical contact cleaner on the attenuator if noisy contacts are indicated.

X3.8.4 Peaks with square tops with omission of small peaks can be caused by a sluggish recorder. If this condition cannot be remedied by adjustment of the gain, check the electronics in the recorder.

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Designation: D 1946 – 90 (Reapproved 1994)$^{\epsilon 1}$

Standard Practice for Analysis of Reformed Gas by Gas Chromatography[1]

This standard is issued under the fixed designation D 1946; 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.

$^{\epsilon 1}$ NOTE—Section 12 was added in December 1994.

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1. Scope

1.1 This practice covers the determination of the chemical composition of reformed gases and similar gaseous mixtures containing the following components: hydrogen, oxygen, nitrogen, carbon monoxide, carbon dioxide, methane, ethane, and ethylene.

1.2 *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 Document

2.1 *ASTM Standard:*

E 260 Practice for Packed Column Gas Chromatography[2]

3. Summary of Practice

3.1 Components in a sample of reformed gas are physically separated by gas chromatography and compared to corresponding components of a reference standard separated under identical operating conditions, using a reference standard mixture of known composition. The composition of the reformed gas is calculated by comparison of either the peak height or area response of each component with the corresponding value of that component in the reference standard.

4. Significance and Use

4.1 The information about the chemical composition can be used to calculate physical properties of the gas, such as heating (calorific) value and relative density. Combustion characteristics, products of combustion, toxicity, and interchangeability with other fuel gases may also be inferred from the chemical composition.

5. Apparatus

5.1 *Detector*—The detector shall be a thermal conductivity type, or its equivalent in stability and sensitivity. The thermal conductivity detector must be sufficiently sensitive to produce a signal of at least 0.5 mV for 1 mol % methane in a 0.5-mL sample.

5.2 *Recording Instruments*—Either strip chart recorders or electronic integrators, or both, are used to display the separated components. Although a strip chart recorder is not required when using electronic integration, it is highly desirable for evaluation of instrument performance.

5.2.1 The recorder, when used, shall be a strip chart recorder with a full-range scale of 5 mV or less (1 mV preferred). The width of the chart shall be not less than 150 mm. A maximum pen response time of 2 s (1 s preferred) and a minimum chart speed of 10 mm/min shall be required. Faster speeds up to 100 mm/min are desirable if the chromatogram is to be interpreted using manual methods to obtain areas.

5.2.2 *Electronic or Computing Integrators*—Proof of separation and response equivalent to that for the recorder is required for displays other than by chart recorder.

5.3 *Attenuator*—If manual methods are used to interpret the chromatogram, an attenuator must be used with the detector output signal to keep the peak maxima within the range of the recorder chart. The attenuator must be accurate to within 0.5 % between the attenuator range steps.

5.4 *Sample Inlet System:*

5.4.1 The sample inlet system must be constructed of materials that are inert and nonadsorptive with respect to the components in the sample. The preferred material of construction is stainless steel. Copper and copper-bearing alloys are unacceptable.

5.4.2 Provision must be made to introduce into the carrier gas ahead of the analyzing column a gas-phase sample that has been entrapped in either a fixed volume loop or tubular section. The injected volume must be reproducible such that successive runs of the same sample agree within the limits of repeatability for the concentration range as specified in 11.1.1.

5.4.3 If the instrument is calibrated with pure components, the inlet system shall be equipped to introduce a sample at less than atmospheric pressure. The pressure-sensing device must be accurate to 0.1 kPa (1 mm Hg).

5.5 *Column Temperature Control:*

5.5.1 *Isothermal*—When isothermal operation is utilized, the analytical columns shall be maintained at a temperature constant to 0.3°C during the course of the sample run and the corresponding reference run.

5.5.2 *Temperature Programming*—Temperature programming may be used, as feasible. The oven temperature shall not exceed the recommended temperature limit for the materials in the column.

5.6 *Detector Temperature Control*—The detector temperature shall be maintained at a temperature constant to 0.3°C

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[1] This practice is under the jurisdiction of ASTM Committee D-3 on Gaseous Fuels and is the direct responsibility of Subcommittee D03.07 on Analysis of Chemical Composition of Gaseous Fuels.

Current edition approved March 30, 1990. Published May 1990. Originally published as 1946 – 62 T. Last previous edition D 1946 – 82.

[2] *Annual Book of ASTM Standards*, Vol 14.02.

during the course of the sample run and the corresponding reference run. The detector temperature shall be equal to, or greater than, the maximum column temperature.

5.7 *Carrier Gas*—The instrument shall be equipped with suitable facilities to provide flow of carrier gas through the analyzer and detector at a flow rate that is constant to 1 % throughout the analysis of the sample and the reference standard. The purity of the carrier gas may be improved by flowing the carrier gas through selective filters prior to its entry into the chromatograph.

5.8 *Columns:*

5.8.1 The columns shall be constructed of materials that are inert and nonadsorptive with respect to the components in the sample. The preferred material of construction is stainless steel. Copper and copper-bearing alloys are unacceptable.

5.8.2 Either an adsorption-type column or a partition-type column, or both, may be used to make the analysis.

NOTE 1—See Practice E 260 for general gas chromatography procedures.

5.8.2.1 *Adsorption Column*—This column must completely separate hydrogen, oxygen, nitrogen, methane, and carbon monoxide. If a recorder is used, the recorder pen must return to the baseline between each successive peak. Equivalent proof of separation is required for displays other than by chart recorder. Figure 1 is an example chromatogram obtained with an adsorption column.

(*1*) Because of similarities in thermal conductivities, helium should not be used as the carrier gas for hydrogen when hydrogen is less than 1 % of the sample. Either argon or nitrogen carrier gas is suitable for both percent and parts per million quantities of hydrogen.

(*2*) The use of a carrier gas mixture of 8.5 % hydrogen and 91.5 % helium will avoid the problem of reversing polarities of hydrogen responses as the concentration of hydrogen in the sample is increased.

(*3*) The precision of measurement of hydrogen can be increased by using a separate injection for hydrogen, using either argon or nitrogen for the carrier gas.

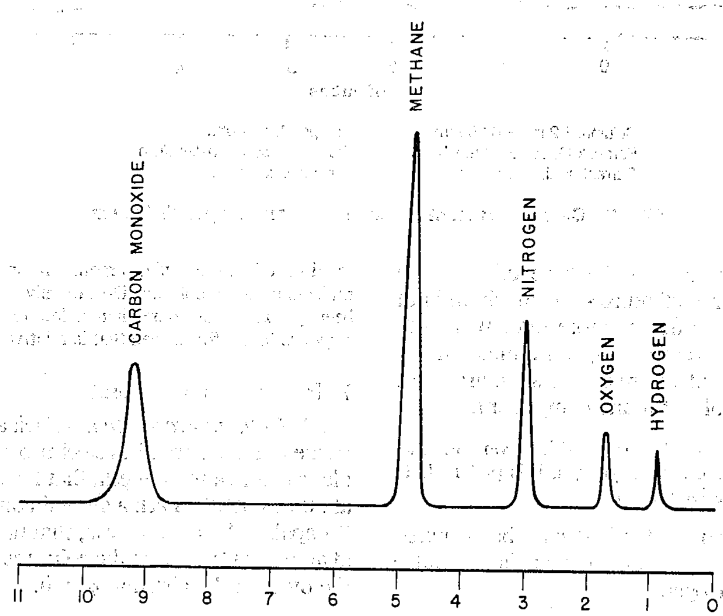
(*4*) Another technique for isolating the hydrogen in a sample is to use a palladium transfer tube at the end of the adsorption column; this will permit only hydrogen to be transferred to a stream of argon or nitrogen carrier gas for analysis in a second thermal conductivity detector.

5.8.2.2 *Partition Column*—This column must separate ethane, carbon dioxide, and ethylene. If a recorder is used, the recorder pen must return to the baseline between each successive peak. Equivalent proof of separation is required for displays other than by chart recorder. Figure 2 is an example chromatogram obtained with a partition column.

5.8.3 *General*—Those column materials, operated either isothermally or with temperature programming, or both, may be utilized if they provide satisfactory separation of components.

6. Reference Standards

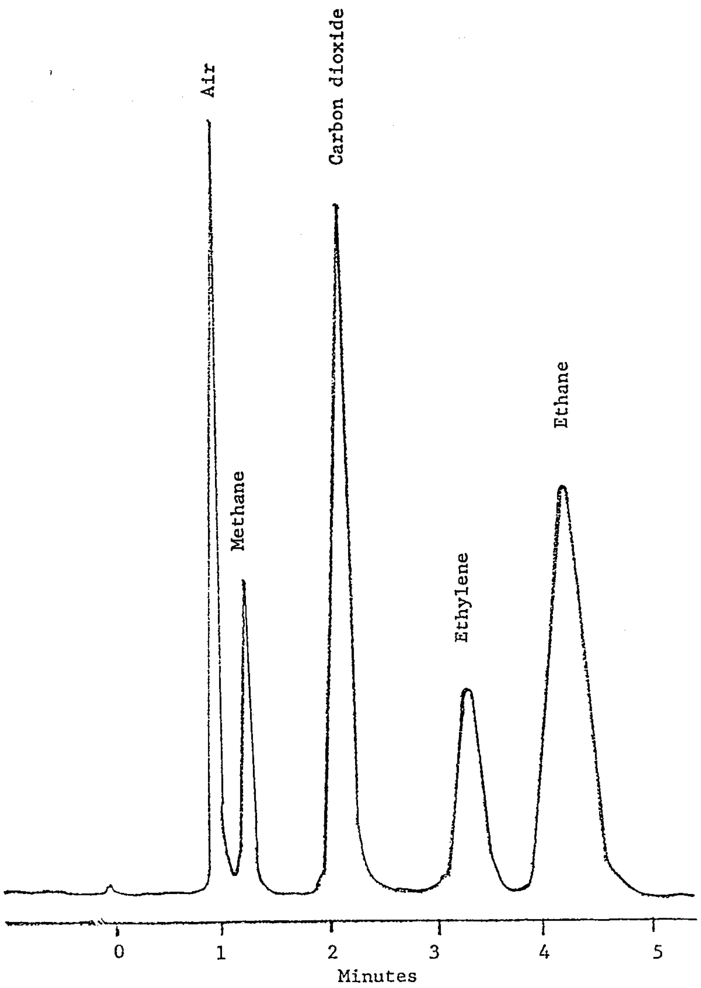
6.1 Moisture-free mixtures of known composition are required for comparison with the test sample. They must contain known percentages of the components, except oxygen (Note 2), that are to be determined in the unknown sample. All components in the reference standard must be



Column: 2 m by 6 mm inside diameter Type 13X molecular sieves, 14 to 30 mesh
Temperature: 35°C

Flow rate: 60 mL helium/min
Sample size: 0.5 mL

FIG. 1 Chromatogram of Reformed Gas on Molecular Sieve Column



Column: 1.2 m by 6.35 mm
Porapak Q, 50 to 80 mesh
Current setting: 225 mA

Temperature: 40°C
Flow rate: 50 mL helium/min
Sample size: 0.5 mL

FIG. 2 Chromatogram of Reformed Gas on Porapak Q Column

homogeneous in the vapor state at the time of use. The fraction of a component in the reference standard should not be less than one half of, nor differ by more than 10 mol % from, the fraction of the corresponding component in the unknown. The composition of the reference standard must be known to within 0.01 mol % for any component.

NOTE 2—Unless the reference standard is stored in a container that has been tested and proved for inertness to oxygen, it is preferable to calibrate for oxygen by an alternative method.

6.2 *Preparation*—A reference standard may be prepared by blending pure components. Diluted dry air is a suitable standard for oxygen and nitrogen.

NOTE 3—A mixture containing approximately 1 % of oxygen can be prepared by pressurizing a container of dry air at atmospheric pressure to 20 atm (2.03 MPa) with pure helium. This pressure need not be measured precisely, as the fraction of nitrogen in the mixture such prepared must be determined by comparison to nitrogen in the reference standard. The fraction of nitrogen is multiplied by 0.280 to obtain the fraction of oxygen plus argon. Argon elutes with oxygen in the molecular sieves column. Do not rely on oxygen standards that have been prepared for more than a few days. It is permissible to use a response factor for oxygen that is relative to a stable component.

7. Preparation of Apparatus

7.1 *Column Preparation*—Pack a 2 to 3-m column (6-mm inside diameter stainless steel tubing) with Type 13× molecular sieves, 14 to 30 mesh, that have been dried 12 h or more at 300 to 350°C. Pack a second column (1 m by 6 mm) with Porapak Q,[3] 50 to 80 mesh, that has been dried 12 h or more at about 150°C. Shape the columns to fit the configuration of the oven in the chromatograph.

NOTE 4—Variations in column material, dimensions, and mesh sizes of packing are permissible if the columns produce separations equivalent to those shown in Figs. 1 and 2. Better performance may be obtained by

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[3] Available from Waters Associates, Inc., Framingham, MA 01701.

using a 2.1-mm stainless steel tubing with corresponding smaller mesh packing materials and substituting Haysep Q for Porapak Q.

7.2 *Chromatograph*—Place the proper column and sample volume in operation for the desired run in accordance with 8.1 and 8.2. For isothermal operation, the column should be maintained at a temperature between 30 and 45°C. When appropriate, column temperatures may be increased. Adjust the operating conditions and allow the instrument to stabilize. Check the stability by making repeat runs on the reference standard to obtain reproducible peak heights as described in 5.4.2 for corresponding components.

8. Procedure

8.1 *Sample Volume*—The sample introduced into the chromatographic column should have a volume between 0.2 and 0.5 mL. Sufficient accuracy can be obtained for the determination of all but the very minor components with this sample size. When increased sensitivity is required for the determination of components present in low concentrations, a sample size of up to 5 mL is permissible. However, components whose concentrations are in excess of 5 % should not be analyzed by using sample volumes greater than 0.5 mL.

8.2 *Chromatograms:*

8.2.1 *Adsorption Column* (Fig. 1)—Obtain a steady base line on the recorder with a constant carrier gas flowrate appropriate to the column diameter. Introduce a sample of the unknown mixture at atmospheric pressure into the chromatograph and obtain a response similar to that of Fig. 1 of the components hydrogen, oxygen, nitrogen, methane, and carbon monoxide, which elute in that order. Repeat with a sample of the reference standard. If oxygen is present in the mixture, run a sample of air, either at an accurately measured reduced pressure, or air freshly diluted with helium, so that the partial pressure of oxygen is approximately equal to that of the oxygen in the mixture being analyzed.

NOTE 5—The peak for carbon monoxide can appear between those of nitrogen and methane if the molecular sieves have become contaminated. If this occurs, replace or regenerate the column packing by heating in accordance with 7.1.

8.2.2 *Partition Column* (Fig. 2)—Establish a steady base line with the helium carrier gas flowing through the Porapak Q column. Introduce a sample of the reference standard, and then a sample of the unknown mixture. Obtain responses similar to that shown in Fig. 2 for carbon dioxide, ethane, and ethylene.

8.2.3 All chromatograms for manual measurement should be run at a sensitivity setting that permits maximum peak height to be recorded for each component.

8.2.4 Column isolation valves may be used to make the entire analysis with a single injection if the separations specified in 5.8.2.1 and 5.8.2.2 are produced.

9. Calculation

9.1 The number of significant digits retained for the quantitative value of each component shall be such that accuracy is neither sacrificed nor exaggerated. The expressed numerical value of any component in the sample should not be presumed to be more accurate than the corresponding certified value of that component in the calibration standard.

9.2 *Manual Measurement*—Measure the response of each component, convert to the same sensitivity for corresponding components in the sample and reference standard, and calculate the mole percent of each component in the sample as follows:

$$C = (A/B)(S)$$

where:

C = mole percent of the component in the sample,
A = response of the component in the sample,
B = response of the component in the standard at the same sensitivity as with A, and
S = mole percent of the component in the reference standard.

9.3 If a helium-diluted air mixture was run for oxygen calibration, calculate the fraction of oxygen in the mixture from the fraction of the nitrogen and the composition of the diluted air. Calculate the fraction of nitrogen in the mixture in accordance with 9.1, using the nitrogen response of the reference standard for comparison. Air composition values of 78.1 % nitrogen and 21.9 % oxygen should be used, as argon (0.9 % in air) elutes with oxygen on the molecular sieves column.

9.4 If air has been analyzed at reduced pressure to calibrate for oxygen, correct the equation for pressure as follows:

$$C = (A/B)(S)(P_a/P_b)$$

where:

P_a = absolute pressure at which air was analyzed, and
P_b = barometric pressure when sample was analyzed, with both pressures being expressed in the same units.

9.5 Normalize the mole percent values by multiplying each value by 100 and dividing by the sum of the original values. The sum of the original values should not differ from 100.0 % by more than 1.0 %.

10. Analysis of the Reference Standard

10.1 If the composition of the reference standard is not known to a sufficient degree of accuracy, analyze it by the use of pure components for calibration. Obtain chromatograms of the standard as described in 8.2, except measure the pressure of each sample introduced to 0.133 kPa (1 mm Hg). When each chromatogram is obtained, calibrate each component by introducing a sample of the pure component at a pressure that closely approximates its partial pressure in the blend (for example, a component whose concentration in the standard is 50 % is analyzed at 50 % of the pressure at which the standard was analyzed). Use a minimum pressure of 0.665 kPa (5 mm Hg) for minor components. Repeat the analysis with the reference standard. Corresponding peak heights should agree within 1 mm or 1 % (whichever is larger) when recorded on a sensitivity setting that allows maximum response on the recorder chart.

10.2 Calculate the composition of the reference standard by the adjustment of responses of like components to the same sensitivity, and calculate the concentration of each component as follows:

$$C = \frac{(100)(R)(P_p)}{(P)(P_r)}$$

where:

C = component concentration, mole percent,

R = response of the component in the reference standard,

P = response of the pure component,

P_p = pressure at which the pure component was analyzed, and

P_r = pressure at which the reference standard was analyzed, with both pressures being expressed in the same absolute units.

10.2.1 Normalize all values as described in 9.4.

11. Precision

11.1 The following data should be used to judge the acceptability of the results:

11.1.1 *Repeatability*—Duplicate results by the same operator should not be considered suspect unless they differ by more than the following amounts:

Component, mol %	Repeatability
0 to 1	0.05
1 to 5	0.1
5 to 25	0.3
Over 25	0.5

11.1.2 *Reproducibility*—Results submitted by different laboratories should not differ by more than the amounts given in 11.1.1 when the same reference standard is used for calibration and the same composition is used for calculations. If calibration is made with pure components or with different reference standards, results submitted by each of two laboratories should not be considered suspect unless the results differ by more than the following amounts:

Component, mol %	Reproducibility
0 to 1	0.1
1 to 5	0.2
5 to 25	0.5
Over 25	1.0

12. Keywords

12.1 gaseous fuels

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Standard Method of Preparing Coal Samples for Analysis[1]

This standard is issued under the fixed designation D 2013; 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 method[2] covers the reduction and division of gross or divided samples, collected in accordance with Methods D 2234, up to and including the individual portions for laboratory analysis.

1.2 Reduction and division procedures are prescribed for coals of the following groups:

1.2.1 *Group A* includes coals that have been cleaned in all sizes.

1.2.2 *Group B* includes all other coals. Unknown coals are to be considered under Group B.

1.2.3 Group A allows smaller weights of laboratory samples to be retained than Group B. These lower weights may be used for particular coals if they have been shown by using the procedure of Annex A1.2 to give a sample preparation and analysis variance which is no more than 20 % of the total allowable variance.

1.3 Two methods are given for preparing the analysis sample for making the moisture determinations:

1.3.1 *Referee Method*—This method shall be used where the possibility of unaccounted changes in moisture content during the reduction and division of the gross or divided sample must be held to a minimum. It is intended to be used for evaluation of nonreferee methods, and for testing of equipment. Only under certain conditions will this referee method be directly applicable to routine test programs.

1.3.2 *Nonreferee Method*—This method may be used for routine work.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 197 Test Method for Sampling and Fineness Test of Pulverized Coal[3]
D 410 Method for Sieve Analysis of Coal[4]
D 431 Test Method for Designating the Size of Coal from its Sieve Analysis[4]
D 2234 Test Methods for Collection of a Gross Sample of Coal[3]
D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke[3]
D 3174 Test Method for Ash in the Analysis Sample of Coal and Coke from Coal[3]
D 3302 Test Method for Total Moisture in Coal[3]
E 11 Specification for Wire-Cloth Sieves for Testing Purposes[5]
E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods[5]

3. Descriptions of Terms Specific to This Standard

3.1 *air drying*—a process of partially drying coal to bring moisture near to equilibrium with the atmosphere in the room in which further reduction and division of the sample is to take place.

3.2 *analysis sample*—final subsample prepared from the original gross or divided sample but reduced to 100 % through No. 60 (250-μm) sieve and divided to not less than 50 g.

3.3 *bias* (*systematic error*)—an error that is consistently negative or consistently positive. The mean of errors resulting from a series of observations which does not tend towards zero.

3.4 *C test*—a standard statistical test for homogeneity of variance[6].

3.5 *divided sample*—a sample that has been reduced in quantity.

3.6 *gross sample*—a sample representing one lot of coal and composed of a number of increments on which neither reduction nor division has been performed.

3.7 *laboratory sample*—the sample, not less than the permissible weight given in Table 1, delivered to the laboratory for further preparation and analysis.

3.8 *precision*—a term used to indicate the capability of a person, an instrument, or a method to obtain repeatable results; specifically, a measure of the chance error as expressed by the variance, the standard error, or a multiple of the standard error (see Practice E 177).

3.9 *representative sample*—a sample collected in such a manner that every particle in the lot to be sampled is equally represented in the gross sample.

3.10 *riffle*—a hand-feed sample divider device that divides the sample into two parts of approximately the same weight.

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[1] This method is under the jurisdiction of ASTM Committee D-5 on Coal and Coke and is the direct responsibility of Subcommittee D05.23 on Sampling.

Current edition approved Aug. 29, 1986. Published October 1986. Originally published as D 2013 – 62 T. Last previous edition D 2013 – 72 (1978)$^{\epsilon 1}$.

[2] For more detailed explanation of this method see Keller, G. E., "Determination of Quantities Needed in Coal Sample Preparation and Analysis," *Transactions*, Vol 232, 1965, pp. 218–226.

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

[4] *Discontinued; see 1988 Annual Book of ASTM Standards*, Vol 05.05.

[5] *Annual Book of ASTM Standards*, Vol 14.02.

[6] Details appear in standard texts. A good text for this purpose is Grubbs, F. E., "An Introduction to Some Precision and Accuracy of Measurement Problems," JTEVA, Vol 10, No. 4, July 1982, pp 133–143.

TABLE 1 Preparation of Laboratory Sample

Crush to pass at least 95 % through sieve	Divide to a minimum weight of, g ^{A}	
	Group A	Group B
No. 4 (4.75-mm)	2000	4000
No. 8 (2.36-mm)	500	1000
No. 20 (850 µm)	250	500
No. 60 (250 µm) (100 % through)	50	50

^{A} If a moisture sample is required, increase the quantity of No. 4 (4.75-mm) or No. 8 (2.36-mm) sieve subsample by 500 g.

3.11 *sample division*—the process whereby a sample is reduced in weight without significant change in particle size.

3.12 *sample preparation*—the process that may include air drying, crushing, division, and mixing of a gross sample for the purpose of obtaining an unbiased analysis sample.

3.13 *sample reduction*—the process whereby a sample is reduced in particle size by crushing or grinding without significant change.

3.14 *significant loss*—any loss that introduces a bias in final results that is of appreciable economic importance to concerned parties.

3.15 *size consist*—the particle size distribution of a coal.

3.16 *standard deviation*—the square root of the variance.

3.17 *subsample*—a sample taken from another sample.

3.18 *systematic error* (see *bias*, 3.3).

3.19 *top size*—the opening of the smallest screen in the series upon which is retained less than 5 % of the sample (see Method D 431).

3.20 *unbiased sample* (*representative sample*)—a sample free of bias.

3.21 *variance*—the mean square of deviations (or errors) of a set of observations; the sum of squared deviations (or errors) of individual observations with respect to their arithmetic mean divided by the number of observations less one (degrees of freedom); the square of the standard deviation (or standard error).

3.22 *variance of analysis*, S_a^2—the variance due to chance errors (deviations) of analysis.

3.23 *variance of division*, S_d^2—the variance due to chance errors (deviations) of sample division.

3.24 *variance of division and analysis*, S_{da}^2—the variance due to the combined chance errors of division and analysis.

3.25 *total variance*, S_o^2—the overall variance resulting from collecting single increments, and including division and analysis of the single increments.

4. Summary of Method

4.1 Three processes of sample division are covered in this method as follows:

4.1.1 *Procedure A*—Riffles are used for division of the sample and mechanical crushing equipment for the reduction of the sample.

4.1.2 *Procedure B*—Mechanical sample dividers are used for the division of the sample and mechanical crushing equipment for the reduction of the sample.

4.1.3 *Combined Procedure A and B*—The two procedures may be combined at any stage of the preparation procedure.

4.2 These procedures include methods to be used whenever residual or total moisture or both, are to be determined, or whenever other laboratory analyses or tests are to be made.

4.3 Preparation of gross or divided samples for analyses or tests consists of air drying (where necessary), particle size reduction, mixing, and dividing the gross or divided sample in stages to a small analysis sample representative of the original gross sample.

5. Significance and Use

5.1 This method is intended to provide an analysis sample of coal from a gross or divided sample that has been collected in accordance with Methods D 2234. In addition, a method to determine the percent air dried moisture loss of the sample is provided. The analysis sample can be used to determine the value of the coal represented, its ability to meet specifications, its environmental impact, as well as for other purposes.

6. Apparatus

6.1 *Air Drying*—The following apparatus may be used:

6.1.1 *Air Drying Oven*—A device for passing slightly heated air over the sample. The oven shall be capable of maintaining a temperature of 10 to 15°C (18 to 27°F) above room temperature with a maximum oven temperature of 40°C (104°F) unless ambient temperature is above 40°C (104°F) in which case ambient temperature shall be used. In case of easily oxidized coals, the temperature shall not be over 10°C (18°F) above room temperature. Air changes shall be at the rate of 1 to 4/min. A typical oven is shown in Fig. 1.

6.1.2 *Drying Floor*—A smooth clean floor in a room free of dust and excessive air currents.

6.1.3 *Drying Pans*—Noncorroding metal pans of sufficient size so that the sample may be spread to a depth of not more than 25 mm (1.0 in.) with sides not more than 38 mm (1.5 in.) high.

6.1.4 *Scale-Gross Sample*—A scale of sufficient capacity and sensitive to 0.023 kg (0.05 lb) in 45.46 kg (100 lb).

6.1.5 *Balance-Laboratory Sample*—A balance of sufficient capacity to weigh the sample and container with a sensitivity of 0.5 g in 1000 g.

6.2 *Crushers or Grinders*—Jaw, cone, or rotary crusher, hammer mill or other suitable crusher to reduce the sample to pass the sieve designated in Table 1. Hard-steel or chilled-iron plate with tamper, sledge, or hand bar for preliminary crushing of any large lumps in the sample before feeding into the crusher.

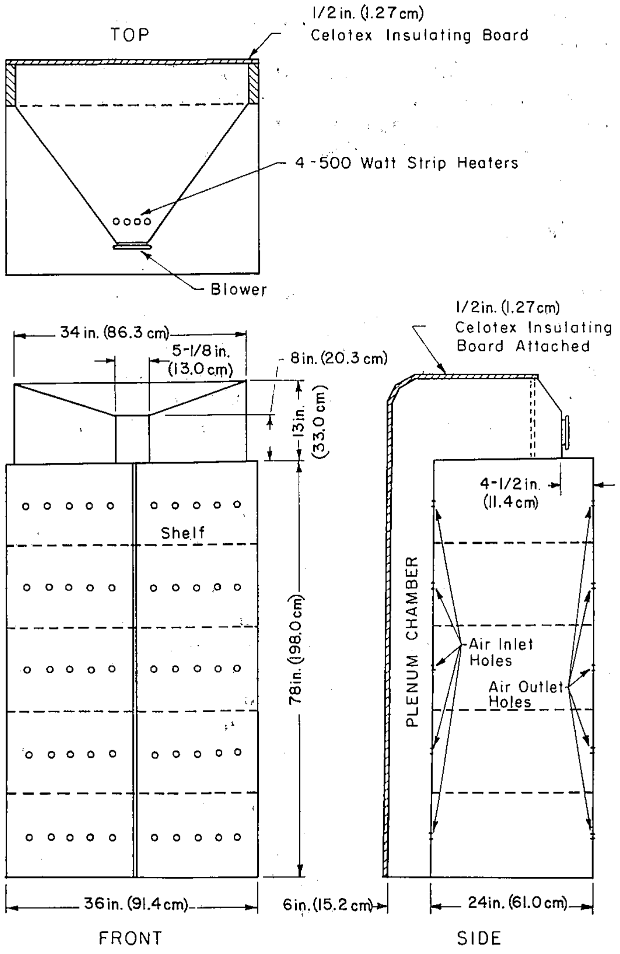
6.3 *Pulverizer or Mill*—For final reduction of laboratory sample to pass the No. 60 (250-µm) sieve, the following equipment may be used:

6.3.1 *Hammer Mill*—Completely enclosed to avoid loss of dust or moisture.

6.3.2 *Porcelain-Jar Ball Mill*—This mill shall be approximately 230 mm (9.0 in.) in diameter and 250 mm (10.0 in.) in height with smooth, hard, well-rounded, flint pebbles or equivalent, that do not appreciably increase the ash content of the sample.

6.4 *Bucking Board* (*Chrome Steel*) *or Mortar* (*Agate or Equivalent*) *and Pestle*—Only for reducing the small fraction of sample, not passing a No. 60 (250-µm) sieve after pulverization.

6.5 *Sample Dividers:*



NOTE—Dimensions are typical but required.

FIG. 1 Air Drying Oven

6.5.1 *Mechanical*—A mechanical sample divider using a reciprocating or rotating cutter, a rotating hopper and spout, a rotating slotted cone, or other acceptable devices for dividing the sample. Typical mechanical sample dividers are shown in Fig. 2. These illustrate four designs but others may be available.

6.5.2 *Riffles*—A manual sample divider which splits the coal stream into a number of alternate elements. Riffle divisions should be at least three times the top size of coal being divided. Typical riffler is shown in Fig. 3. It is preferable that feed chutes and enclosed riffles be used. The slope of feed chutes and riffles must be at least 60°.

6.5.2.1 *Feed Scoop*—A feed scoop or pan having straight sides and equal to the effective width of the riffle shall be used to feed the stand-type riffle.

6.5.2.2 *Feed Chute*—A feed chute shall be used as shown in Fig. 3. The discharge opening of the feed chute shall be the same width as the riffle opening.

6.6 *Mixing Wheel*—One type of a mechanical device used for mixing the analysis sample. In this device, the samples are in closed containers attached to the rim of a wheel at an angle of 45° with the horizontal wheel shaft. The wheel provides space for a number of containers depending on its diameter and is turned slowly by a small motor and reduction gear. The wheel should be rotated at a speed so that the particles fall gently from top to bottom of the container, mixing the sample thoroughly. The container should be about half full and never more than two thirds full in order to obtain good mixing of the sample.

6.7 *Sieves*—A set of sieves whose dimensions are in accordance with Specification E 11, of the following sizes, with cover and receiver:

No.	Size
4	4.75 mm
8	2.36 mm
20	850 µm
60	250 µm

6.8 *Laboratory Sample Containers*—Heavy vapor-impervious bags, properly sealed, or noncorroding cans such as those with an airtight, friction top or screw top sealed with a rubber gasket and pressure-sensitive tape for use in storage and transport of the laboratory sample. Glass containers, sealed with rubber gaskets, may be used but care must be taken to avoid breakage in transport.

7. Precautions

7.1 *General*—The preparation of the gross or divided sample shall be done by trained and experienced personnel. Sample preparation should be checked at intervals by the methods described in Annex A1 or A2. It is necessary that the variance of sample division and analysis S_{da}^2 be not more than 20 % of the total variance of sampling, division, and analysis S_o^2.

7.1.1 The sample preparation operations should be performed in an enclosed space, roofed, cool, and free from excessive air movements.

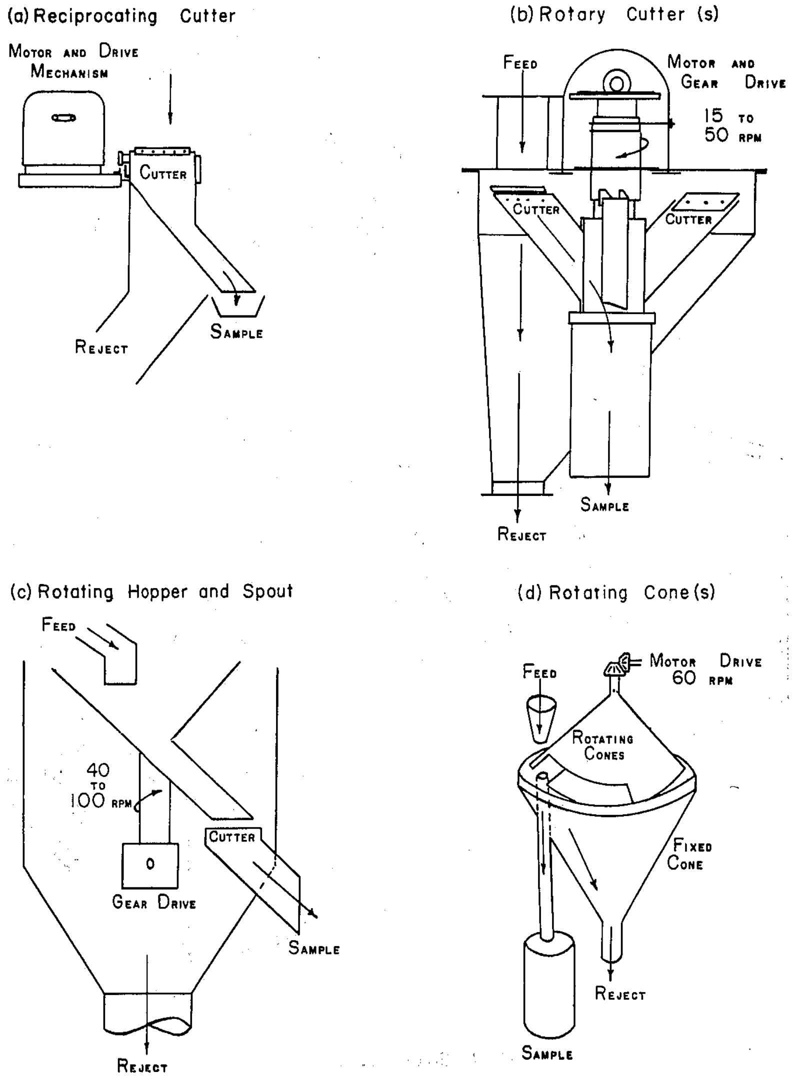
7.2 *Number of Tests*—Before preparing the gross or divided sample, the number and nature of the analysis and tests should be considered. A separate moisture laboratory sample may be required, and portions may be required for grindability and other tests. Also, a reserve sample may be desired in case a check analysis or test is required.

7.3 Since most coals oxidize on exposure to air, the air drying procedure should not be prolonged past the time necessary to bring its moisture to equilibrium with the air in the room in which further reduction and division are to be made. The sample shall be allowed to attain room temperature before weighing and further reduction.

7.4 In collecting, handling, reducing, and dividing the sample, all operations shall be done rapidly and in as few operations as possible, since moisture loss depends on several factors other than total moisture content, such as time required for crushing, atmospheric temperature and humidity, and type of crushing equipment.

7.5 While awaiting preparation, the uncrushed gross or divided sample shall be protected from moisture change due to exposure to rain, snow, wind, and sun, on contact with absorbent materials.

7.6 Whenever subsamples are stored or transported, the containers and subsample shall be weighed, equilibrated to the new atmosphere by air-drying, and the weight loss or gain shall be used in the calculation of moisture content.



(a) Reciprocating Cutter—Fig. 2(*a*) shows a section of a cutter which is moved across a stream of coal. At regular intervals the cutter movement is reversed and a sample increment is collected on each trip through the coal stream.

(b) Rotating Cutter—Fig. 2(*b*) shows two cutters attached to a hollow, rotating shaft. Each cutter is designed to extract increments from the feed and to discharge these into the hollow shaft. One or more cutters may be used.

(c) Rotating Hopper and Spout—Fig. 2(c) shows the totaling hopper that receives the crushed sample and discharges it through a spout over one or more stationary cutters.

(d) Rotating Cone—A sampler developed by the British National Coal Board. Two slotted cones are locked together and rotated on a vertical shaft so that on each revolution the common slot operating intercepts the falling stream of coal and collects an increment.

FIG. 2 Mechanical Sample Dividers

7.7 Whenever a distinct change of humidity occurs during the course of preparation of an air-dried subsample, the subsample should be weighed and its moisture equilibrated with the new atmosphere, and the weight loss or gain used in the calculation of moisture content.

8. Sieve Tests

8.1 The errors of sample division are sensitive to the top size (see 3.19) and, therefore, it is important to make a periodic sieve test of the product of the sample crusher. Sieve tests (see 6.7) shall be made and reported in accordance with Method D 410, except when more than 50 % passes the No. 8 (2.36-mm) sieve. Sieve tests on the portions passing the No. 8 (2.36-mm) sieve shall be made in accordance with Test Method D 197.

9. Procedure

9.1 *Weights*—The minimum allowable weight of the sample at any stage depends on the size consist, the variability of the constituent sought, and the degree of precision desired (Table 1).

9.2 *Air Drying:*

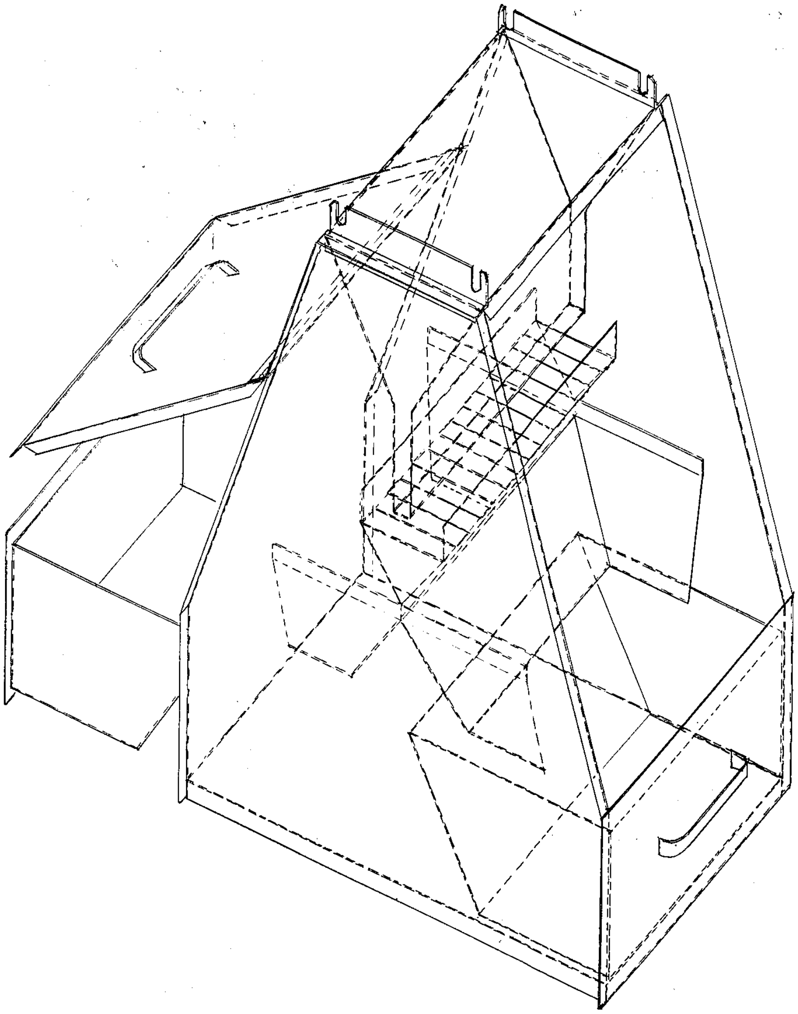


FIG. 3 Sample Divider (Riffle)

9.2.1 *Gross or Divided Samples*—Weigh and spread the referee moisture sample, or a sample too wet to crush without significant loss of moisture, in pans, if an air drying oven is available, or on a drying floor to a depth of not more than twice the top size of the coal. The coal may be stirred, without loss of coal particles, to speed up air drying. Continue air drying until the loss in weight of the total gross or divided sample is not more than 0.1 %/h. Avoid excessive drying time.

9.2.2 *Laboratory Samples*—Weigh the sample, plus pan, plus container, if one is used. Spread the sample in the pan to a depth not to exceed 25 mm (1.0 in.); place it in the oven along with the container and air dry until the loss in weight is not more than 0.1 %/h. Avoid excessive drying. If an oven is not available, the sample may be air-dried in a room free from dust and excessive air currents. Stirring at intervals will lessen air-drying time.

9.3 *Reduction and Division:*

9.3.1 Samples may require air drying in order to feed properly through the reduction and dividing equipment.

9.3.2 In the reduction and division of gross or divided samples for which total moisture content is to be determined, the precautions in 7.3 through 7.7 must be followed.

9.3.3 *Procedure A—Manual Riffling:*

9.3.3.1 Reduce the gross or divided sample to a top size of No. 4 (4.75-mm) or No. 8 (2.36-mm) sieve taking precautions as outlined in Section 7.

9.3.3.2 Determine the number of passes required in the riffling operation from the total weight of the gross sample and the minimum permissible weight in accordance with Table 1.

9.3.3.3 Divide the crushed sample by using a large riffle. Riffles properly used will reduce sample variability but cannot eliminate it. A typical enclosed riffle is shown in Fig. 3 and described in 6.5.2. Pass the coal through the riffle from a feed scoop, feed bucket, or riffle pan having a lip or opening the full width of the riffle. When using any of the above containers to feed the riffle, spread the coal evenly in the container, raise the container, and hold it with its front edge resting on top of the feed chute, then slowly tilt it so that the coal flows in a uniform stream through the hopper straight down over the center of the riffle into all the slots, thence into the riffle pans, one-half of the sample being collected in a pan. Under no circumstances shovel the sample into the riffle, or dribble into the riffle from a small-mouthed container. Do not allow the coal to build up in or above the riffle slots. If it does not flow freely through the slots, shake or vibrate the riffle to facilitate even flow.

9.3.3.4 If the initial crushing was only to No. 4 (4.75-mm) sieve size, reduce to No. 8 (2.36-mm) sieve size after dividing to not less than the quantity specified in Table 1 for a No. 4 (4.75-mm) sieve size.

9.3.3.5 After reducing to No. 8 (2.36-mm) sieve size, divide the subsample by riffling to not less than the quantity specified in Table 1 for a No. 8 (2.36-mm) sieve size.

9.3.3.6 With suitable pulverizing equipment (see 6.3), reduce the No. 8 (2.36-mm) sieve size subsample to a No. 60 (250-µm) sieve size. Divide the ground subsample by riffling, using the small riffle (see 6.5.2) until a minimum of 50 g is obtained. Quickly pass the subsample through a No. 60 (250-µm) sieve. Reduce the particles retained on the screen, on a bucking board or mortar and pestle to pass the sieve, and add to what passed through the sieve and mix thoroughly. This is the analysis sample.

9.3.3.7 As an alternative to the procedure of 9.3.3.6 above, the No. 8 (2.36-mm) sieve size subsample may be reduced to pass 95 % through a No. 20 (850-µm) sieve. Divide this subsample by riffling with the small riffle to not less than the quantity specified in Table 1, and then reduce to No. 60 (250-µm) sieve size as described in 9.3.3.6.

9.3.3.8 Thoroughly mix, preferably by mechanical means, the analysis sample, weighing not less than 50 g, before extracting portions for analysis (see 6.6).

9.3.4 *Procedure B—Mechanical Division:*

9.3.4.1 Reduce the gross or divided sample in stages and divide by suitable mechanical sample dividers (see 6.5.1) to quantities not less than those shown in Table 1.

9.3.4.2 Mechanical division of the sample consists of automatically collecting a large number of increments of the properly reduced sample. Distribute this large number of increments equally throughout the entire discharge from the sample crusher because crushers can introduce appreciable segregation. At each stage of division, take at least 60 increments.

NOTE—It is recommended that, in the case of mechanical division where an increment is not thoroughly mixed with other increments prior to division, a portion of each increment be collected by the subsequent stage increment collection process.

9.3.4.3 Thoroughly mix the analysis sample, 100 % through No. 60 (250-µm) sieve and weighing not less than 50 g, in accordance with 9.3.3.8 prior to extracting portions for analysis.

9.4 *Reduction and Division of Moisture Samples:*

9.4.1 Two procedures for reduction and division of gross samples for use in moisture determinations are given in 9.4.2, Referee Method, and 8.4.3, Nonreferee Method.

9.4.2 *Referee Method*—See 1.3.1 and Fig. 4.

9.4.2.1 Before any sample reduction operations are performed, weigh, air-dry, and reweigh the entire gross or divided sample in accordance with 9.2.1. The percentage loss is A.

9.4.2.2 Reduce the gross sample to No. 4 (4.75-mm) or No. 8 (2.36-mm) with suitable crushing equipment and divide to quantity limits in Table 1 plus a minimum of 500 g. This is the laboratory sample.

9.4.2.3 Air-dry the laboratory sample in accordance with 9.2.2. This air-dry loss is A'.

9.4.2.4 If the gross or divided sample was reduced originally to No. 4 (4.75-mm), air-dry and reduce to No. 8 (2.36-mm). Divide to quantity limits in Table 1 plus 500 g.

9.4.2.5 Divide out the moisture subsample and determine residual moisture in accordance with Test Methods D 3302, Section 2. This is R.

9.4.2.6 If an analysis sample is required, continue reduction and division in accordance with 9.3.3.6 and 9.3.3.7.

9.4.2.7 Calculate the total moisture, M, as follows:

$$M' = [R(100 - A')/100] + A'$$
$$M = [M'(100 - A)/100] + A$$

where:

M = total moisture,
M' = moisture (laboratory sample),
A = air-dry loss gross or divided sample,
A' = air-dry loss (laboratory sample), and
R = residual moisture.

9.4.3 *Nonreferee Method*—See 1.3.2 and Fig. 5.

9.4.3.1 If the sample is too wet to reduce to No. 4 (4.75-mm) or No. 8 (2.36-mm), air-dry the gross or divided sample in accordance with 9.2.1. Complete the preparation and calculations in accordance with 9.4.2.2 through 9.4.2.7.

9.4.3.2 If the sample is dry enough to reduce to No. 4 (4.75-mm) or No. 8 (2.36-mm), reduce the gross or divided sample with suitable crushing equipment and divide to quantity limits in Table 1 plus 500 g. This is the laboratory sample.

9.4.3.3 *Air-Dry Laboratory Sample*—The percentage air-dry loss is A.

9.4.3.4 If the sample was reduced to No. 4 (4.75-mm) air-dry, reduce to No. 8 (2.36-mm) and divide to quantity limits in Table 1 plus 500 g.

9.4.3.5 Divide out the moisture sample from No. 8 coal and determine the residual moisture in accordance with Test Methods D 3302, Section 2. This is R.

9.4.3.6 If an analysis sample is required, continue the reduction and division in accordance with 9.3.3.6, 9.3.3.7, and 9.3.3.8.

9.4.3.7 Calculate the total moisture, M, as follows:

$$M = [R(100 - A)/100] + A$$

where:

M = total moisture,
A = air-dry loss, and
R = residual moisture.

10. Precision and Bias

10.1 The precision of sample preparation (and analysis) can be checked by following Annexes A1 and A2. Since this method does not produce a numerical result, determination of bias is not applicable.

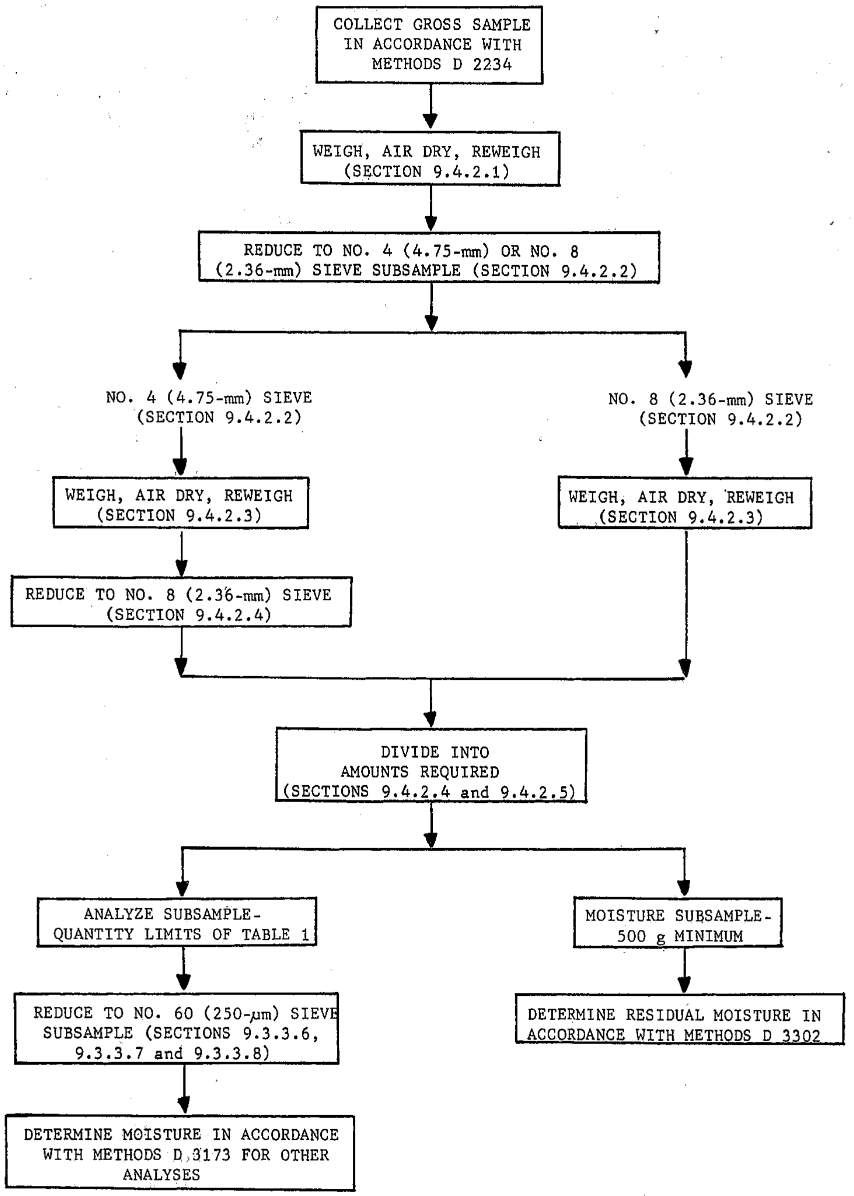


FIG. 4 Gross Sample Preparation for Moisture Determination (Referee Method)

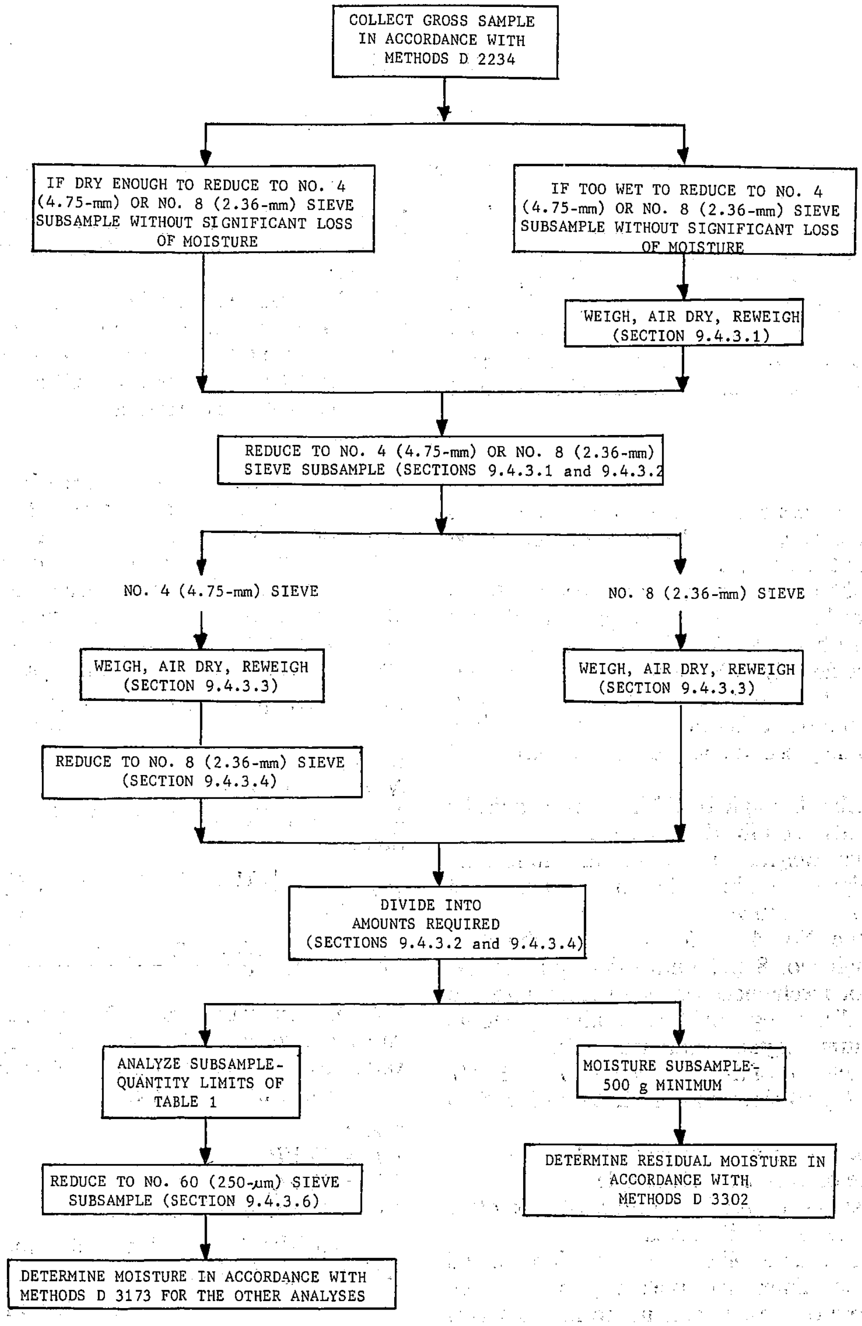


FIG. 5 Gross Sample Preparation for Moisture Determination (Nonreferee Method)

ANNEXES

(Mandatory Information)

A1. METHOD OF CHECKING THE PRECISION OF SAMPLE PREPARATION AND ANALYSIS

A1.1 Scope

A1.1.1 This method covers procedures for checking precision of sample preparation and analysis at the various stages. The data obtained from tests using consistent sample preparation and analysis method are used to estimate the random errors in the various stages of sample division and analysis.

A1.1.2 Coals used in each series of tests should be of similar ash content.

A1.2 Procedure

A1.2.1 Reduce the gross sample to 95 % through No. 4 (4.75-mm) sieve and divide, using either riffles or mechanical sample dividers, into two equal parts.

A1.2.2.1 Many laboratories are crushing directly to No. 8 (2.36-mm) size instead of to No. 4; but for purpose of test it is usually best to use both No. 4 and 8 sizes since we can assume that crushing directly to No. 8 would give a variance no greater, and probably less, than crushing to No. 4 and then to No. 8. If, however, it is desired to crush directly to No. 8, follow the same procedure as if crushed to No. 4 and then to No. 8.

A1.2.2 Divide each subsample by riffling or mechanically to no less than weights as outlined in Table 1.

A1.2.2.1 Individual weights should not vary more than ±20 % from the weights given in Table 1 and the average of all tests should be within ±10 % of the weights.

A1.2.3 Reduce the No. 4 (4.75-mm) sieve laboratory sample 95 % through No. 8 (2.36-mm) sieve and divide, using either riffles or mechanical sample dividers, into two equal parts without discarding. Divide each subsample to no less than the minimum weights as outlined in Table 1.

A1.2.4 Reduce each part of the No. 8 subsample to 100 % through No. 60 (250-µm) sieve and divide to no less than 50 g.

A1.2.5 Determine ash in accordance with Test Methods D 3174, in duplicate on each analysis sample.

A1.2.5.1 This test can be used for sulfur, Btu, or other determinations, instead of ash, if desired.

A1.2.5.2 If possible, the duplicate determinations should be made at different times and preferably by different analysts. The purpose of these tests is not to find out how accurate a laboratory can be, but to find out actual variances of preparation and analysis in the normal routine of a laboratory following a prescribed procedure.

A1.2.6 Treat three sets of ten samples each in the above manner.

A1.2.6.1 Make calculations on the first set of ten samples so that the variance for each of the stages may be checked and corrective action, if needed, may be taken.

A1.2.6.2 Continue this cycle of tests until three successive sets of ten samples are satisfactory.

A1.3 Calculation

A1.3.1 The analysis of variance is based upon the calculations of mean squared differences with the eight determinations for each sample taken in different combinations. Calculate the variances of these combinations: VP, the variance of the difference between duplicate analyses; VQ, the variance of the difference between the averages of duplicate analyses; VR, the variance of the difference between the average of each four analyses, as follows:

$$VP = (1/4N)\,\Sigma[(X1 - X2)^2 + (X3 - X4)^2 + (Y1 - Y2)^2 + (Y3 - Y4)^2]$$

where:

N = number of tests.

$X1, X2, X3, X4, Y1, Y2, Y3, Y4$ = individual ash determinations.

$$VQ = \left(\frac{1}{2N}\right)\Sigma\left[\left(\frac{X1 + X2}{2} - \frac{X3 + X4}{2}\right)^2 + \left(\frac{Y1 + Y2}{2} - \frac{Y3 + Y4}{2}\right)^2\right]$$

$$VR = (1/N)\Sigma\left[\left(\frac{X1 + X2 + X3 + X4}{4} - \frac{Y1 + Y2 + Y3 + Y4}{4}\right)^2\right]$$

A1.3.2 The variances can be resolved further in terms of variance due to the first stage of sample preparation, $V1$; variance due to the second stage of sample preparation, $V2$; and the variance of analysis, Va.

where:

$Va = \frac{1}{2} VP$,

$V2 = \frac{1}{2} VQ - \frac{1}{4} VP$,

$V1 = \frac{1}{2} VR - \frac{1}{4} VQ$.

A1.3.3 The total variance of sample preparation and analysis, S_{da}^2, is given by the equation:

$$S_{da}^2 = Va + V2 + V1$$

A1.3.4 The calculations of the variances of sample preparation are illustrated in Table A1.1.

TABLE A1.1 Illustrations of the Calculation of the Variances[A] of Sample Preparation at the Various Stages and Analysis

Test No.	*X* 1	*X* 2	Difference	Difference²	*X* 3	*X* 4	Difference	Difference²
1	12.13	12.10	0.03	0.0009	12.03	12.05	−0.02	0.0004
2	10.67	10.73	−0.06	0.0036	10.69	10.78	−0.09	0.0081
3	10.93	11.10	−0.17	0.0289	11.36	11.45	−0.09	0.0081
4	12.05	12.02	0.03	0.0009	12.17	12.23	−0.06	0.0036
5	12.74	12.70	0.04	0.0016	12.71	12.76	−0.05	0.0025
6	12.47	12.30	0.17	0.0289	12.21	12.14	0.07	0.0049
7	11.94	11.99	−0.05	0.0025	12.08	12.17	−0.09	0.0081
8	12.52	12.63	−0.11	0.0121	12.76	12.82	−0.06	0.0036
9	12.01	12.05	−0.04	0.0016	11.94	11.77	0.17	0.0289
10	10.96	10.88	0.08	0.0064	11.37	11.40	−0.03	0.0009
Total	118.42	118.50		0.0874	119.32	119.57		0.0691
Average	11.84	11.85			11.93	11.96		

Test No.	*Y* 1	*Y* 2	Difference	Difference²	*Y* 3	*Y* 4	Difference	Difference²
1	12.00	12.01	−0.01	0.0001	12.00	12.00	0.00	0.0000
2	10.53	10.65	−0.12	0.0144	10.60	10.62	−0.02	0.0004
3	11.37	11.47	−0.10	0.0100	11.22	11.35	−0.13	0.0169
4	12.13	12.10	0.03	0.0009	12.01	12.04	−0.03	0.0009
5	12.60	12.60	0.00	0.0000	12.51	12.40	0.11	0.0121
6	12.09	12.15	−0.06	0.0036	12.18	12.20	−0.02	0.0004
7	11.93	11.87	0.06	0.0036	11.71	11.73	−0.02	0.0004
8	12.57	12.57	0.00	0.0000	12.58	12.61	−0.03	0.0009
9	11.81	11.88	−0.07	0.0049	11.70	11.84	−0.14	0.0196
10	11.57	11.48	0.09	0.0081	11.54	11.36	0.18	0.0324
Total	118.60	118.78		0.0456	118.05	118.15		0.0840
Average	11.86	11.88			11.81	11.82		

Test No.	*X*(1 + 2)/2	*X*(3 + 4)/2	Difference	Difference²	*Y*(1 + 2)/2	*Y*(3 + 4)/2	Difference	Difference²
1	12.11	12.04	0.07	0.0056	12.00	12.00	0.00	0.0000
2	10.70	10.73	−0.03	0.0012	10.59	10.61	−0.02	0.0004
3	11.01	11.40	−0.39	0.1521	11.42	11.28	0.13	0.0182
4	12.03	12.20	−0.16	0.0272	12.11	12.02	0.09	0.0081
5	12.72	12.73	−0.01	0.0002	12.60	12.45	0.14	0.0210
6	12.38	12.17	0.21	0.0441	12.12	12.19	−0.07	0.0049
7	11.96	12.12	−0.16	0.0256	11.90	11.72	0.18	0.0324
8	12.57	12.79	−0.21	0.0462	12.57	12.59	−0.02	0.0006
9	12.03	11.85	0.17	0.0306	11.84	11.77	0.07	0.0056
10	10.92	11.38	−0.46	0.2162	11.52	11.45	0.07	0.0056
Total	118.46	119.44		0.5491	118.69	118.10		0.0969
Average	11.85	11.94			11.87	11.81		

Test No.	*X*(1 + 2 + 3 + 4)/4	*Y*(1 + 2 + 3 + 4)/4	Difference	Difference²
1	12.07	12.00	0.07	0.0056
2	10.71	10.60	0.11	0.0138
3	11.21	11.35	−0.04	0.0203
4	12.11	12.07	0.04	0.0022
5	12.72	12.52	0.20	0.0400
6	12.28	12.15	0.12	0.0156
7	12.04	11.81	0.23	0.0552
8	12.68	12.58	0.10	0.100
9	11.94	11.80	0.13	0.0182
10	11.15	11.48	−0.33	0.1122
Total	118.95	118.39		0.2932
Average	11.90	11.84		

$VP = \frac{1}{40}(0.0874 + 0.0691 + 0.0456 + 0.0840) = 0.0071$

$VQ = \frac{1}{20}(0.5491 + 0.0969) = 0.0323$

$VR = \frac{1}{10}(0.2932) = 0.0293$

Then:

$Va = \frac{1}{2}(0.0071) = 0.0035$

$V_2 = \frac{1}{2}(0.0323) - \frac{1}{4}(0.0071) = 0.0144$

$V_1 = \frac{1}{2}(0.0293) - \frac{1}{4}(0.0323) = 0.0066$

$S_{da}^2 = \quad = 0.0035 + 0.0144 + 0.0066 = 0.0245$

[A] This table contains data taken from a computer printout with rounding errors that are not involved in the over-all calculation, data taken at intermediate steps are not consistent within limits of these rounding errors. Thus, the difference 0.07^2 shows a result of 0.0056 which is correct when all places are carried in the calculation.

A2. METHOD FOR DETERMINING THE OVER-ALL VARIANCE OF DIVISION AND ANALYSIS[4]

A2.1 Scope

A2.1.1 Legitimate estimates of the variance of division and analysis, S_{da}^2, can only be made using data obtained from tests that were run using consistent division and analysis methods. Coals used in these variance tests should be of similar ash content. Any gross change in the division and analysis methods or in the ash characteristics of the test coal will nullify the test results.

A2.2 Procedure

A2.2.1 The following four-step method uses the regular gross or divided samples obtained from normal sampling operations:

A2.2.1.1 Crush the gross sample to the same mesh as that normally obtained when preparing the gross sample for processing,

A2.2.1.2 Divide the sample into four equal parts, according to the normal routine laboratory procedure,

A2.2.1.3 Reduce the four subsamples to laboratory analysis samples, and

A2.2.1.4 Analyze each analysis sample for dry ash content.

A2.2.2 Calculate the variance of division and analysis for each gross or divided sample from the "within set sums of squares" for the replicate determinations as follows:

$$S_{da}^2 = [\Sigma x^2 - (\Sigma x)^2/4]/3 \qquad (5)$$

where:

S_{da}^2 = variance of division and analysis,
x^2 = sum of the squares of the four ash results, and
$(\Sigma x)^2$ = sum of the ash results, quantity squared.

A2.2.3 Make progressive checks as the work is carried out by using the data in groups of five. In any group of five estimates of S_{da}^2 based on four subsamples for each estimate, the ratio of the largest estimate to the average of the group should not exceed 2.99, in 19 out of 20 cases. Investigate values in excess of this ratio before proceeding with the test. In addition, after completing 30 sets, by groups of five, the ratio of the largest group average to the over-all average should not exceed 1.88, in 19 cases out of 20. If these criteria are met, the variance of division and analysis may be taken as the over-all average S_{da}^2 of the 30 sets of data. If these criteria are not met, follow the procedure described in Method D 2013 for the necessary information to improve techniques of division and analysis.

A2.2.4 *Example*—A complete example illustrating the procedure for determining the variance of division and analysis is given in Table A2.1. In this example, gross sample No. 24, the highest individual ash sample in the group, (19.28 % ash) has an unusually high variance of division and analysis. The behavior of samples 21 to 30 indicates that trouble can be expected when the ash exceeds 15 % (see Table A2.1).

TABLE A2.1 Determination of Variance of Division and Analysis—Use of Four Analysis Samples for Each Gross Sample

NOTE—10 % ash was subtracted from each of the ash results listed to simplify the calculations.

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
Gross Sample Number	Analysis Samples				Σx	Σx^2	$(\Sigma x)^2/4$	(6)–(7)	(8)/3 = Sda^2	Average Sets of 5 $S_{da}{}^2$	C_i[A]	C_i[B]
	1	2	3	4								
1	1.22	1.37	1.56	1.71	5.86	8.7230	8.5849	0.1381	0.0460		1.62	
2	1.29	1.17	1.70	1.57	5.73	8.3879	8.2082	0.1797	0.0599		2.11	
3	1.56	1.66	1.58	1.64	6.44	10.3752	10.3684	0.0068	0.0023		0.08	
4	5.63	5.57	5.93	5.52	22.65	128.3571	128.2556	0.0015	0.0005		0.02	
5	3.90	3.87	3.58	3.56	14.91	55.6769	55.5770	0.0999	0.0333		1.17	
Average	...	...	...	...	12.78	...	...	...	...	0.0284	...	0.61
6	0.64	0.42	0.80	0.73	2.59	1.7589	1.6770	0.0819	0.0273		1.12	
7	2.47	2.44	2.74	2.68	10.33	26.7445	26.6772	0.0673	0.0227		0.93	
8	3.70	3.53	3.43	3.43	14.09	49.6807	49.6320	0.0487	0.0162		0.66	
9	3.59	3.73	4.13	3.80	15.25	58.2979	58.1406	0.1573	0.0524		2.15	
10	2.14	2.17	2.25	2.11	8.67	18.8031	18.7922	0.0109	0.0036		0.15	
Average	...	...	...	...	12.55	...	...	...	...	0.0244	...	0.52
11	5.71	5.61	5.61	5.71	22.64	128.1524	128.1424	0.0100	0.0033		0.09	
12	3.21	3.40	2.86	2.90	12.37	38.4537	38.2542	0.1995	0.0665		1.87	
13	4.99	4.80	5.51	4.93	20.23	102.6051	102.3132	0.2919	0.0973		2.74	
14	3.26	3.15	3.17	3.09	12.67	40.1471	40.1322	0.0149	0.0050		0.14	
15	3.48	3.65	3.59	3.53	14.25	50.7819	50.7656	0.0163	0.0054		0.15	
Average	...	...	...	...	14.11	...	...	...	...	0.0355	...	0.76
16	2.89	2.84	2.85	2.89	11.47	32.8923	32.8902	0.0021	0.0007		0.02	
17	2.35	2.48	2.90	2.71	10.44	27.4270	27.2484	0.1786	0.0595		1.86	
18	4.23	3.92	4.13	4.05	16.33	66.7187	66.6672	0.0515	0.0172		0.54	
19	5.46	5.13	5.13	5.38	21.10	111.3898	111.3025	0.0873	0.0291		0.91	
20	3.15	2.98	3.42	3.47	13.02	42.5402	42.3801	0.1601	0.0534		1.67	
Average	...	...	...	...	13.62	...	...	...	...	0.0320	...	0.69
21	2.88	2.81	2.80	2.59	11.08	30.7386	30.6916	0.0470	0.0157		0.17	
22	4.94	4.32	4.40	4.39	18.05	81.6981	81.4506	0.2945	0.0982		1.05	
23	4.04	4.28	4.47	4.48	17.27	74.6913	74.5632	0.1281	0.0427		0.46	
24	8.38	8.28	8.93	9.28	34.87	304.6461	303.9792	0.6669	0.2223		2.39	
25	6.93	6.97	6.37	6.54	26.81	179.9543	179.6940	0.2603	0.0868		0.93	
Average	...	...	...	...	15.40	...	...	...	...	0.0931	...	2.00[C]
26	4.52	4.27	3.66	4.07	16.52	68.6238	68.2276	0.3962	0.1321		2.02	
27	4.53	4.46	4.54	4.65	18.18	82.6466	82.6281	0.0185	0.0062		0.09	
28	2.18	2.42	2.45	2.31	9.36	21.9474	21.9024	0.0450	0.0150		0.23	
29	8.84	9.21	8.69	8.55	35.29	311.5883	311.3460	0.2423	0.0808		1.24	
30	5.03	4.73	5.47	5.11	20.34	103.7068	103.4289	0.2779	0.0926		1.42	
Average	...	...	...	...	14.98	...	...	...	...	0.0653	...	1.40
Over-all average $S_{da}{}^2$	...	...	...	...	...	...	...	...	...	0.0465	...	

[A] "C" for individuals in subgroup. Divide individual $S_{da}{}^2$ values (Column 9) by average $S_{da}{}^2$ (Column 10). Results should be below 2.99 in 19 cases out of 20.

[B] "C" for subgroup averages. Divide average $S_{da}{}^2$ (Column 10) by over-all averages $S_{da}{}^2$. Result should be below 1.88 in 19 cases out of 20.

[C] Above limit of 1.88.

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Standard Test Method for Gross Calorific Value of Coal and Coke by the Adiabatic Bomb Calorimeter[1]

This standard is issued under the fixed designation D 2015; 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.

1. Scope

1.1 This test method covers the determination of the gross calorific value of coal and coke by the adiabatic bomb calorimeter.

1.2 The values stated in SI units and British thermal units are to be regarded as the standard. The values given in parentheses are for information only.

1.3 *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 Section 8.

1.4 All accountability and quality control aspects of Guide D 4621 apply to this standard.

2. Referenced Documents

2.1 *ASTM Standards:*

D 121 Terminology of Coal and Coke[2]

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 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke[2]

D 3177 Test Methods for Total Sulfur in the Analysis Sample of Coal and Coke[2]

D 3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases[2]

D 4239 Test Method for Sulfur in the Analysis Sample of Coal and Coke Using High Temperature Tube Furnace Combustion Methods[2]

D 4621 Guide for Accountability and Quality Control in the Coal Analysis Laboratory[2]

E 1 Specification for ASTM Thermometers[4]

E 144 Practice for Safe Use of Oxygen Combustion Bombs[5]

3. Terminology

3.1 *Definitions:*

3.1.1 *calorific value, n*—the heat produced by combustion of a unit quantity of a substance under specified conditions.

3.1.1.1 *Discussion*—It is expressed in this test method in British thermal units per pound (Btu/lb). Calorific value may also be expressed in calories per gram (cal/g) or in the International System of Units (SI), joules per gram (J/g), when required. The unit equivalents are given in Table 1.

3.1.2 *gross calorific value (gross heat of combustion at constant volume) Q_v (gross)*—see Terminology D 121.

3.1.3 *net calorific value (net heat of combustion at constant pressure) Q_p (net)*—see Terminology D 121.

3.1.4 *calorimeter—as used in this test method*, consists of the bomb and its contents, the calorimeter vessel (bucket) with stirrer, the water in which the bomb is immersed, and the portions of the thermometer and the ignition leads within the calorimeter vessel.

3.2 *Descriptions of Terms Specific to This Standard:*

3.2.1 *corrected temperature rise*—the temperature change of the calorimeter caused by the process that occurs inside the bomb, that is, the observed temperature change corrected for various effects as noted in 10.4.1.

NOTE 1—Temperature is measured in either degrees Celsius or degrees Fahrenheit. Thermometer corrections should be applied. Temperatures may be recorded in ohms or other arbitrary units instead of degrees. Consistent units must be used in standardization and the actual calorific value determination. If arbitrary units other than degrees Celsius or Fahrenheit are used, the temperature interval over which all tests are made, must not vary so much that an error greater than 0.001°C would be caused.

3.2.2 *energy equivalent, heat capacity, or water equivalent*—the energy required to raise the temperature of the calorimeter one arbitrary unit. This is the quantity that, when multiplied by the corrected temperature rise, then adjusted for extraneous heat effects, and divided by the mass of the sample, gives the gross calorific value.

NOTE 2—Energy units for quantities listed throughout this test method are such that the number of energy units per gram of sample corresponds exactly to the number of British thermal units per pound of sample. For brevity these are referred to as British thermal units. The actual energies are smaller than those stated by the ratio of the number of pounds per gram (1/453.59). The energy equivalent of the calorimeter has the units (British thermal units per pound) times (grams per degree). Conversion to other units is discussed in Appendix X1.2. Time is expressed in minutes. Mass is expressed in grams.

4. Summary of Test Method

4.1 Calorific value is determined in this test method by

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[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.

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

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

[4] *Annual Book of ASTM Standards*, Vol 14.03.

[5] *Annual Book of ASTM Standards*, Vol 14.02.

TABLE 1 Calorific Value

1 Btu = 1055.06 J	1 Btu/lb = 2.326 J/g
1 Calorie[A] = 4.1868 J	1.8 Btu/lb = 1.0 cal/g

[A] International tables calorie.

burning a weighed sample, in oxygen, in a calibrated adiabatic bomb calorimeter under controlled conditions. The calorimeter is standardized by burning benzoic acid. The calorific value of the sample is computed from temperature observations made before, during and after combustion, making proper allowances for heat contributed by other processes, and for thermometer and thermochemical corrections.

NOTE 3—Oxidation after sampling of susceptible low-rank coal or lignite may result in a reduction of calorific value. Unnecessary exposure of the sample to air from the time of sampling or delay in analysis shall be avoided.

5. Significance and Use

5.1 The gross calorific value is used to compute the total calorific content of the quantity of coal represented by the sample for payment purposes, provided the buyer and the seller mutually agree upon this.

5.2 The gross calorific value is used in computing the calorific value versus sulfur content to determine if the coal meets regulatory requirements for industrial fuels.

5.3 The gross calorific value may be used for evaluating the effectiveness of beneficiation processes, or for research purposes.

6. Apparatus and Facilities

6.1 *Test Space,* shall be a room or area free from drafts and that can be kept at a reasonably uniform temperature for the time required for the determination. The apparatus should be shielded from direct sunlight and radiation from other heat sources. Thermostatic control of room temperature and controlled relative humidity are desirable.

6.2 *Combustion Bomb,* shall be constructed of materials that are not affected by the combustion process or products sufficiently to introduce measurable heat input or alteration of end products. 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 of 20 MPa (3000 psig) at room temperature without stressing any part beyond its elastic limit.

6.3 *Balance,* shall be a laboratory balance having capability to weigh the sample to the nearest 0.0001 g. The balance should be checked periodically to determine is accuracy.

6.4 *Calorimeter Vessel,* shall be made of metal 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 calorimeter temperature more than 0.01°C (0.02°F) 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 low-heat conductivity.

6.5 *Jacket,* shall be a double-walled, water-filled jacket fully enclosing the calorimeter. The sides, top, and bottom of the calorimeter vessel shall be approximately 10 mm from the inner wall of the jacket to minimize convection currents. Mechanical supports for the calorimeter vessel shall provide as little thermal conduction as possible. The jacket shall have a device for stirring the water thoroughly and at a uniform rate with minimum heat input.

6.6 *Thermometers,* used to measure temperature in the calorimeter and jacket shall be any of the following types or combinations thereof:

6.6.1 *Liquid-in-Glass Thermometers,* conforming to the requirements for ASTM Thermometers 56C, 56F, 116C, or 117C as prescribed in Specification E 1. The thermometers shall be tested for accuracy against a known standard (preferably by the National Institute of Standards and Technology). For Thermometers 56C and 56F the calibration should be at intervals no larger than 2.0°C or 2.5°F over the entire graduated scale. The maximum difference in correction between any two test points shall be no more than 0.02°C or 0.05°F. For Thermometers 116C and 117C, the calibration should be at intervals no larger than 0.5°C over the entire calibrated range. The maximum difference in correction between any two test points shall not be more than 0.02°C.

6.6.2 *Beckman Differential Thermometer,* (glass enclosed scale, adjustable), having a range of approximately 6°C in 0.01°C subdivisions reading upward and conforming to the requirements for Thermometer 115C, as prescribed in Specification E 1, may be used. Each of these thermometers shall be tested for accuracy against a known standard (preferably by the National Institute of Standards and Technology) at intervals no larger than 1°C over the entire graduated scale. The maximum difference in the correction between any two test points shall not be more than 0.02°C.

6.6.3 *Other Thermometers,* of an accuracy equal to or better than 0.001°C, such as platinum resistance or linear thermistors are preferred if properly calibrated. A Wheatstone bridge and galvanometer capable of measuring resistance to 0.0001 Ω are necessary for use with 25-Ω platinum resistance thermometers.

6.7 *Thermometer Accessories*—A magnifier is required for reading liquid-in-glass thermometers to one tenth of the smallest scale division. This shall have a lens and holder designed so as to introduce no significant errors due to parallax.

6.8 *Sample Holder,* shall be an open crucible of platinum, quartz, or acceptable base-metal alloy. Base-metal alloy crucibles are acceptable, if after a few preliminary firings, the weight does not change significantly between tests.

6.9 *Ignition Wire,* shall be 100 mm of 0.16 mm diameter (No. 34 B & S gage) nickel-chromium (Chromel C) alloy or iron wire. Platinum or palladium wire, 0.10 mm diameter (No. 38 B & S gage), may be used, provided constant ignition energy is supplied. The length, or mass, of the ignition wire shall remain constant for all calibrations and calorific value determinations.

6.10 *Ignition Circuit,* for ignition purposes shall provide 6 to 16 V alternating or direct current to the ignition wire. An ammeter or pilot light is required in the circuit to indicate when current is flowing. A step-down transformer, connected to an alternating current lighting circuit or batteries, may be used.

6.11 *Buret,* used for the acid titration shall have 0.1-mL divisions.

6.12 *Automated Controller and Temperature Measuring Accessories,* may be used.

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 Analytical 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 *Reagent Water*—Reagent water conforming to Type II of Specification D 1193, shall be used for preparation of reagents and washing of the bomb interior.

7.3 *Benzoic Acid,* (C_6H_5COOH), shall be the National Institute of Standards and Technology benzoic acid. The crystals shall be pelleted before use. Commercially prepared pellets may be used provided they are made from National Institute of Standards and Technology benzoic acid. The value of heat of combustion of benzoic acid for use in the calibration calculations shall be in accordance with the value listed in the National Institute of Standards and Technology certificate issued with the standard.

7.4 *Methyl Orange, Methyl Red, or Methyl Purple Indicator,* may be used to titrate the acid formed during combustion. The indicator used shall be the same for both calibration and calorific value determinations.

7.5 *Oxygen,* shall be free of combustible matter. Only oxygen manufactured from liquid air, guaranteed to be greater than 99.5 % pure, should be used. Oxygen made by the electrolytic process may contain a small amount of hydrogen rendering it unfit without purification.

7.6 *Sodium Carbonate Standard Solution,* (Na_2CO_3), should be dried for 24 h at 105°C. Dissolve 20.9 g in water and dilute to 1 L. One millilitre of this solution is equivalent to 10.0 Btu in the nitric acid (HNO_3) titration.

8. Hazards

8.1 The following precautions are recommended for safe calorimeter operation. Additional precautions are given in Practice E 144. Also consult the calorimeter manufacturer's installation and operating manuals before using the calorimeter.

8.2 The mass of coal or coke sample and the pressure of the oxygen admitted to the bomb must not exceed the manufacturer's recommendations.

8.3 Inspect the bomb parts carefully after each use. Check the bomb for thread wear on any closures; if an inspection reveals any wear, replace the worn parts or return the bomb to the factory for testing or replacement of the defective parts. It is good practice to replace the o-rings and seals, inspect screw cap threads, and hydrostatically test the bomb as per the manufacturer's recommendations.

8.4 The oxygen supply cylinder should be equipped with an approved type of safety device, such as a reducing valve, in addition to the needle valve and pressure gage used in regulating the oxygen feed to the bomb. Valves, gages, and gaskets must meet industry safety code. Suitable reducing valves and adaptors for 3 to 4-MPa (300 to 500-psi) discharge pressure are obtainable from commercial sources of compressed gas equipment. The pressure gage shall be checked periodically for accuracy.

8.5 During ignition of a sample, the operator must not permit any portion of her or his body to extend over the calorimeter.

8.6 When combustion aids are employed, extreme caution must be exercised not to exceed the bomb manufacturer's recommendations and to avoid damage to the bomb. Do not fire loose fluffy material such as unpelleted benzoic acid, unless thoroughly mixed with the coal sample.

8.7 Do not fire the bomb if the bomb has been dropped or turned over after loading, or if there is evidence of a gas leak when the bomb is submerged in the calorimeter water.

8.8 For manually operated calorimeters, the ignition circuit switch shall be of the momentary double-contact type, normally open, except when held closed by the operator. The switch should be depressed only long enough to fire the charge.

9. Sample

9.1 The sample shall be the material pulverized to pass a 250-µm (No. 60) sieve, prepared in accordance with either Practice D 346 for coke, or Method D 2013 for coal.

9.2 A separate portion of the analysis sample should be analyzed simultaneously for moisture content in accordance with Method D 2013 and Test Method D 3173, so that calculation to other bases can be made.

9.3 Sulfur analysis shall be made in accordance with Test Methods D 3177.

10. Standardization

10.1 The calorimeter is standardized by combustion of benzoic acid.

10.2 Determine the energy equivalent as the average of a series of ten individual test runs. To be acceptable the relative standard deviation of the series shall be 0.15 % or less of the average energy equivalent (see Table 2). For this purpose, any individual test may be discarded if there is evidence of incomplete combustion. If, after considering the possibility of outliers utilizing criterion established in Practice E 178, this limit is not met, one should review operation of the calorimeter for any assignable cause which should be corrected before repeating the series.

10.3 *Procedure:*

10.3.1 Regulate the weights of the pellets of benzoic acid in each series to yield approximately the same temperature rise as that obtained with the coal tested in the same laboratory. The usual range of masses is 0.9 to 1.3 g. Weigh

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[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.

TABLE 2 Standard Deviations for Calorimeter Standardization[A]

Standardization Number	Column A	Column B	Column C
	Energy Equivalent (Btu/lb) × (g/°C)	Code to 4400 (Column A − 4400)	(Column B)^2
1	4412	12	144
2	4407	7	49
3	4415	15	225
4	4408	8	64
5	4404	4	16
6	4406	6	36
7	4409	9	81
8	4410	10	100
9	4412	12	144
10	4409	9	81
SUM		92	940

Average = $\bar{X} = \Sigma X/10 = (92/10) + 4400 = 4409$

Variance = $s^2 = \dfrac{\Sigma \text{ Column C} - [(\Sigma \text{ Column B})^2/n]}{n-1} = \dfrac{940 - [(92)^2/10]}{9} = 10.4$

Standard deviation = $s = \sqrt{\text{variance}} = \sqrt{10.4} = 3.22$

[A] In this example the values of energy equivalent are typical for a calorimeter calibrated so that, if the energy equivalent is multiplied by the temperature rise in degrees Celsius per gram of sample, the calorific value of the sample will be obtained in British Thermal units per pound.

the pellet to the nearest 0.0001 g in the sample holder in which it is to be burned, and record the weight as the mass.

10.3.2 Rinse the bomb, invert to drain, and leave undried. Add 1.0 mL of water to the bomb prior to assembly for a determination.

10.3.3 Connect a measured length of ignition wire to the ignition terminals, with enough slack to allow the ignition wire to maintain contact with the sample.

10.3.4 Assemble the bomb and charge it with oxygen to a consistent pressure between 2 to 3 MPa (20 to 30 atm). This pressure must remain the same for each calibration and each calorific-value determination. Admit the oxygen slowly into the bomb so as not to blow powdered material from the sample holder. If the pressure exceeds the specified pressure, do not proceed with the combustion. Instead, detach the filling connection, exhaust the bomb in the usual manner, and discard the sample.

10.3.5 Fill the calorimeter vessel (bucket) with the measured (or weighed) quantity of water adjusted from 1.0 to 2.0°C (2.0 to 4.0°F) below room temperature, but not lower than 20°C (68°F). Use the same mass of water in each test weighed to +0.5 g. For 2000-mL calorimeters, the proper quantity can be obtained by use of a volumetric flask calibrated to deliver 2000 ± 0.5 mL. As the density of water varies with temperature, make suitable corrections if the water temperature varies from the temperature at which the flask was calibrated. Place the assembled bomb in the calorimeter vessel. Check that no oxygen bubbles are leaking from the bomb. Place the calorimeter vessel in the jacket; connect the electrodes; place the stirrers, thermometers, and cover in position. Start the stirrers and continue to operate them throughout the determination. Examine the thermometers for liquid separation and correct any separation before proceeding. The starting temperature should be within ±0.5°C (0.9°F) of that used in analysis of coal or coke samples.

NOTE 4—Check all liquid-in-glass thermometers at least daily for defects, for example, cracked glass, etc.

10.3.6 Allow 5 min for attainment of equilibrium. Adjust the jacket temperature to match the calorimeter temperature within 0.01°C (0.02°F) and maintain for 3 min. Use a magnifier when using ASTM Bomb Calorimeter Thermometers 56C or 56F, and estimate all readings (except those during the rapid-rise period) to the nearest 0.002°C or 0.005°F. Estimate ASTM Thermometers 115C, 116C, or 117C readings to 0.001°C, and 25 Ω resistance thermometer readings to the nearest 0.0001 Ω. Tap mercury thermometers (for instance, with a pencil) just before reading to avoid errors caused by mercury sticking to the walls of the capillary. Take calorimeter temperature readings at one-minute intervals until the same temperature, within one-tenth of the smallest thermometer subdivision, is observed in three successive readings. Record this "initial temperature", t_1, 20°C (68°F) or higher, to within one-tenth of the smallest thermometer subdivision and ignite the charge. Adjust the jacket temperature to match the calorimeter temperature during the period of rise; keep the two temperatures as nearly equal as possible during the rapid rise and adjust to within 0.01°C (0.02°F) when approaching the final equilibrium temperature. Take calorimeter temperature readings at 1-min intervals until the same temperature, within one-tenth of the smallest thermometer subdivision, is observed in three successive readings. Record this as the "final temperature", t_f.

10.3.7 Open the cover and remove the bomb. Release the pressure at a uniform rate, such that the operation will require not less than 1 min. Open the bomb and examine the bomb interior. Discard the test if unburned sample or sooty deposits are found. Wash the interior of the bomb with distilled water containing the titration indicator, until the washings are free of acid, and titrate the washings with standard sodium carbonate solution.

10.3.8 Remove and measure, or weigh, the combined pieces of unburned ignition (firing) wire and subtract from the original length, or weigh to determine the wire consumed in firing. If the wire is weighed, remove the ball of oxidized metal from the end of each piece of wire before weighing.

10.4 *Calculations:*

10.4.1 *Temperature Rise*—Using data obtained as prescribed in 10.3.6, compute the corrected temperature rise, t, as follows:

$$t = t_f - t_i + C_e + C_s \qquad (1)$$

where:

t = corrected temperature rise, °C or °F,

t_i = initial temperature reading at time of firing, °C or °F,

t_f = final temperature reading, °C or °F,

C_e = thermometer emergent stem correction, if required (see Note 5 and Annex A1.1.4), and

C_s = thermometer setting correction, if required (see Note 5 and Annex A1.1.3).

NOTE 5—With all mercury-in-glass thermometers, it is necessary to make corrections if the total calorific value is altered by 5.0 Btu or more. This represents a change of 0.001°C or 0.002°F in a calorimeter using approximately 2000 g of water. Beckmann thermometers also require a setting correction and an emergent stem correction (see Annex A1.1.3 and A1.1.4). Solid-stem ASTM Thermometers 56C and 56F do not require emergent stem corrections if all tests, including standardization, are performed within the same 5.5°C (10°F) interval. If operating temperatures range beyond this limit, a differential emergent stem correction (see Annex A1.1.4) must be applied to the corrected temperature rise, t, in all tests including standardization.

10.4.2 *Thermochemical Corrections* (see Appendix X1.1, X1.2, and X1.3)—Compute the following for each test:

e_1 = correction for the heat of formation of HNO_3, Btu. Each millilitre of standard Na_2CO_3 is equivalent to 10.0 Btu, and

e_2 = correction for heat of combustion of firing wire, Btu (Note 6).
= 0.41 Btu/mm or 2.6 Btu/mg for No. 34 B & S gage Chromel C wire.
= 0.49 Btu/mm or 3.2 Btu/mg for No. 34 B & S gage iron wire.

NOTE 6—There is no correction for platinum wire provided the ignition energy is constant.

10.4.3 Compute the calorimeter energy equivalent, E, by substituting in the following:

$$E = [(Hg) + e_1 + e_2]/t \qquad (2)$$

where:

E = calorimeter energy equivalent (Note 7),
H = heat of combustion of benzoic acid, as stated in the National Institute of Standards and Technology Certificate, Btu/lb in air,
g = mass (weight in air) of benzoic acid, g,
e_1 = titration correction (10.4.2),
e_2 = fuse wire correction (10.4.2), and
t = corrected temperature rise.

NOTE 7—Using the units and corrections as given in 10.4.1 and 10.4.2, the energy equivalent of the calorimeter is such that the calorific value of the coal sample will be obtained directly in British thermal units per pound when the mass of sample is taken in grams. The units of the energy equivalent are therefore: (British thermal units per pound) times (grams per degree).

10.5 Repeat the procedure for a total of ten determinations. Compute the standard deviation as illustrated in Table 2.

11. Restandardization

11.1 Make checks on the energy equivalent value after changing the oxygen supply, after changing any part of the calorimeter, and at least once a month otherwise.

11.1.1 If a single new determination differs from the old value by 6 Btu/°C (4 Btu/°F), the old standard is suspect, thereby requiring a second test.

11.1.2 The difference between the two new determinations must not exceed 8 Btu/°C (5 Btu/°F), and the average of the two new determinations must not differ from the old standard by more than 4 Btu/°C (3 Btu/°F). If these requirements are met, do not change the calorimeter standard.

11.1.3 If the requirements given in 11.1.2 are not met, two more determinations must be run. The range of the four values must not exceed 14 Btu/°C (8 Btu/°F), and the average of the four new determinations must not differ from the old standard value by more than 3 Btu/°C (2 Btu/°F). If these requirements are met, do not change the calorimeter standard.

11.1.4 If the requirements given in 11.1.3 are not met, a fifth and sixth determination must be run. The range of the six new values must not exceed 17 Btu/°C (10 Btu/°F), and the average of the six new values must not differ from the old standard value by more than 2 Btu/°C (2 Btu/°F). If these requirements are met, do not change the calorimeter standard.

TABLE 3 Summary of Numerical Requirements

NOTE—Test values exceeding table limits require additional runs.[A]

Number of Runs	Maximum Range of Results		Maximum Difference between $\bar{X}_1$ and $\bar{X}_2$[B]	
	Btu/°C	Btu/°F	Btu/°C	Btu/°F
1	. . .	. . .	±6	±4
2	8	5	±4	±3
4	14	8	±3	±2
6	17	10	±2	±2
10	20	12	±1	±1

[A] Values in this table have been rounded off after statistical calculation, and are therefore not precisely in a ratio from 1.8 to 1.0.

[B] $\bar{X}_1$ = average of original standard. $\bar{X}_2$ = average of check runs.

11.1.5 If the requirements given in 11.1.4 are not met, four more determinations must be run to complete a series of ten runs. The range of these ten results must not exceed 20 Btu/°C (12 Btu/°F), and the average of the ten new standards must not differ from the old standard by more than 1 Btu/°C (1 Btu/°F). If these requirements are met, do not change the calorimeter standard.

11.1.6 If the requirements given in 11.1.5 are not met, the average value from the ten new values must be used for the new standard energy equivalent, provided that the standard deviation of the series does not exceed 6.5 Btu/°C (3.6 Btu/°F).

11.2 The summary of the numerical requirements at each stage of restandardization is given in Table 3.

12. Procedure for Coal and Coke Samples (Note 8)

12.1 Thoroughly mix the analysis sample of coal or coke in the sample bottle and carefully weigh approximately 1 g of it into the sample holder. Weigh the sample to the nearest 0.0001 g. Make each determination in accordance with the procedure described in 10.3.2 through 10.3.8.

NOTE 8—For anthracite, coke, and coal of high ash content, that do not readily burn completely, one of the following procedures are recommended: (*1*) The inside of the sample holder is lined completely with ignited asbestos in a thin layer pressed well down in the angles, and the sample is then sprinkled evenly over the surface of the asbestos. (*2*) The mass of the sample may be varied to obtain good ignition. If the mass is varied, it will be necessary to recalibrate the calorimeter so that the water equivalent will be based on the same temperature rise as that obtained with the sample weight. (*3*) A known amount of benzoic acid may be mixed with the sample. Proper allowance must be made for the heat of combustion of benzoic acid when determining the calorific value of the sample.

NOTE 9—For the calorific value of coke, it is necessary to use 3-MPa (30-atm) pressure for both standardization and analysis.

12.2 Determine the sulfur content of the sample by any of the procedures described in Test Methods D 3177.

13. Calculation (Note 2)

13.1 Compute the corrected temperature rise, t, as shown in 10.4.1.

13.2 *Thermochemical Corrections* (Appendix X1)—Compute the following for each test:

e_1 = correction for the heat of formation of HNO_3, Btu. Each millilitre of standard sodium carbonate is equivalent to 10.0 Btu,

e_2 = correction for heat of combustion of ignition wire, Btu,
= 0.41 Btu/mm or 2.6 Btu/mg for No. 34 B & S gage Chromel C wire,

= 0.49 Btu/mm or 3.2 Btu/mg for No. 34 B & S gage iron wire, and
e_3 = correction for difference between heat of formation of H_2SO_4 from the heat of formation of HNO_3, Btu,
= 23.7 times percent of sulfur in sample times mass of sample, g.

14. Calorific Value (Note 10)

14.1 *Gross Calorific Value*—Calculate the gross calorific value (gross heat of combustion at constant volume), Q_v (gross), as follows:

$$Q_v \text{ (gross)} = [(tE) - e_1 - e_2 - e_3]/g \qquad (3)$$

where:
Q_v (gross) = gross calorific value, Btu/lb,
t = corrected temperature rise calculated in 13.1, °C or °F,
E = energy equivalent calculated in 10.4.3,
e_1, e_2, e_3 = corrections as prescribed in 13.2, and
g = mass of sample, g.

NOTE 10—This calculation gives calorific value in British thermal units per pound. To obtain calorific value in joules per gram, see Appendix X2.

14.2 *Net Calorific Value*—Calculate the net calorific value (net heat of combustion at a constant pressure), Q_p (net), as follows:

$$Q_p \text{ (net)}_{ar} = Q_v \text{ (gross)}_{ar} - 5.72\ (H_{ar} \times 9) \qquad (4)$$

where:
Q_p (net)$_{ar}$ = net calorific value at constant pressure, cal/g
Q_v (gross)$_{ar}$ = gross calorific value at constant volume, as-received basis, cal/g, and
H_{ar} = total hydrogen as-received basis, where hydrogen includes the hydrogen in sample moisture, %.

NOTE 11—Example for converting from the as-determined (air-dried) sample basis to the as-received net calorific value basis:[7]

Calories, as determined (gram/Cal$_{ad}$) = 7506
Calories, as received (gram/Cal$_{ar}$) = 7056
Moisture, as determined (M_{ad}) = 2.13
Moisture, as received (M_{ar}) = 8.00
Hydrogen, as determined (H_{ad}) = 5.00

To convert H_{ad} to H_{ar}:

$$H_{ar} = \left[(H_{ad} - 0.1119\ M_{ad}) \times \frac{100 - M_{ar}}{100 - M_{ad}}\right] + 0.1119\ M_{ar}$$

$$= \left[(5.00 - 0.1119 \times 2.13) \times \left(\frac{100 - 8.00}{100 - 2.13}\right)\right] + 0.1119 \times 8.00$$

$$H_{ar} = 5.37$$

Q_p (net)$_{ar}$ = 7056 − 5.72 (5.37 × 9)
= 7056 − 276
= 6780 cal/g (International Table Calories)
= 12204 Btu/lb
= 28390 J/g
= 28.39 MJ/kg

15. Report

15.1 The results of the calorific value may be reported on any of a number of bases, differing from each other in the manner that moisture is treated.

15.2 Use the percent moisture in the sample passing a 250-μm (No. 60) sieve (Test Method D 3173) to calculate the results of the analysis sample to a dry basis.

15.3 Procedures for converting the value obtained on the analysis sample to other bases are described in Practice D 3180.

16. Precision and Bias

16.1 *Precision*—The relative precision of this test method for the determination of gross calorific value (Btu) covers the range from 7,112 to 8,120 cal/g (12,700 to 14,500 Btu/lb) for bituminous coals and from 4,922 to 7,140 cal/g (8,790 to 12,750 Btu/lb) for subbituminous and lignite coals.

16.1.1 *Repeatability*—The difference in absolute value between two consecutive test results, carried out on the same sample of 250-μm (No. 60) pulp, in the same laboratory, by the same operator, using the same apparatus, 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 both, of the test results. The repeatability interval for this test method is 28 cal/g (50 Btu/lb) on a dry basis.

16.1.2 *Repeatability*—The difference in absolute value between test results, obtained in the same laboratory, by the same operator, using the same riffle, determined on a single test specimen 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 repeatability limit for more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the repeatability limit, there is reason to question one, or both, of the test results. The repeatability limit for this test method on a dry basis is:

Bituminous coals	39 cal/g (69 Btu/lb)
Subbituminous and lignite coals	33 cal/g (59 Btu/lb)

16.1.3 *Reproducibility*—The difference in absolute value of replicate determinations, carried out in different laboratories on representative 250-μm (No. 60) samples, prepared from the same bulk sample after the last stage of reduction, 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 both, of the test results. The reproducibility interval for this test method is 56 cal/g (100 Btu/lb) on a dry basis.

16.1.4 *Reproducibility*—The difference in absolute value between test results obtained in different 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 limit for more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the reproducibility limit, there is reason to question one, or both, of the test results. The reproducibility limit for this test method on a dry basis is:

Bituminous coals	60 cal/g (107 Btu/lb)
Subbituminous and lignite coals	78 cal/g (140 Btu/lb)

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[7] For a comprehensive theoretical derivation of calculations for converting gross calorific value at constant volume to net calorific value at constant pressure, request Research Report RR: D05-1014.

NOTE 7—Supporting data for 2.36-mm (No. 8) coal has been filed at ASTM Headquarters and may be obtained by requesting RR:DO5-1015.

NOTE 8—The precision for 250-µm (No. 60) coal is currently being evaluated.

16.2 *Bias*—The equipment used in this test method for measuring gross calorific value has no bias because it is standardized with a compound having a known heat of combustion. This procedure may involve tests that produce varying levels of heat formation not accounted for in standardization. If the thermochemical corrections for heat of formation are not done correctly, a bias may be present in the determination.

ANNEX

(Mandatory Information)

A1. THERMOMETRIC CORRECTIONS

A1.1 Thermometer Corrections

A1.1.1 It is necessary to make the following individual corrections, if not making the correction would result in an equivalent change of 5.0 Btu or more.

A1.1.2 *Calibration Correction* shall be made in accordance with the calibration certificate furnished by the calibration authority.

A1.1.3 *Setting Correction* is necessary for the Beckmann thermometer. It shall be made in accordance with the directions furnished by the calibration authority.

A1.1.4 *Differential Emergent Stem Correction*—The calculation of differential stem correction depends upon the way the thermometer was calibrated and how it was used. Two conditions are possible:

A1.1.4.1 *Thermometers Calibrated in Total Immersion and Used in Partial Immersion*—This emergent stem correction is made as follows:

$$\text{Correction} = C_e = K\,(t_f - t_i)\,(t_f + t_i - L - T) \qquad \text{(A1.1)}$$

where:

C_e = emergent stem correction,
K = 0.00016 for thermometers calibrated in °C,
= 0.0009 for thermometers calibrated in °F,
L = scale reading to which the thermometer was immersed,
T = mean temperature of emergent stem, °C or °F,
t_i = initial temperature reading, °C or °F, and,
t_f = final temperature reading, °C or °F.

NOTE A1.1—*Example:* Assume the point L, to which the thermometer was immersed was 16°C; its initial reading, t_i, was 24.127°C, its final reading, t_f, was 27.876, the mean temperature of the emergent stem, T was 26°C; then:

$$\begin{aligned}&\text{Differential stem correction, } C_e\\ &= 0.00016\,(28 - 24)\,(28 + 24 - 16 - 26)\\ &= +\,0.0064^\circ\text{C.}\end{aligned}$$

A1.1.4.2 *Thermometers Calibrated and Used in Partial Immersion, but at a Different Temperature than the Calibration Temperature*—This emergent stem correction is made as follows:

$$\text{Correction} = C_e = K\,(t_f - t_i)\,(t_c - t_o) \qquad \text{(A1.2)}$$

where:

C_e = emergent stem correction,
K = 0.00016 for thermometers calibrated in °C,
= 0.00009 for thermometers calibrated in °F,
t_i = initial temperature reading, °C or °F,
t_f = final temperature reading, °C or °F,
t_o = observed stem temperature, °C or °F, and
t_c = stem temperature at which the thermometer was calibrated, °C or °F.

NOTE A1.2—*Example:* Assume the initial reading, t_i, was 80°F, the final reading, t_f, was 86°F, and that the observed stem temperature, t_o, was 82°F, and calibration temperature, t_c, was 72°F then:

$$\begin{aligned}&\text{Differential stem correction}\\ &= 0.00009\,(86 - 80)\,(82 - 72)\\ &= 0.005^\circ\text{F}\end{aligned}$$

APPENDIXES

(Nonmandatory Information)

X1. THERMOCHEMICAL CORRECTIONS

X1.1 *Energy of Formation of Nitric Acid*—A correction, e_1, (10.4.2 and 13.2), is applied for the acid titration. This correction is based on the assumptions (*1*) that all the acid titrated is HNO_3 formed by the following reaction: 1/2 N_2 (gas) + 5/4 O_2 (gas) + 1/2 H_2O (liquid) = HNO_3 (in 500 mol H_2O), and (*2*) that the energy of formation of HNO_3 in approximately 500 mol of water under bomb conditions is −59.0 kJ/mol.[8]

X1.1.1 A convenient concentration of Na_2CO_3 is 0.394 *N* (20.9 g Na_2CO_3/1000 mL) which gives e_1 = 10 times *V*, where *V* is the volume of Na_2CO_3 in millilitres. The factor 10.0 (0.394 × 59.0 = 2.326) is to be used for calculating calorific value in British thermal units per pound. For other units see Table X2.1. When H_2SO_4 is also present, a part of the correction for H_2SO_4 is contained in the e_1 correction and remainder in the e_3 correction.

X1.2 *Energy of Formation of Sulfuric Acid*—By definition (see Terminology D 121) the gross calorific value is obtained when the product of the combustion of sulfur in the sample is SO_4 (in grams). However, in actual bomb combustion process, all the sulfur is found as H_2SO_4 in the bomb washings. A correction, e_3 (see 13.2) is applied for the sulfur that is converted to H_2SO_4. This correction is based upon the energy of formation of H_2SO_4 in solutions, such as will be present in the bomb at the end of a combustion. This energy is taken as −295.0 kJ/mol.[9] A correction of 2 times 59.0 kJ/mol of sulfur was applied in the e_1 correction, so the additional correction necessary is 295.0 − (2 times 59.0) = 177 kJ/mol, or 5.52 kJ/per gram of sulfur in the sample (55.2 J times weight of sample in grams times percent sulfur in sample). This causes e_2 to be 23.7 times weight of sample in grams times percent sulfur in sample. The factor 23.7 (equals 55.2/2.326), for e_3 (see 13.2) is to be used for calculating calorific value in British thermal units per pound. For other units, see Appendix X2. The values above are based on a coal containing about 5 % sulfur and about 5 % hydrogen. The assumption is also made that the H_2SO_4 is dissolved entirely in the water condensed during combustion of the sample.

X1.2.1 If a 1-g sample of such a fuel is burned, the resulting H_2SO_4 condensed with water formed on the walls of the bomb, will have a ratio of about 15 mol of water to 1 mol of H_2SO_4. For this concentration, the energy of the reaction SO_2 (gas) + ½ O_2 + H_2O (liquid) = H_2SO_4 (in 15 moles of H_2O) under the conditions of the bomb process is −295.0 kJ/mol.[10] Basing the calculation upon a sample of comparatively large sulfur content reduces the possible overall errors, because, for small percent of sulfur, the correction is smaller.

X1.3 *Fuse (Ignition) Wire*—Calculate the energy contributed by burning the fuse wire in accordance with the directions furnished by the supplier of the wire. For example, the energy of the combustion of No. 34 B & S gage Chromel C wire is 6.0 J/mg or approximately 0.95 J/mm. For calculating e_2 for use in Eqs 2 and 3, these give e_2 = 0.41 times length (mm) of wire or e_2 = 2.6 times weight (mg) of wire. The energy required to melt a platinum wire is constant for each experiment if the same amount of platinum wire is used. As the energy is small, its effect is essentially cancelled out in the relationship between the standardization experiments and the calorific value determinations, and it can be neglected. The factors listed above for e_2 (10.4.2 and 13.2) are suitable for calculating calorific value in British thermal units per pound. For other units, see Appendix X2.

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[8] Calculated from data in National Bureau of Standards Technical Note 270-3.

[9] Calculated from data in National Bureau of Standards Circular 500.

[10] Mott, R. A. and Parker, C., "Studies in Bomb Calorimetry IX—Formation of Sulfuric Acid," *Fuel*, Vol 37, 1958, p. 371.

X2. REPORTING RESULTS IN OTHER UNITS

X2.1 *Reporting Results in Joules per Gram:*

X2.1.1 The gross calorific value can be expressed in joules per gram, calories per gram, or British thermal units per pound. The relationships between these units are given in Table 1.

X2.1.2 Because the energy of combustion of the reference material is measured and certified by the National Institute of Standards and Technology (NIST) in joules per gram, the most straightforward usage of the reference material would lead to the calorific value of the fuel in joules per gram. To carry out this procedure, make the changes outlined in X2.1.3 through X2.1.5.

X2.1.3 For calculating energy equivalent, substitute Eq X2.1 for Eq 2:

$$E = [(H'g) + e_1']/t \qquad \text{(X2.1)}$$

where the meanings of the symbols in Eq X2.1 are the same as in Eq 2 except that:

E' = energy equivalent in units of joules per temperature unit,

H' = the heat of combustion of reference material in units of joules per gram weight in air (J/g from the certificate for the NIST benzoic acid), and

e_1' and e_3' = corrections in units of joules, (see Table X2.1).

X2.1.4 For calculating gross calorific value, substitute Eq X2.2 for Eq 3:

$$Q_v\ \text{(gross)} = [(t_E') - e_1' - e_2']/g \qquad \text{(X2.2)}$$

where the meanings of the symbols in Eq X2.2 are the same as in Eq 3 except that:

Q_v (gross) = gross calorific value with units of joules per gram (weight in air),

E' = energy equivalent units, of joules per temperature unit, and

e_1', e_2', and e_3' = corrections in units of joules (see Table X2.1).

X2.1.5 *Precision:*

X2.1.5.1 *Repeatability*—Duplicate results by the same laboratory, using the same operator and equipment, should not be considered suspect unless they differ by more than 120 J/g.

X2.1.5.2 *Reproducibility*—The results submitted by two or more laboratories (different equipment, operators, date of test, and different portions of the same sample) should not be considered suspect unless the results differ by more than 240 J/g.

TABLE X2.1 Alternative Thermochemical Correction Factors (Units in Joules)[A]

Correction	Multiplication Factor	Multiply By
e_1' (HNO_3)	20 J/mL	mL of 0.34 *N* Na_2CO_3
e_3' (H_2SO_4)	55.2 J/cgS	percent of sulfur in sample times mass of sample in grams
e_2' (fuse wire) or	0.95 J/mm	length (mm) of No. 34 B & S gage Chromel C wire
e_2' (fuse wire)	1.14 J/mm	length (mm) of No. 34 B & S gage iron wire
e_2' (fuse wire) or	6.0 J/mg	mass (mg) of Chromel C wire
e_2' (fuse wire)	7.4 J/mg	mass (mg) of iron wire

[A] To be used in Eqs X2.1 and X2.2 only.

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Standard Test Methods for Cyanides in Water[1]

This standard is issued under the fixed designation D 2036; 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 cover the determination of cyanides in water. The following test methods are included:

	Sections
Test Method A—Total Cyanides after Distillation	12 to 18
Test Method B—Cyanides Amenable to Chlorination[2] by Difference	19 to 25
Test Method C—Weak Acid Dissociable Cyanides	26 to 32
Test Method D—Cyanides Amenable to Chlorination without Distillation (Short-Cut Method)	33 to 39

1.2 Cyanogen halides may be determined separately.

NOTE 1—Cyanogen chloride is the most common of the cyanogen halide complexes as it is a reaction product and is usually present when chlorinating cyanide-containing industrial waste water. For the presence or absence of CNCl, the spot test method given in Annex A1 can be used.

1.3 These test methods do not distinguish between cyanide ions and metallocyanide compounds and complexes. Furthermore, they do not detect the cyanates.

NOTE 2—The cyanate complexes are decomposed when the sample is acidified in the distillation procedure.

1.4 The cyanide in cyanocomplexes of gold, platinum, cobalt and some other transition metals is not completely recovered by these test methods.

1.5 Only a few organo-cyanide complexes are recovered, and those only to a minor extent.

1.6 Part or all of these test methods have been used successfully with reagent water and various waste waters. It is the user's responsibility to assure the validity of the test method for the water matrix being tested.

1.7 Separation of the cyanide from interfering substances prior to electrochemical determination (see 16.5 for ion chromatography procedure) should be conducted when using Test Method A-total cyanides after distillation or Test Method B-cyanides amenable to chlorination by the difference when sulfur, thiocyanate, or other sulfur containing compounds are present.

1.8 *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.* Specific hazard statements are given in Note 3, Note 4, Note 6, and Note 7, 5.1, and Section 9.

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 Methods of Committee D-19 on Water[3]

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

D 3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water[3]

D 4210 Practice for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data[3]

D 5788 Guide for Spiking Organics into Aqueous Samples[3]

D 5789 Practice for Writing Quality Control Specifications for Standard Test Methods for Organic Constituents[3]

E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals[4]

E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared Spectrophotometers[5]

3. Terminology

3.1 Definitions—For definitions of terms used in these test methods, refer to Terminology D 1129.

3.2 *Abbreviations:*

3.2.1 *HPLC*—High Performance Liquid Chromatography

3.2.2 *IC*—Ion Chromatography

4. Summary of Test Methods

4.1 The cyanide as hydrocyanic acid (HCN) is released from compounds by means of reflux distillation and absorbed in sodium hydroxide solution. The conditions used for the distillation distinguish the type of cyanide. The sodium cyanide in the absorbing solution can be determined colorimetrically,

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[1] These test methods are under the jurisdiction of ASTM Committee D-19 on Water and are the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

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[2] For an explanation of the term cyanides amenable to alkaline chlorination, see Lancy, L. E. and Zabban, W., "Analytical Methods and Instrumentation for Determining Cyanogen Compounds," *Papers on Industrial Water and Industrial Waste Water, ASTM STP 337*, 1962, pp. 32–45.

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

[4] *Annual Book of ASTM Standards*, Vol 03.05.

[5] *Annual Book of ASTM Standards*, Vol 03.06.

by titration or by selective ion electrode.

4.2 Test Method A, Total Cyanides, is based on the decomposition of nearly all cyanides in the presence of strong acid, magnesium chloride catalyst, and heat during a 1-h reflux distillation.

4.3 Test Method B, Cyanide Amenable to Chlorination, is based on chlorinating a portion of the sample under controlled conditions followed by the determination of total cyanide in both the original and chlorinated samples. Cyanides amenable to chlorination are calculated by difference.

4.3.1 This test method can be affected by compounds that are converted during chlorination to color-producing compounds or react with the reagents used, and cause interference in the procedure employed to determine cyanide in the absorption solution.

4.4 Test Method C, Weak Acid Dissociable Cyanides, is based on the decomposition of cyanides in the presence of weak acid, zinc acetate and heat during a 1-h reflux distillation.

4.5 Test Method D, Cyanide Amenable to Chlorination without Distillation, is a direct colorimetric procedure.

4.6 The minimum concentration of cyanide in the absorption solution that can be accurately determined colorimetrically is 0.005 mg/L, by titration 0.4 mg/L and by selective ion electrode 0.05 mg/L. Pretreatment including distillation tends to increase these concentrations to a degree determined by the amount of manipulation required and the type of sample.

4.7 Round-robin data indicate the following minimum concentrations: colorimetric 0.03 mg/L; titration 1.0 mg/L; and selective ion electrode 0.03 mg/L.

5. Significance and Use

5.1 Cyanide is highly toxic. Regulations have been established to require the monitoring of cyanide in industrial and domestic wastes and in surface waters (Appendix X1).

5.2 Test Method D is applicable for natural water and clean metal finishing or heat treatment effluents. It may be used for process control in wastewater treatment facilities providing its applicability has been validated by Test Method B or C.

5.3 The spot test outlined in Annex A1 can be used to detect cyanide and thiocyanate in water or wastewater, and to approximate its concentration.

6. Interferences

6.1 Common interferences in the analysis for cyanide include oxidizing agents, sulfides, aldehydes, glucose and other sugars, high concentration of carbonate, fatty acids, thiocyanate, and other sulfur containing compounds.

6.2 It is beyond the scope of these test methods to describe procedures for overcoming all of the possible interferences that may be encountered.

6.3 When the procedures must be revised to meet specific requirements, recovery data must be obtained by the addition of known amounts of cyanide to the sample.

7. Apparatus

7.1 *Distillation Apparatus*—The reaction vessel shall be a 1-L round bottom flask, with provision for an inlet tube and a condenser. The inlet tube shall be a funnel with an 8-mm diameter stem that extends to within 6 mm of the bottom of the flask. The condenser, which is recommended, shall be a reflux-type, cold finger, or Allihn. The condenser shall be connected to a vacuum-type absorber which shall be in turn connected to a vacuum line which has provision for fine control. The flask shall be heated with an electric heater. Examples of the apparatus are shown in Fig. 1. Equivalent apparatus is acceptable provided cyanide recoveries of 100 ± 4 % are documented.

7.2 *Spectrophotometer or Filter Photometer*, suitable for measurement in the region of 578 nm, using 1.0-, 2.0-, 5.0-, and 10.0-cm absorption cells. Filter photometers and photometric practices used in these test methods shall conform to Practice E 60. Spectrophotometers shall conform to Practice E 275.

7.3 *Selective Ion Meter*, or a pH meter with expanded millivolt scale equipped with a cyanide activity electrode and a reference electrode.

7.4 *Mixer*, magnetic, with a TFE-fluorocarbon-coated stirring bar.

7.5 *Buret*, Koch, micro, 2- or 5-mL, calibrated in 0.01 mL.

7.6 *Ion Chromatograph*, high performance ion chromatograph equipped with a 10-μL sample solution injection device and pulsed-electrochemical detector.

7.7 *Chromatography Column*, Dionex IonPac AS7 anion-~~exchange, 4 × 250 mm and matching guard column or equiva-~~lent.

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 of the Committee on Analytical Reagents of the American Chemical Society,

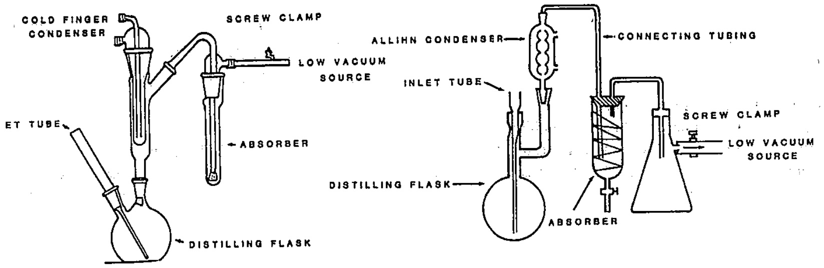

FIG. 1 Cyanide Distillation Apparatus

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.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type II grade of Specification D 1193.

8.3 *Acetic Acid* (1 + 9)—Mix 1 volume of glacial acetic acid with 9 volumes of water.

8.4 *Acetate Buffer*—Dissolve 410 g of sodium acetate trihydrate ($NaC_2H_3O_2 \cdot 3H_2O$) in 500 mL of water. Add glacial acetic acid to yield a solution pH of 4.5, approximately 500 mL.

8.5 *Barbituric Acid.*

8.6 *Calcium Hypochlorite Solution* (50 g/L)—Dissolve 5 g of calcium hypochlorite ($Ca(OCl)_2$) in 100 mL of water. Store the solution in an amber glass bottle in the dark. Prepare fresh monthly.

8.7 *Chloramine-T Solution* (10 g/L)—Dissolve 1.0 g of the white-colored, water-soluble grade powder chloramine-T in 100 mL of water. Prepare fresh weekly.

8.8 *Cyanide Solution, Stock* (1 mL = 250 μg CN^-)—Dissolve 0.6258 g of potassium cyanide (KCN) (**Warning**—see Note 3) in 40 mL of sodium hydroxide solution (40 g/L). Dilute to 1 L with water. Mix thoroughly. Standardize with standard silver nitrate solution following the titration procedure (see 16.2).

Note 3—**Warning**—Because KCN is highly toxic, avoid contact or inhalation (see Section 9).

8.8.1 *Cyanide I Solution, Standard* (1 mL = 25 μg CN^-)—Dilute a calculated volume (approximately 100 mL) of KCN stock solution to 1 L with NaOH solution (1.6 g/L).

8.8.2 *Cyanide II Solution, Standard* (1 mL = 2.5 μg CN^-)—Dilute exactly 100 mL of KCN standard solution I to 1 L with NaOH solution (1.6 g/L).

8.8.3 *Cyanide III Solution, Standard* (1 mL = 0.25 μg CN^-)— Dilute exactly 100 mL of KCN standard solution II to 1 L with NaOH solution (1.6 g/L). Prepare fresh solution daily and protect from light.

8.8.4 *Cyanide IV Solution, Standard* (1 mL = 0.025 μg CN^-)— Dilute exactly 100 mL of KCN standard solution III to 1 L with NaOH solution (1.6 g/L). Prepare fresh solution daily and protect from light.

8.9 *Hydrogen Peroxide Solution*, 3 %—Dilute 10 mL of 30 % hydrogen peroxide (H_2O_2) to 100 mL. Prepare fresh weekly.

8.10 *Isooctane, Hexane, Chloroform* (solvent preference in the order named).

8.11 *Lead Carbonate* ($PbCO_3$), *Lead Acetate* ($Pb(C_2H_3O_2)_2 \cdot 3H_2O$), or *Lead Nitrate* ($Pb(NO_3)_2$)—Lead acetate and lead nitrate can be put in solution with water, if desired, at a suggested concentration of 50 g/L.

8.12 *Lime*, hydrate ($Ca(OH)_2$), powder.

8.13 *Magnesium Chloride Solution*—Dissolve 510 g of magnesium chloride ($MgCl_2 \cdot 6H_2O$) in water and dilute to 1 L.

8.14 *Potassium Iodide-Starch Test Paper.*

8.15 *Pyridine-Barbituric Acid Reagent*— Place 15 g of barbituric acid in a 250-mL volumetric flask and add just enough water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine and mix. Add 15 mL of hydrochloric acid (sp gr 1.19), mix, and cool to room temperature. Dilute to volume with water and mix until all of the barbituric acid is dissolved. This solution is usable for about 6 months if stored in a cold dark place.

8.16 *Rhodanine Indicator Solution* (0.2 g/L)—Dissolve 0.02 g of (p-dimethylaminobenzylidene) in 100 mL of acetone.

8.17 *Silver Nitrate Solution, Standard* (0.01 *N*)—Dissolve 1.6987 g of silver nitrate ($AgNO_3$) in water and dilute to 1 L. Mix thoroughly. Store in a dark container.

8.18 *Sodium Arsenite Solution* (20 g/L)—Dissolve 2 g of $NaAsO_2$ in 100 mL of water.

Note 4—**Warning**—This material has appeared on lists of suspected and known carcinogens. Avoid contact with skin.

8.19 *Sodium Hydroxide Solution* (40 g/L)—Dissolve 40 g of sodium hydroxide (NaOH) in water and dilute to 1 L with water.

8.20 *Sodium Hydroxide Solution* (1.6 g/L)—Dilute 40 mL of NaOH solution (40 g/L) to 1 L.

8.21 *Sulfamic Acid Solution* (133 g/L)—Dissolve 133 g of sulfamic acid in water and dilute to 1 L.

8.22 *Sodium Thiosulfate Solution* (500 g/L)—Dissolve 785 g of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) in water and dilute to 1 L.

8.23 *Sulfuric Acid* (1 + 1)—Slowly and carefully add 1 volume of sulfuric acid (H_2SO_4, sp gr 1.84) to 1 volume of water, stirring and cooling the solution during the addition.

8.24 *Zinc Acetate Solution* (100 g/L)—Dissolve 120 g of zinc acetate [$Zn(C_2H_3O_2)_2 \cdot 2H_2$] in 500 mL of water. Dilute to 1 L.

8.25 *IC Eluent Solution* (100 mM sodium hydroxide, 500 mM sodium acetate, and 0.5 % (v/v) ethylenediamine)—Dissolve 136.1 g of sodium acetate in 800-mL water. Transfer to a 2000-mL volumetric flask, add 10 mL of ethylenediamine, and dilute to mark. Sparge the solution with helium for 20 min. Add 10.4 mL of 50 % sodium hydroxide solution and allow the sparging to continue for and additional 5 min to mix.

8.26 *Ethylene diamine.*

8.27 *Helium.*

8.28 *Sodium Hydroxide Solution* (50 % W/W). Dissolve 100 g NaOH in 100 g of water or purchase a 50 % solution.

8.29 *Sodium Acetate.*

9. Hazards

9.1 **Caution**—Because of the toxicity of cyanide, great care must be exercised in its handling. Acidification of cyanide solutions produces toxic hydrocyanic acid (HCN). All manipulations must be done in the hood so that any HCN gas that might escape is safely vented.

9.2 **Warning**—Many of the reagents used in these test methods are highly toxic. These reagents and their solutions

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[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.

must be disposed of properly.

10. Sample and Sample Preservation

10.1 Collect the sample in accordance with Practices D 3370.

10.2 Minimize exposure of samples to ultraviolet radiation that causes photodecomposition of some metal cyanide complexes and may significantly increase the concentration of free cyanide in the sample. It is recommended that all manipulations of the sample be performed in a well-ventilated hood under incandescent light.

10.3 Oxidizing agents (chlorine) will destroy the cyanide in storage. Sulfide can convert the cyanide to thiocyanate, especially at the pH of the stabilized sample. The presence of either oxidizing agents or sulfides should be determined before the addition of sodium hydroxide preservation or further analysis.

10.3.1 *Oxidizing Agents*—Test for the presence of chlorine by placing a drop of the sample on a strip of potassium iodide-starch test paper which has been previously moistened with the acetic acid solution. Darkening (bluish) of the test paper normally indicates the presence of chlorine. (Manganese dioxide, nitrosyl chloride, etc., if present, may also cause discoloration of the test paper.) Add sodium arsenite solution dropwise to the sample and retest. In the event that a bluish discoloration is still perceptible, repeat the sodium arsenite addition.

10.3.2 *Sulfide*—Test for the presence of sulfide by placing a drop of the sample on a strip of lead acetate test paper which has been previously moistened with the acetic acid solution. Darkening of the test paper indicates the presence of sulfide. The presence of sulfide can be assumed to indicate the absence of oxidizing agents in the sample. Sulfide is removed by treating the sample with small increments of powdered lead carbonate or with the dropwise addition of lead nitrate or lead acetate solution. Black lead sulfide precipitates in samples containing sulfide. Repeat the operation until no more lead sulfide forms, as indicated by testing the supernatant liquid with lead acetate test paper. Immediately filter through dry paper into a dry beaker and stabilize the sample according to 10.4 or 10.5.

10.4 If the sample cannot be analyzed immediately, stabilize it by the addition of sodium hydroxide (NaOH) pellets to a pH of 12 to 12.5 and store it in a closed bottle (dark bottle if available) in a dark and cool environment.

Note 5—It has been determined that the use of hydrated lime, $Ca(CO)_3$, for the stabilization of effluents high in carbonate content lowers the recovery of total cyanide from samples. The task group responsible for this standard is pursuing further revision to this section.

11. Elimination of Interferences

11.1 The following treatments are for the removal or reduction of substances that can interfere in the various methods. Care must be taken to keep time of pretreatment at a minimum to avoid loss of cyanide (see 9.1).

11.2 Fatty acids that distill and form soaps in the absorption solution can be removed by extraction. Acidify the sample with dilute (1 + 9) acetic acid to a pH 6 to 7, (**Caution**—see Note 6). Extract with *iso*octane, hexane or chloroform (preference in order named), with a solvent volume equal to 20 % of the sample volume. One extraction is usually sufficient to reduce the fatty acids below the interference level. Avoid multiple extractions or a long contact time at low pH in order to keep the loss of HCN to a minimum. When the extraction is complete, immediately raise the pH of the sample to 12 to 12.5 with NaOH solution.

Note 6—**Caution:** Perform this operation in the hood and leave the sample there until it is made alkaline after the extraction.

11.3 Aldehydes combine with cyanides to form cyanohydrins which can hydrolyze to acids under distillation conditions. Hydrogen cyanide is not liberated and is not available for quantitative determination in the absorption solution. The formation of cyanohydrins also interferes in the direct colorimetric determination (Test Method D and spot test). Identification and removal of aldehydes is described in Appendix X2.

11.3.1 Glucose and other sugars if present in the sample can also form cyanohydrins with cyanide at the pH of preservation.

11.4 Carbonate in high concentration can affect the distillation procedure by causing the violent release of carbon dioxide with excessive foaming when acid is added prior to distillation, and by lowering the pH of the absorption solution. Calcium hydroxide is added slowly with stirring to a pH of 12 to 12.5. After the precipitate settles, the supernatant liquid is decanted and used for the determination of cyanide.

11.4.1 However, if the sample contains insoluble complex cyanide compounds, they will not be included in the determination. In this event, a measured amount of well-mixed treated sample can be filtered quantitatively through a glass-fiber or a membrane filter (47-mm or less). The filter is rinsed with dilute (1 + 9) acetic acid until the effervescence ceases, and the entire filter with the insoluble material is added to the filtrate prior to distillation.

11.5 Nitrite and nitrate in the sample can react under conditions of the distillation with other contaminants present to form cyanides. The addition of an excess of sulfamic acid to the sample prior to the addition of sulfuric acid will eliminate this interference.

11.6 Thiocyanate and other sulfur containing compounds can decompose during distillation. Sulfur, hydrogen sulfide, sulfur dioxide, etc., formed can be distilled into the absorption solution. The addition of lead ion to the absorption solution before distillation followed by filtration of the solution before the titration or the colorimetric procedure is used will eliminate sulfur and sulfide interference. Absorbed sulfur dioxide forms sodium sulfite which reacts with chloramine-T in the colorimetric determination. Test for the presence of chloramine-T by placing a drop of solution on a strip of potassium iodide test paper previously moistened with dilute acetic acid. If the test is negative, add chloramine-T until a positive test is obtained.

11.6.1 Cyanide can be measured in the presence of sulfur containing compounds by using IC to separate the interferences from the cyanide (16.5).

11.7 Thiocyanate in the presence of ferric ion is quantitatively determined by the colorimetric procedure. Test Method D outlines a procedure for masking any cyanide amenable to chlorination in order to determine thiocyanate by difference.

11.8 Substances which contribute color or turbidity interfere with Test Method D.

TEST METHOD A—TOTAL CYANIDES AFTER DISTILLATION

12. Scope

12.1 This test method covers the determination of cyanides in water, including the iron cyanide complexes (total cyanide).

12.2 The cyanide in some cyano complexes of transition metals, for example, cobalt, gold, platinum, etc., is not determined.

12.3 Either the titration, colorimetric or selective ion electrode procedure can be used to quantify the cyanide concentration.

12.4 This test method has been used successfully on reagent and surface water and coke plant, refinery, and sanitary waste waters. It is the user's responsibility to assure the validity of the test method for the water matrix being tested.

13. Interferences

13.1 All the chemical compounds listed in Section 6 can interfere.

13.2 For the removal of these interferences, proceed as instructed in Sections 10 and 11.

14. Apparatus

14.1 The schematic arrangement of the distillation system is shown in Fig. 1.

14.2 For the required apparatus, refer to Section 7.

15. Reagents and Materials

15.1 Refer to Section 8.

16. Procedure

16.1 *Distillation Procedure*:

16.1.1 Set up the apparatus as shown in Fig. 1.

16.1.2 Add 10.0 mL of NaOH solution (40 g/L) to the absorber. Dilute with water to obtain an adequate depth of liquid. Do not use more than 225 mL of total volume in the absorber.

16.1.3 Attach the absorber to the vacuum and connect to the condenser.

16.1.4 Place 500 mL of the sample in the flask. If cyanide content is suspected to be more than 10 mg/L, use an aliquot so that no more than 5 mg of cyanide is in the distilling flask and dilute to 500 mL with water. Annex A1 describes a procedure for establishing the approximate cyanide content. Verify a negative reaction in the spot-plate technique by using 500 mL of the sample.

16.1.5 Connect the flask to the condenser.

16.1.6 Turn on the vacuum and adjust the air flow to approximately 1 bubble per second entering the boiling flask through the air-inlet tube.

16.1.7 Add 20 mL of magnesium chloride solution (8.13) through the air inlet tube. If the sample contains nitrite or nitrate, add 15 mL of sulfamic acid solution (8.21).

16.1.8 Rinse the air-inlet tube with a few mL of water and allow the air flow to mix the content of the flask for approximately 3 min.

16.1.9 Carefully add 50 mL of H_2SO_4 solution (1 + 1) through the air-inlet tube.

NOTE 7—**Warning:** Add slowly; heat is generated and foaming may occur.

16.1.10 Turn on the condenser cooling water. Heat the solution to boiling, taking care to prevent the solution from backing into the air-inlet tube.

16.1.11 Maintain the air flow as in 16.1.6.

16.1.12 Reflux for 1 h.

16.1.13 Turn off the heat, but maintain the air flow for at least an additional 15 min.

16.1.14 Quantitatively transfer the absorption solution into a 250-mL volumetric flask. Rinse absorber and its connecting tubes sparingly with water and add to the volumetric flask.

16.1.15 Dilute to volume with water and mix thoroughly.

16.1.16 Determine the concentration of cyanide in the absorption solution by one of the four procedures (16.2, 16.3, 16.4, or 16.5).

16.2 *Titration Procedure*:

16.2.1 Place 100 mL of the absorption solution or an accurately measured aliquot diluted to 100 mL with NaOH solution (1.6 g/L) in a flask or beaker.

16.2.2 Add 0.5 mL of rhodanine indicator solution.

16.2.3 Titrate with standard silver nitrate solution (8.17) using a microburet to the first change from yellow to salmon pink.

16.2.4 Titrate a blank of 100 mL of NaOH solution (1.6 g/L) (8.20).

16.2.5 Record the results of the titration and calculate the cyanide concentration in the original samples according to Eq 1 (17.1).

16.3 *Colorimetric Procedure*:

16.3.1 *Standardization*:

16.3.1.1 Prepare a series of cyanide standards based on the cell path which is used (Table 1). For this purpose use 50-mL glass-stoppered volumetric flasks or graduated cylinders.

16.3.1.2 Follow 16.3.2.2 through 16.3.2.6 of the procedure.

16.3.1.3 Calculate the absorption factor (17.2.1).

16.3.2 *Procedure*:

16.3.2.1 Pipet an aliquot of the absorption liquid, such that the concentration falls within the standardization range, into a 50-mL glass-stoppered volumetric flask or graduated cylinder.

16.3.2.2 Dilute to 40 mL with the NaOH solution (1.6 g/L).

16.3.2.3 Place 40 mL of NaOH solution (1.6 g/L) in a flask

TABLE 1 Guide for Selection of Appropriate Cell Paths

Standard Solution No.	Millitres of Standard Solution	Final Concentration, µg CN/mL	Cell Length, cm		
	50 mL		1.0	5.0	10.0
IV	5.0	0.0025			X
IV	10.0	0.0050		X	X
IV	15.0	0.0075		X	X
IV	20.0	0.0100		X	X
IV	25.0	0.0125		X	X
IV	30.0	0.0150		X	X
IV	40.0	0.0200		X	
III	5.0	0.0250	X	X	
III	10.0	0.0500	X		
III	15.0	0.0750	X		
III	20.0	0.1000	X		
III	25.0	0.1250	X		
III	30.0	0.1500	X		
	0.0 (blank)		X	X	X

or cylinder for a blank. (Carry out the following steps of the procedure on the blank also.)

16.3.2.4 Add 1 mL of chloramine-T solution and 1 mL of acetate buffer, stopper, mix by inversion two or three times, and allow to stand for exactly 2 min.

16.3.2.5 Add 5 mL of pyridine-barbituric acid reagent, dilute to volume with water, mix thoroughly, and allow to stand exactly 8 min for color development.

16.3.2.6 Measure at the absorbance maximum at 578 nm. Measure absorbance (*A*) versus water.

16.3.2.7 Calculate the concentration of cyanide (mg CN/L) in the original sample following equations given in 17.2.

16.4 *Selective Ion Electrode Procedure*:

16.4.1 *Standardization*:

16.4.1.1 Place 100-mL aliquots of standard solutions I, II, III, and IV in 250-mL beakers.

16.4.1.2 Follow 16.4.2.2 and 16.4.2.3.

16.4.1.3 Pipet 10- and 50-mL aliquots of standard solution IV into 250-mL beakers and dilute to 100 mL with NaOH solution (1.6 g/L).

16.4.1.4 Follow 16.4.2.2 and 16.4.2.3 of the procedure, starting with the lowest concentration.

16.4.1.5 Plot concentration values of the standardizing solutions on the logarithmic axis of semilogarithmic graph paper versus the potentials developed in the standardizing solutions on the linear axis. Follow manufacturer's instructions for direct-reading ion meters.

16.4.2 *Procedure*:

16.4.2.1 Place 100 mL of the absorption solution (or an accurately measured aliquot diluted to 100 mL with NaOH solution (1.6 g/L)) in a 250-mL beaker.

NOTE 8—Check a small portion of the solution for sulfide. If it is present, add either the $PbCO_3$ or $Pb(C_2H_3O_2)_2$ before inserting the electrodes.

16.4.2.2 Place the beaker on a magnetic stirrer, place a TFE-fluorocarbon-coated stirring bar in the solution, stir at a predetermined constant rate, and maintain constant temperature.

16.4.2.3 Insert the cyanide specific ion electrode and the reference electrode in the solution and measure potential or the cyanide concentration following the manufacturer's instructions.

16.4.2.4 Use values found from the graph or direct-reading ion meter to calculate the concentration in the original sample following Eq 5 (17.3).

16.5 *Ion Chromatography Procedure:*

16.5.1 *Standardization:*

16.5.1.1 Place 2-mL of standard solutions I, II, III, and IV into HPLC autosampler vials if using an autosampler, or other capped glass vial if using a manual injector.

16.5.1.2 Follow 16.5.2.1 through 16.5.2.4 to standardize the IC detector response by injection of 10 µL of each standard solution.

NOTE 9—A 10-µL injection was used for the interlaboratory study. Other levels can be used provided the analyst confirms the precision and bias is equivalent with that generated using the 10-µL injection.

16.5.1.3 Measure the area under the cyanide peak. This is the detector response.

16.5.1.4 Plot concentration values of the standard solution versus detector response. Follow manufacturer's instruction for IC systems with computer controlled data stations.

16.5.2 *Procedure:*

16.5.2.1 Set the ion chromatograph to operate at the following conditions or as required for instrument being used:

(*a*) *Flow Rate*: 1.0 mL/min.

(*b*) *Pulsed-Electrochemical Detector* operated in a dc amperometric mode with a silver-working-electrode set at − 0.05 V in relation to a standard Ag/AgCl-reference electrode or an equivalent detector.

(*c*) *Column,* Dionex IonPac As 10 anion-exchange, 4 × 250 mm and matching guard column or equivalent.

(*d*) *Temperature*: Ambient.

(*e*) *Sample size:* 10 µL.

16.5.2.2 Prime the IC pump and ensure that the flow rate is 1.0 mL/min. Allow the detector to warm up for 30-60 min to stabilize the baseline.

16.5.2.3 Inject 10-µL of sample solution into the IC system.

16.5.2.4 Cyanide will elute in the retention time frame of 7.5-9.0 min depending upon column effective equivalency, eluant preparation, and temperature effects. Sulfide will elute in the 4.0-6.0 min time frame and will pose no interference with the cyanide analysis.

16.5.2.5 Measure the area under the cyanide peak. This is the detector response.

16.5.2.6 Use values found from the graph or data station to calculate the concentration in the original sample following Eq 5 (17.3).

17. Calculation

17.1 *Titration Procedure*—Calculate the concentration in milligrams of CN per litre in the original sample using Eq 1:

$$\text{mg CN/L} = [(A - B) \times N\,\text{AgNO}_3 \times 0.052/\text{mL original sample}] \times (250/\text{mL aliquot used}) \times 10^6 \quad (1)$$

where:

A = $AgNO_3$ solution to titrate sample, mL, and
B = $AgNO_3$ solution to titrate blank, mL.

17.2 *Colorimetric Procedure*—Calculate the concentration in milligrams of CN per litre as follows:

17.2.1 *Slope and Intercept of Standard Curve*—Calculate the slope on the standard curve, *m*, and the intercept on *c*-axis, *b*, using Eq 2 and Eq 3, respectively:

$$m = \frac{n\Sigma ca - \Sigma c\Sigma a}{n\Sigma a^2 - (\Sigma a)^2} \quad (2)$$

$$b = \frac{\Sigma a^2\Sigma c - \Sigma a\Sigma ac}{n\Sigma a^2 - (\Sigma a)^2} \quad (3)$$

where:

a = absorbance of standard solution,
c = concentration of CN^- in standard, mg/L, and
n = number of standard solutions.

17.2.1.1 the blank concentration, 0.0 mg CN^-/L, and the absorbance of the blank must be included in the calculation of slope and intercept.

17.2.2 *Concentration*—Calculate the concentration of cyanides using Eq 4:

$$\text{CN, mg/L} = (ma_1 + b) \times \frac{59}{X} \times \frac{250}{Y} \quad (4)$$

where:

a_1 = absorbance of sample solution,
X = aliquot of absorbance solution, mL, and
Y = original sample, mL.

17.3 *Selective-Ion Electrode and Ion Chromatography Procedures*—Calculate the concentration in milligrams of CN per litre using Eq 5:

$$\text{CN, mg/L} = \text{CN mg/L from graph or meter} \times (100/\text{aliquot}) \times (250/\text{mL original sample}) \quad (5)$$

18. Precision and Bias [7]

18.1 *Precision*:

18.1.1 *Colorimetric*—Based on the results of nine operators in nine laboratories, the overall and single-operator precision of this test method within its designated range may be expressed as follows:

Reagent Water	$S_T = 0.06x + 0.003$
	$S_o = 0.11x + 0.010$
Selected Water Matrices	$S_T = 0.04x + 0.018$
	$S_o = 0.04x + 0.008$

18.1.2 *Electrode*—Based on the results of six operators in five laboratories, the overall and single-operator precision of this test method within its designated range may be expressed as follows:

Reagent Water	$S_T = 0.06x + 0.003$
	$S_o = 0.03x + 0.008$
Selected Water Matrices	$S_T = 0.05x + 0.008$
	$S_o = 0.03x + 0.012$

18.1.3 *Titrimetric*—Based on the results of six operators in three laboratories, the overall and single-operator precision of this test method within its designated range may be expressed as follows:

Reagent Water	$S_T = 0.04x + 0.038$
	$S_o = 0.01x + 0.018$
Selected Water Matrices	$S_T = 0.06x + 0.711$
	$S_o = 0.04x + 0.027$

18.1.4 *Ion Chromatography Procedure*—Based on the results of eight operators in seven laboratories, the overall and single-operator precision of this test method within its designated range may be expressed as follows:

$$\text{xbar} = 1.04x + 0.35$$
$$S_T = 0.057x + 3.19$$
$$S_o = 0.020x + 3.90$$

A weighted linear regression was used since the absolute error increased with concentration. More weight was given to the smaller (lower error) concentrations than to the larger (higher error) ones. The weighting factor used was 1/s.d. ^{2} for each of the concentration levels (**1**).[8]

18.1.5 where:

S_T = overall precision,
S_o = single operator precision, and
x = cyanide concentration, mg/L.

18.1.6 Since this is an existing test method which has results from a minimum of three laboratories for a total of six operators, it does not require further collaborative testing in accordance with Practice D 2777.

18.2 *Bias*—Recoveries of known amounts of cyanide from Reagent Water Type II and selected water matrices are shown in Table 2 and Table 3. Data from Table 4 will be added to Table 2 on Reagent Water (Test Method A.)

18.3 The precision and bias information given in this section may not apply to waters of untested matrices.

TEST METHOD B—CYANIDES AMENABLE TO CHLORINATION BY THE DIFFERENCE

19. Scope

19.1 This test method covers the determination of cyanides amenable to chlorination in water.

19.2 Iron cyanides are the most commonly encountered compounds not amenable to chlorination.

19.3 This test method has been used on reagent, surface, and industrial waste waters. It is the user's responsibility to assure the validity of the test method for the water matrix being tested.

20. Interferences

20.1 All the chemical compounds listed in Section 6 can interfere.

20.2 For the removal of these interferences, proceed as instructed in Sections 10 and 11.

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[7] Supporting data are available from ASTM Headquarters. Request RR: D19-1131.

[8] The boldface numbers in parentheses refer to the list of references at the end of this standard.

TABLE 2 Reagent Water (Test Method A)

Technique	Amount Added, mg/L	Amount Found, mg/L	n	S_t	Bias	%Bias	Statistical Significance, 95 % CL
Colorimetric	0.060	0.060	26	0.0101	0.000	0	No
	0.500	0.480	23	0.0258	−0.020	−4	No
	0.900	0.996	27	0.0669	0.096	11	Yes
Electrode	0.060	0.059	18	0.0086	−0.001	2	No
	0.500	0.459	18	0.0281	−0.041	−8	Yes
	0.900	0.911	18	0.0552	0.011	1	No
	5.00	5.07	18	0.297	0.07	1	No
Titrimetric	2.00	2.10	18	0.1267	0.10	5	Yes
	5.00	4.65	18	0.2199	−0.35	−7	Yes
	5.00	5.18	18	0.2612	0.18	4	Yes

TABLE 3 Selected Water Matrices (Test Method A)

Technique	Amount Added, mg/L	Amount Found, mg/L	n	S_t	Bias	%Bias	Statistical Significance, 95 % CL
Colorimetric	0.060	0.060	25	0.0145	0.000	0	No
	0.500	0.489	26	0.0501	−0.011	−3	No
	0.900	0.959	24	0.0509	0.059	7	Yes
Electrode	0.060	0.058	14	0.0071	−0.002	−3	No
	0.500	0.468	21	0.0414	−0.032	−6	No
	0.900	0.922	19	0.0532	0.022	2	No
	5.00	5.13	20	0.2839	0.13	3	No
Titrimetric	2.00	2.80	18	0.8695	0.80	40	Yes
	5.00	5.29	18	1.1160	0.29	6	No
	5.00	5.75	18	0.9970	0.75	15	Yes

TABLE 4 Final Statistical Summary for Cyanide Round Robin

	Sample A	Sample D	Sample B	Sample E	Sample C	Sample F	A + Sulfide	D + Sulfide
Number of retained values	7	7	7	7	7	7	7	7
True Concentration (C),µ g/L	251	217	866	736	43.3	34.6	251	217
Mean Recovery (XBAR)	250	222	958	801	44	39	248	221
Percent Recovery	99.5	10.2	111	109	100	110	99.0	102
Overall Standard Deviation, (st)	17.8	20.1	58.8	41.7	7.3	4.6	18.4	13.2
Overall Relative Standard Deviation,%	7.10	9.08	6.14	5.21	16	12	7.39	5.95
Number of retained pairs	7	7	7	7	7	7	7	7
Single-Operator Standard Deviation, (so)	9.35		18.0		4.6		8.54	
Analyst Relative Deviation,%	4.01		2.12		11		3.72	
Bias	−0.46	2.11	10.61	8.83	2.6	13	−1.02	2.04

20.3 This test method can be affected by compounds that are converted during chlorination to volatile compounds which are collected in the absorption solution and can interfere in the final determination.

21. Apparatus

21.1 The schematic arrangement of the distillation system is shown in Fig. 1.

21.2 For the required apparatus, refer to Section 7.

22. Reagents and Materials

22.1 Refer to Section 8.

23. Procedure

23.1 *Sample Preparation*—Divide the sample into two equal portions of 500 mL or less. Determine the total cyanide in one portion as indicated in 23.2. Place the other portion in a 1-L beaker and chlorinate as outlined in the following steps.

NOTE 10—Protect the solution in the beaker from ultraviolet radiation by wrapping the beaker with aluminum foil or black paper and cover with a wrapped watch glass during chlorination.

23.1.1 Place the beaker on a magnetic stirrer, insert a TFE fluorocarbon-coated stirring bar in the beaker, and start stirring.

23.1.2 If necessary, adjust the pH to between 11 and 12 with NaOH solution (40 g/L).

23.1.3 Add $Ca(OCl)_2$ solution (50 g/L) 3 drops at a time until there is an excess of chlorine indicated on a strip of potassium iodide-starch test paper previously moistened with acetic acid solution.

23.1.4 Maintain the pH and excess chlorine for 1 h while stirring. Add $Ca(OCl)_2$ solution or NaOH solution, or both, 2 drops at a time when necessary.

23.1.5 At the end of the hour remove any residual chlorine by the dropwise addition of $NaAsO_2$ solution (2 g/100 mL) or by adding 8 drops of H_2O_2 solution (3 %) followed by 4 drops of $Na_2S_2O_3$ solution (500 g/L). Test with potassium iodide-starch test paper.

23.2 Follow steps 16.1.1 through 16.1.16 for Test Method A.

24. Calculation

24.1 Calculate the total cyanide in each portion of the sample following Eq 1, Eq 4, or Eq 5.

24.2 Calculate the concentration of cyanide amenable to chlorination using Eq 6:

$$\text{CN, mg/L} = G - H \qquad (6)$$

where:

G = cyanide, determined in the unchlorinated portion of the sample, mg/L, and
H = cyanide determined in the chlorinated portion of the sample, mg/L.

25. Precision and Bias [7]

25.1 *Precision*:

25.1.1 *Colorimetric*—Based on the results of eight operators in seven laboratories, the overall and single-operator precision of this test method within its designated range may be expressed as follows:

Reagent Water $S_T = 0.18x + 0.005$
$S_o = 0.06x + 0.003$
Selected Water Matrices $S_T = 0.20x + 0.009$
$S_o = 0.05x + 0.005$

25.1.2 *Titrimetric*—Based on the results of six operators in three laboratories, the overall and single-operator precision of this test method within its designated range may be expressed as follows:

Reagent Water $S_T = 0.01x + 0.439$
$S_o = 0.241 - 0.03x$
Selected Water Matrices $S_T = 0.12x + 0.378$
$S_o = 0.209 - 0.01x$

25.1.3 where:

S_T = overall precision,
S_o = single operator precision, and
x = cyanide concentration, mg/L.

25.2 *Bias*—Recoveries of known amounts of cyanide amenable to chlorination from reagent water Type II and selected water matrices were as shown in Table 5 and Table 6.

25.3 The precision and bias information given in this section may not apply to waters of untested matrices.

TEST METHOD C—WEAK ACID DISSOCIABLE CYANIDES

26. Scope

26.1 This test method covers the determination of cyanide compounds and weak acid dissociable complexes in water.

26.2 The thiocyanate content of a sample usually does not cause interference.

26.3 Any of the three procedures, titration, colorimetric, or selective ion electrode, can be used to determine the cyanide content of the absorption solution. The lower limits of detectability are the same as for Test Method A.

26.4 This test method has been used successfully on reagent and surface water and coke plant, refinery and sanitary waste waters. It is the user's responsibility to assure the validity of the test method for the water matrix being tested.

27. Interferences

27.1 All the chemical compounds listed in Section 6 can interfere.

27.2 For the removal of these interferences proceed as instructed in Sections 10 and 11.

28. Apparatus

28.1 The schematic arrangement of the distillation system is shown in Fig. 1.

28.2 The required equipment, instruments, and parts are listed in Section 7.

29. Reagents and Materials

29.1 Refer to Section 8.

29.2 *Methyl Red Indicator Solution.*

30. Procedure

30.1 *Distillation Procedure*:

30.1.1 Set up the apparatus as shown in Fig. 1.

30.1.2 Add 10.0 mL of NaOH solution (40 g/L) to the absorber. Dilute with water to obtain an adequate depth of liquid. Do not use more than 225 mL of total volume in the absorber.

30.1.3 Attach the absorber to the vacuum and connect to the condenser.

30.1.4 Place 500 mL of sample in the flask. If cyanide content is suspected to be more than 10 mg/L, use an aliquot so that no more than 5 mg of cyanide are in the flask, and dilute to 500 mL with water.

30.1.5 Connect the flask to the condenser.

30.1.6 Turn on the vacuum and adjust the air flow to approximately 1 bubble per second entering the boiling flask through the air-inlet tube.

30.1.7 Add 20 mL each of the acetate buffer and zinc acetate solutions through the air-inlet tube. Add 2 or 3 drops of methyl red indicator solution.

30.1.8 Rinse the air-inlet tube with a few mL of water and allow the air flow to mix the content of the flask. (If the solution is not pink, add acetic acid (1 + 9) dropwise through the air-inlet tube until there is a permanent color change.)

30.1.9 Turn on the condenser cooling water, heat the solution to boiling, taking care to prevent the solution from backing into the air inlet tube.

30.1.10 Maintain the air flow as in 30.1.6.

30.1.11 Reflux for 1 h.

30.1.12 Turn off the heat, but maintain the air flow for at least an additional 15 min.

30.1.13 Quantitatively transfer the absorption solution into a 250-mL volumetric flask. Rinse the absorber and its connecting tubes sparingly with water and add to volumetric flask.

30.1.14 Dilute to volume with water and mix thoroughly.

30.1.15 Determine the concentration of cyanide in the absorption solution by one of the three procedures desceibed in 16.2, 16.3, or 16.4.

31. Calculation

31.1 Calculate the concentration of weak acid dissociable cyanide in the sample following Eq 1, Eq 4, or Eq 5.

32. Precision and Bias [7]

32.1 *Precision:*

32.1.1 *Colorimetric*—Based on the results of nine operators in nine laboratories, the overall and single-operator precision

TABLE 5 Reagent Water (Test Method B)

Technique	Amount Added, mg/L	Amount Found, mg/L	n	S_t	Bias	% Bias	Statistical Significance, 95 % CL
Colorimetric	0.008	0.009	21	0.0033	0.001	13	No
	0.019	0.023	20	0.0070	0.004	21	Yes
	0.080	0.103	20	0.0304	0.018	23	Yes
	0.191	0.228	21	0.0428	0.037	19	Yes
Titrimetric	1.00	0.73	18	0.350	−0.27	−27	Yes
	1.00	0.81	18	0.551	−0.19	−19	No
	4.00	3.29	18	0.477	−0.71	−18	Yes

TABLE 6 Selected Water Matrices (Test Method B)

Technique	Amount Added, mg/L	Amount Found, mg/L	n	S_t	Bias	% Bias	Statistical Significance, 95 % CL
Colorimetric	0.008	0.013	17	0.0077	0.005	63	Yes
	0.019	0.025	18	0.0121	0.006	32	Yes
	0.080	0.100	18	0.0372	0.020	25	Yes
	0.191	0.229	18	0.0503	0.038	20	Yes
	1.00	1.20	18	0.703	0.20	20	No
Titrimetric	1.00	1.10	18	0.328	0.10	10	No
	4.00	3.83	18	0.818	−0.17	−4	No

of this test method within its designated range may be expressed as follows:

Reagent Water $S_T = 0.09x + 0.010$
$S_o = 0.08x + 0.005$
Selected Water Matrices $S_T = 0.08x + 0.012$
$S_o = 0.05x + 0.008$

32.1.2 *Electrode*—Based on the results of six operators in five laboratories, the overall and single-operator precision of this test method within its designated range may be expressed as follows:

Reagent Water $S_T = 0.09x + 0.004$
$S_o = 0.02x - 0.009$
Selected Water Matrices $S_T = 0.08x + 0.005$
$S_o = 0.02x + 0.004$

32.1.3 *Titrimetric*—Based on the results of six operators in three laboratories, the overall and single-operator precision of this test method within its designated range may be expressed as follows:

Reagent Water $S_T = 0.532 - 0.10x$
$S_o = 0.151 - 0.01x$
Selected Water Matrices $S_T = 0.604 - 0.06x$
$S_o = 0.092 + 0.02x$

32.1.4 where:

S_T = overall precision,
S_o = single-operator precision,and
x = cyanide concentration, mg/L.

32.2 *Bias*—Recoveries of known amounts of cyanide from reagent water Type II and selected water matrices were as shown in Table 7 and Table 8.

32.3 The precision and bias information given in this section may not apply to waters of untested matrices.

TEST METHOD D—CYANIDES AMENABLE TO CHLORINATION WITHOUT DISTILLATION, SHORT-CUT METHOD

33. Scope

33.1 This test method covers the determination of free CN^- and CN^- complexes that are amenable to chlorination in water. The procedure does not measure cyanates nor iron cyanide complexes. It does, however, determine cyanogen chloride and thiocyanate.

33.2 Modification is outlined for its use in the presence of thiocyanate.

34. Interferences

34.1 All chemical compounds as listed in Section 6 can interfere.

34.2 For removal of these interferences, proceed as instructed in Sections 10 and 11.

34.3 The thiocyanate ion which reacts with chloramine-T will give a positive error equivalent to its concentration as cyanide.

34.4 Color and turbidity can interfere.

34.4.1 When color or turbidity producing substances are present, it is recommended that Test Method B or C be used.

34.4.2 Color and turbidity can be extracted from some samples with chloroform without reduction of the pH.

34.4.3 It is possible with some samples to compensate for color and turbidity by determining the absorbance of a second sample solution to which all reagents except chloramine-T have been added.

34.5 Reducing compounds such as sulfites can interfere by preferentially reacting with chloramine-T.

34.6 The color intensity and absorption is affected by wide variations in the total dissolved solids content of the sample.

TABLE 7 Reagent Water (Test Method C)

Technique	Amount Added, mg/L	Amount Found, mg/L	n	S_t	Bias	% Bias	Statistical Significance, 95 % CL
Colorimetric	0.030	0.030	25	0.0089	0.000	0	No
	0.100	0.117	27	0.0251	0.017	17	Yes
	0.400	0.361	27	0.0400	−0.039	−10	Yes
Electrode	0.030	0.030	21	0.0059	0.000	0	No
	0.100	0.095	21	0.0163	−0.005	−5	No
	0.400	0.365	21	0.0316	−0.035	−9	No
	1.000	0.940	21	0.0903	−0.060	−6	No
Titrimetric	1.00	1.35	18	0.4348	0.35	35	Yes
	1.00	1.38	18	0.3688	0.38	38	Yes
	4.00	3.67	18	0.1830	0.33	−8	No

TABLE 8 Selected Water Matrices (Test Method C)

Technique	Amount Added, mg/L	Amount Found, mg/L	*n*	S_t	Bias	% Bias	Statistical Significance, 95 % CL
Colorimetric	0.030	0.029	15	0.0062	0.001	3	No
	0.100	0.118	24	0.0312	0.018	18	Yes
	0.400	0.381	23	0.0389	−0.019	−5	Yes
Electrode	0.030	0.029	20	0.0048	−0.001	−3	No
	0.100	0.104	21	0.0125	0.004	4	No
	0.400	0.357	21	0.0372	−0.043	−11	No
	1.000	0.935	21	0.0739	−0.065	−7	No
Titrimetric	1.00	1.55	18	0.5466	0.55	55	Yes
	1.00	1.53	18	0.4625	0.53	53	Yes
	4.00	3.90	18	0.3513	−0.10	−3	No

34.6.1 For samples containing high concentrations of dissolved solids, 3 000 to 10 000 mg/L, add 6 g of NaCl to each litre of NaOH solution (1.6 g/L) used to prepare the standards. For samples containing dissolved solids concentration greater than 10 000 mg/L, add sufficient NaCl to the NaOH solution to approximate the dissolved solids content.

35. Apparatus

35.1 *Spectrophotometer or Filter Photometer*, suitable for measurements in the region of 578 nm, using 1.0-cm absorption cells. Filter photometers and photometric practices used in these test methods shall conform to Practice E 60. Spectrophotometers shall conform to Practice E 275.

35.2 *Water Bath*, capable of maintaining temperature at 27± 1°C.

36. Reagents and Materials

36.1 Refer to Section 8.

36.2 *Pyridine-Barbituric Acid Reagent*— For the preparation of this reagent, refer to 8.15; however, for this test method, prepare a fresh solution weekly. Longer storage affects the results of the test.

36.3 *EDTA Solution* (18.5 g/L)—Dissolve 18.5 g of the disodium salt of ethylenediamine tetraacetic acid dihydrate in water and dilute to 1 L.

36.4 *Formaldehyde Solution* (10 %)—Dilute 27 mL of formaldehyde (37 %) to 100 mL.

36.5 *Hydrochloric Acid* (HCl) (sp gr 1.19) (1 + 9)—Slowly add 1 volume of concentrated HCl (sp gr 1.19) to 9 volumes of water, stirring during the addition.

36.6 *Phosphate Buffer* Solution (138 g/L)—Dissolve 159 g of sodium dihydrogen phosphate ($NaH_2PO_4{\cdot}H_2O$) in water, dilute to 1 L and refrigerate.

36.7 *Sodium Carbonate* (Na_2CO_3), anhydrous.

36.8 *Sodium Chloride* (NaCl), crystals.

37. Standardization

37.1 From the cyanide standard solutions, pipet a series of aliquots containing from 0.5 to 5.0 µg of cyanide in volumes not exceeding 20 mL into 50-mL volumetric flasks.

37.2 Dilute each solution to 20 mL with NaOH solution (1.6 g/L). Follow 38.3 through 38.7 of the procedure.

37.3 Calculate the absorption factor (17.2.1).

38. Procedure

38.1 Adjust the pH of a small volume of sample (50 mL) to between 11.4 and 11.8. If the addition of acid is needed, add a small amount (0.2 to 0.4 g) of sodium carbonate and stir to dissolve. Then add dropwise while stirring HCl solution (1 + 9). For raising the pH, use NaOH solution (40 g/L).

38.2 Pipet 20.0 mL of the sample into a 50-mL volumetric flask. If the cyanide concentration is greater than 0.3 mg/L, use a smaller aliquot and dilute to 20 mL with NaOH solution (1.6 g/L). Do not exceed the concentration limit of 0.3 mg/L.

38.3 To ensure uniform color development, both in calibration and testing, it is necessary to maintain a uniform temperature. Immerse the flasks in a water bath held at 27 ± 1°C for 10 min before adding the reagent chemicals and keep the samples in the water bath until all the reagents have been added.

38.4 Add 4 mL of phosphate buffer and swirl to mix. Add one drop of EDTA solution, and mix.

38.5 Add 2 mL of chloramine-T solution and swirl to mix. Place 1 drop of sample on potassium iodide-starch test paper which has been previously moistened with acetate buffer solution. Repeat the chloramine-T addition if required. After exactly 3 min, add 5 mL of pyridine-barbituric acid reagent and swirl to mix.

38.6 Remove the samples from the water bath, dilute to volume and mix. Allow 8 min from the addition of the pyridine-barbituric acid reagent for color development.

38.7 Determine the absorbance at 578 nm in a 1.0-cm cell versus water.

38.8 Calculate the concentration of cyanide as milligrams per litre, in the original sample following equations given in 17.2.

38.9 If the presence of thiocyanate is suspected, pipet a second 20-mL aliquot of pH-adjusted sample solution into a 50-mL volumetric flask. Add 3 drops of 10 % formaldehyde solution. Mix and allow to stand 10 min. Place in a water bath at 27 ± 1°C for an additional 10 min before the addition of the reagent chemicals and hold in the bath until all reagents have been added.

38.10 Continue with 38.4 through 38.7.

38.11 Calculate the concentration of cyanide, in milligrams per litre, in the original sample following equations given in 17.2.

38.12 In the presence of thiocyanate, cyanide amenable to chlorination is equal to the difference between the concentration of cyanide obtained in 38.8 and that obtained in 38.11.

39. Precision and Bias [9]

39.1 *Precision*:

39.1.1 Based on the results of 14 operators in nine laboratories, the overall and single-operator precision of this test method within its designated range may be expressed as follows:

Reagent Water	S_T	=	$0.10x + 0.006$
	S_o	=	$0.07x + 0.005$
Selected Water Matrices	S_T	=	$0.11x + 0.007$
	S_o	=	$0.02x + 0.005$

39.1.2 where:

S_T = overall precision,
S_o = single-operator precision,and
x = cyanide concentration, mg/L.

39.2 *Bias*—Recoveries of known amounts of cyanide from reagent water Type II, seven creek waters, one diluted sewage (1 + 20) and one industrial waste water are as shown in Table 9 and Table 10.

39.3 This precision and bias information may not apply to waters of untested matrices.

40. Quality Assurance/Quality Control

40.1 *Verification of Systems for Quantifying Cyanide in the Distillate*:

40.1.1 *Titration Procedure*:

40.1.1.1 Standardize the silver nitrate solution with Potassium Chloride, NIST, at least every six months.

40.1.1.2 Titrate 100-mL aliquots of Cyanide I Solution Standard and 100-mL aliquots of Sodium Hydroxide Solution (1.6 g/L) each time the procedure is used. Duplicate titrations should check within 0.05 mL.

40.1.2 *Colorimetric Procedure*:

40.1.2.1 Prepare a series of cyanide standards, including zero (blank), based on the expected concentration range of the samples, and follow the standardization each time new reagents are prepared or every six months.

40.1.2.2 The slope (m) of the standard curve should check the theoretical value:

1.0-cm cell, 0.22–0.24 mg CN/L/a; 5.0-cm cell, 0.044–0.048 mg CN/L/a; 10.0-cm cell, 0.022–0.024 mg CN/L/a

40.1.2.3 At least one standard solution and one blank should be checked each time the procedure is used.

40.1.3 *Selective Ion Electrode Procedure*:

40.1.3.1 Follow the standardization procedure each time new standard solutions are prepared.

40.1.3.2 The slope of the curve should check within 90 % of the theoretical value: 59.2 mV/decade.

40.1.3.3 At least two standard solutions and one blank should be checked each time the procedure is used.

40.1.4 *Ion Chromatographic Procedure*:

40.1.4.1 At least three standard solutions and one blank should be checked each time the procedure is used.

40.1.4.2 Calibrate the ion chromatograph each time the procedure is used or whenever the eluent is changed. If the response or retention time for cyanide varies from the expected value by more than ± 10 % a new calibration curve must be prepared.

40.1.4.3 One midrange standard solution and a blank should be checked each time the procedure is used or at least every 20 samples. If the response or retention time varies from the expected value by more than ± 10 % repeat the test using fresh standards.

40.2 *Verification of the Distillation Procedure*:

40.2.1 The distillation is performed following the method protocol on duplicate solutions containing known amounts of cyanide and duplicate blanks followed by the quantification procedure which will be used.

NOTE 11—With careful selection of concentration all four quantification procedures can be performed on the same distillate solution. (See Guide D 5788).

40.2.2 The recoveries should be 100 ± 10 % based on the verification data obtained for the quantifying procedures. The precision must be within the limits specified in the method for single operator standard deviation.

40.3 *Demonstration of Analyst Proficiency*:

40.3.1 Demonstrate the competence of the analyst before these methods are used to generate reportable work (See Practice D 5789).

40.3.2 Verify the procedure(s) to be used by analyzing cyanide standard solutions in the expected range.

40.3.3 Analyze in duplicate six samples of known or nearly the same concentration by the complete method expected to be used, such as distillation, chlorination, etc., plus colorimetric, electrode titration or ion chromatograph.

40.3.4 Calculate the standard deviation of the data in accordance with Guide D 3856 and Practices D 4210 and D 5789. If the value obtained is within the that given in the procedure for single operator precision, the analyst can be considered competent.

NOTE 12—If this is the first data generated in the laboratory, construct a preliminary control chart (see Guide D 3856 and Practice D 4210).

40.4 *Demonstration of Laboratory Proficiency*:

40.4.1 Analyze samples in duplicate until at least 40 data points are accumulated for each method or combination of

TABLE 9 Reagent Water (Test Method D)

Amount Added, mg/L		Amount Found, mg/L	n	S_t	Bias	% Bias	Statistical Significance, 95 % CL
CN	SCN						
0.005		0.007	42	0.0049	0.002	40	Yes
0.027		0.036	41	0.0109	0.009	25	Yes
0.090		0.100	42	0.0167	0.010	11	Yes
0.090	0.080	0.080	39	0.0121	−0.010	11	Yes
0.270		0.276	42	0.0320	0.006	2	No

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[9] Supporting data are available from ASTM Headquarters. Request RR: D19 - 1074.

TABLE 10 Selected Water Matrices (Test Method D)

Amount Added, mg/L		Amount Found, mg/L	*n*	S_t	Bias	% Bias	Statistical Significance, 95 % CL
CN	SCN						
0.005		0.003	40	0.0042	−0.002	40	Yes
0.027		0.026	42	0.0093	−0.001	4	No
0.090		0.087	42	0.0202	−0.003	3	No
0.090	0.080	0.068	37	0.0146	−0.022	24	Yes
0.270		0.245	41	0.0319	−0.025	9	Yes

methods used (see Practice D 4210).

40.4.2 Construct control charts with upper and lower limits from the data obtained (see Guide D 3856 and Practice D 4210).

40.4.3 To monitor precision and bias analyze the following in duplicate: a standard solution, a sample of known value, a spiked sample, a field blank, and a method blank each day (or every 20 routine samples).

40.4.4 Calculate the relative range value (*R*) for each set of duplicate analyses. If the *R*s are greater than the upper control limit, the precision is judged out-of-control, and the analysis should be discontinued until the problem is resolved.

40.4.5 Calculate the percent recovery (*P*) for the standard and the spiked sample. If the recoveries are not within 100 ± 10 %, the analyses should be discontinued until the reason is found.

41. Keywords

41.1 colorimetric; cyanides amendable to chlorination; distillation; ion chromatography; ion electrode; titration; total cyanide; weak acid dissociable cyanides

ANNEX

(Mandatory Information)

A1. SPOT TEST FOR SAMPLE SCREENING

A1.1 Scope

A1.1.1 The spot test procedure allows a quick screening of the sample to establish if more than 0.05 mg/L (ppm) of cyanides amenable to chlorination, cyanogen chloride, or thiocyanate are present in water, waste water, and saline water.

A1.1.2 The test may also be used to establish the presence and absence of cyanogen chloride by omitting the addition of chloramine-T.

A1.1.3 With the addition of formaldehyde to the sample, the amenable cyanide can be masked and under these conditions, the test is specific to thiocyanate. It is possible therefore to distinguish between the presence of cyanide and thiocyanate or possibly judge the relative levels of concentration for each.

A1.1.4 With practice or dilution, the test can be used to estimate the approximate concentration range of these compounds, judging from the color development and comparing it to similarly treated samples of known concentration.

A1.2 Interferences

A1.2.1 All the chemical compounds listed in Section 6, with the exception of the nitrites, may interfere. For their removal, refer to Sections 10 and 11.

A1.2.2 The thiocyanate ion reacts in the same manner as the cyanide. The cyanide can be masked and then the test is specific for thiocyanate.

A1.2.3 The presence of large amounts of reducing substances in the sample interferes by consuming the chloramine-T added. Repeat the chloramine-T addition, if necessary.

A1.3 Apparatus

A1.3.1 *Spot Plate*, porcelain with 6 to 12 cavities preferred.

A1.4 Reagents and Materials

A1.4.1 Refer to Sections 8 and 36.

A1.4.2 *Formaldehyde*, 37 %, pharmaceutical grade.

A1.4.3 *Hydrochloric Acid* (1 + 9)

Mix 1 volume of concentrated (HCl (sp gr 1.19) with 9 volumes of water.

A1.4.4 *Sodium Carbonate*, anhydrous Na_2CO_3.

A1.5 Procedure

A1.5.1 If the solution subject to spot tests is alkaline in a pH range greater than 10, neutralize a 20 to 25-mL portion.

A1.5.1.1 Add 1 drop of phenolphthalein indicator solution. If the sample remains colorless, proceed to A1.5.2.

A1.5.1.2 If the sample turns red, add approximately 250 mg of sodium carbonate and mix to dissolve.

A1.5.1.3 Add HCl (1 + 9) dropwise while mixing until colorless.

A1.5.2 Place 3 drops of sample and 3 drops of reagent water (for a blank) on a white spot plate.

A1.5.3 To each cavity, add 1 drop of chloramine-T solution and mix with a clean stirring rod.

A1.5.4 To each cavity add 1 drop of phosphate buffer.

A1.5.5 Add 1 drop of pyridine-barbituric acid solution to each and again mix with a stirring rod.

A1.5.6 After 1 min, the sample spot will turn pink to red if 0.05 mg/L or more of CN is present. The blank spot will be faint yellow due to the color of the reagents. Until familiarity with the spot test is gained, it may be advisable to use, instead of the reagent water blank, a standard solution containing 0.05 mg/L CN for color comparisons. This standard can be made up by diluting the KCN standard solution (8.8.3).

A1.5.7 If the presence of thiocyanate is suspected, test a second sample pretreated as follows: Heat a 20 to 25-mL sample in a water bath at 50°C; add 0.1 mL of formaldehyde and hold for 10 min. This treatment will mask up to 5 mg CN/L.

A1.5.8 Repeat the spot test with the treated sample. Color development indicates the presence of thiocyanate. Comparing the intensity of the colors in the two spot tests is useful in judging whether both compounds are present and, if so, the relative concentration of cyanide and thiocyanate.

APPENDIXES

(Nonmandatory Information)

X1. CYANIDE

X1.1 *Introductory Comments*—Cyanides are used extensively in metal finishing processes and heat treatment of steel, and are a significant constituent of wastes from coke oven and blast furnace operations. As a toxic contaminant of effluents, they usually appear in the waste waters from quenching, gas scrub waters, and rinse water effluent from electroplating plants. The toxic effects of cyanide are so severe and established toxicity levels so low (<0.1 mg/L) that regulatory concern and waste treatment efforts by industry need dependable analytical procedures and a better understanding of the various cyanide complexes that may be encountered.

X1.2 *Molecular Hydrogen Cyanide, Cyanides Amenable to Chlorination, Iron Cyanides:*

X1.2.1 Toxicological investigations by Doudoroff and others have indicated that the acute toxicity of polluted water is caused by the molecular hydrogen cyanide (undissociated HCN) as opposed to the cyanide ion (CN) that may be equally present (**2–4**).Actually, Milne suggested complexing the molecular HCN with metal salts as a waste treatment process (**5**).

X1.2.2 A number of analytical methods were proposed to allow a quantitative distinction for the molecular HCN to establish the acute toxicity levels of surface waters when cyanide toxicity is suspected (**6–10**). The first question we have to raise when evaluating these various analytical procedures is whether the premise regarding the distinction between molecular or undissociated HCN hydrogen cyanide on the one hand and cyanide ions on the other hand is valid or not. The distinction desired is actually the dissociated CN^- as distinct from the CN^- tightly bound in the metal complex. Another term referred to by the authors in reference is "free cyanide." This term doesn't have any toxicological significance and is commonly used in the electroplating industry and refers to the cyanide ion that can be titrated with silver nitrate (Liebig Titration), forming an insoluble silver cyanide precipitate when the free cyanide available for complexing the silver is exhausted.

X1.2.3 Lancy and Zabban have shown (**11**) that in solutions containing the various metal cyanide complexes, the difference in cyanide ion activity is due to the difference in measurable dissociation constants for each of the metal cyanide complexes investigated.

X1.2.4 Critical evaluation of the toxicity investigations with various metal cyanide complexes reveals that these reports confirm the great differences in dissociation by the various metal cyanide complexes.

X1.2.5 Both Milne (**12**) and Doudoroff (**13**) show that in the critical concentration of 0.01 to 0.5 mg/L of CN at a pH of 7.5, HCN formation is favored and will be maintained if depleted by further dissociation of the cyanide complex. Lowering the pH (that is, increasing the hydrogen ion concentration by 0.3 pH units) doubles the HCN content.

X1.2.6 Doudoroff has found that the toxicity of zinc-, cadmium-, and copper-cyanide compounds is probably greater than equal concentrations of sodium cyanide. The synergistic toxic effects, when both zinc and copper ions are combined with cyanide, are known. Additional evidence regarding the toxicity of copper, silver, and nickel cyanide complexes in low concentrations was reported (**3,13,14**). Doudoroff, on the other hand, shows that the iron cyanides do not dissociate to any measurable extent and therefore are not toxic to fish(**2,3,15**).

X1.2.7 Differentiation between toxic and nontoxic cyanide was designated "cyanides amenable to chlorination" by Lancy and Zabban (**16**). Differentiation is based on the oxidizing effect of chlorine. Resistance of the iron cyanide compounds to oxidation is due to lack of dissociation rendering them nontoxic to fish. Test for "Cyanides Amenable to Chlorination Without Distillation" is based on rapid dissociation of cyanide and complexing with chloramine-T. First, the sample aliquot is prepared in the very low concentration ranges, aiding dissociation which is accelerated by complexing the cyanide ion with chloramine-T. The latter frees additional cyanide ion to reestablish the equilibrium that was disturbed. The pH is reduced significantly by adding the pyridine-barbituric acid reagent (pH 5 to 5.5), and the sample is previously heated to accelerate the dissociation and complexing with chloramine-T. The test therefore has the necessary ability to measure certain undissociated cyanides, which could be converted by dissociation to toxic cyanides as a result of pH changes or dilution of the sample.

X1.2.8 All metal cyanide complexes are in equilibrium with the hydrolyzed HCN molecule, the concentration being dependent on the pH of the water and the dissociation constant of the particular metal cyanide complex present. The tightest complex is formed with iron. Since there is little dissociation, we may say that the ferrocyanide and ferricyanide compounds are themselves nontoxic **(17,18).**The iron cyanide complex is so tight that the standard alkaline chlorination procedure will not affect it. Reported analytical data showing a slight reduction in ferrocyanide content, either in the chlorination step or recovery in the colorimetric analysis procedure, is most likely due to impurity in the reagent or the handling of the sample. Analytical-grade ferrocyanide when dissolved always contains some dissociated CN^-(HCN). The sample has to be handled carefully to avoid any photodecomposition which will appear as an oxidizable portion of the total ferrocyanide present**(19–21).** All other metal cyanide compounds will be chlorinated at a slower rate due to the slow dissociation of the metal cyanide complex. The equilibrium of the metal cyanide complex and molecular HCN is continuously upset, and as the dissociation occurs, the hypochlorite ion will react with the cyanide ion, leading to further dissociation of the metal cyanide complex and then allowing further oxidation by chlorination. This implies a time dependence regarding the chlorination reaction with the cyanide ion that is complexed by such metals as silver, gold, and nickel. The chlorination of nickel cyanide at a concentration of 20 mg/L CN, as an example, may not be complete after 1 h even when hypochlorite was added at a 10 % excess of the stoichiometric amount **(16,22,23).**Because iron cyanide complexes are not destroyed by the practical methods of "alkaline chlorination" and cyanide in contact with iron salts causes iron cyanide to be always present in metal finishing waste, the question of proper waste treatment, or its lack, was many times raised when analyzing industrial waste using the standard analytical procedures. There is important practical value, therefore, that a distinction be made and analytical procedures be developed for" Cyanides Amenable to Chlorination" **(11,16).** As it has been established that the ferrocyanide complex is not toxic**(2,3,17,18)** it might be assumed that a low-cyanide concentration of 1 to 10 mg/L; if not amenable to chlorination such as iron cyanides, would have no toxic effect on the environment. However, this assumption is based on the following two factors:

X1.3 *The Iron Cyanides Undergo Dissociation from Photodecomposition* **(18** and **21).**

X1.3.1 Under strong sunlight, 10 mg/L iron cyanide, expressed as CN^-, may release 1 mg/L HCN in 1 h (Fig. X1.1).

X1.4 *Dilution and Dispersion of the Treated Waste in the Receiving Waters:*

X1.4.1 The kind of dilution, mixing in the diluting stream, clarity of the receiving waters, and the quantity of HCN release that may be expected are dependent upon particular environmental conditions, considering that only the top layers of the receiving waters will be subject to the strong sunlight to cause decomposition. Oxidation by air and bacterial decomposition in the receiving waters will be additional factors mitigating against the development of toxic concentration levels.

X1.4.2 Deliberate complexing of simple cyanides with iron salts as an economical means of waste treatment naturally should be unacceptable. Higher concentrations of iron cyanides, in view of the foregoing, require treatment. Suitable processes for the oxidative destruction of iron cyanides are available **(24)**, leading to the complete destruction of the cyanide and precipitation of iron oxide. Insoluble iron cyanide precipitates are soluble in alkali. Therefore, their being insoluble under normal conditions is not an ensurance that the environment is protected.

X1.5 *Cyanogen Chloride:*

X1.5.1 Presently the destruction of cyanide compounds in waste treatment processes is done by oxidation with hypochlorite (OCl^-) because the oxidation reaction is rapid and can be carried to completion using near stoichiometric equivalent of the reacting chemical. The chlorination reaction has to be conducted at an alkaline pH because the first reaction product formed is cyanogen chloride, a toxic gas, having very low solubility. The toxicity of cyanogen chloride may exceed the toxicity of HCN, both in water and in the atmosphere (<0.1 mg/L) **(25,26)**. Cyanogen chloride hydrolyzes at an alkaline pH to cyanate (CNO^-). The rate of hydrolysis is dependent on the pH conditions and the available excess chlorine, the higher the

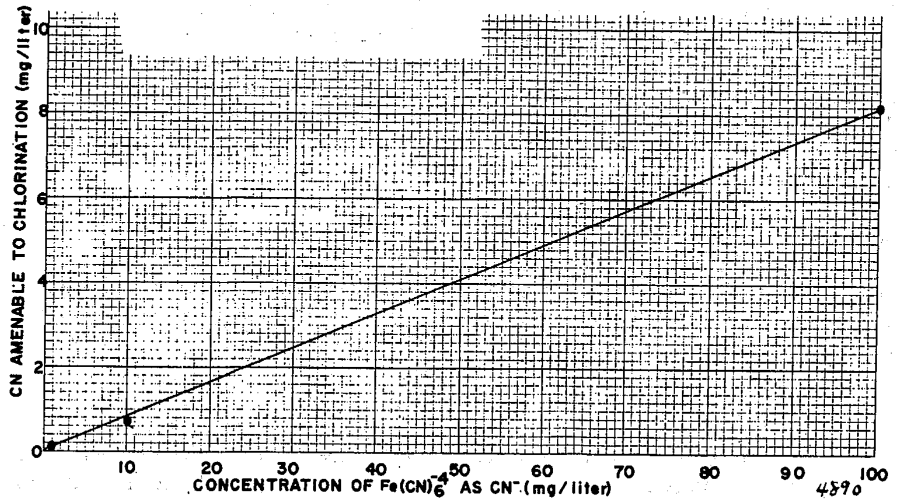

FIG. X1.1 Photodecomposition Rates for $Fe(CN)_6^{4}$ in Direct Sunlight, 20°C, pH 7, in Buffered Distilled Water, 75 mm Solution Layer, 1 h Exposure pH or the more chlorine present, the faster will the reaction go to completion. At a pH of 9, with no excess chlorine present, cyanogen chloride may persist in the treated water for more than 24 h **(27–29).** In view of the low solubility of cyanogen chloride and the time dependence for its hydrolysis, it is desirable to maintain the alkalinity during chlorination at pH 11 or higher. A pH of 12 to 13 may be required when the chlorination reaction is carried out on a waste water containing high concentrations of cyanide (>100 mg/L). The low solubility of cyanogen chloride is reduced further by the reaction heat generated upon addition of chlorine. The vapor pressure of the cyanogen chloride gas is increased. Rapid hydrolysis of the cyanogen chloride is the only means available to avoid the escape of cyanogen chloride into the atmosphere. When conducting continuous treatment of an effluent, the pH of the waste stream is lowered after a few minutes of reaction time because a neutral effluent has to be discharged. After the pH is reduced, any cyanogen chloride that has not yet undergone hydrolysis will escape as the toxic cyanogen chloride in the effluent. At pH 11 and at 10°C, the half-life period of cyanogen chloride before hydrolysis to CNO^-, and in the absence of excess chlorine, is 12.5 min **(27–29).** It is regrettable that the importance of this reaction and these conditions are not appreciated by Regulatory Agencies and waste treatment engineers. Analysis for cyanogen chloride is not performed, whereas concern is shown for the possible cyanate content of a treated waste. An analytical procedure for the distinction between HCN, ferro- and ferricyanide, respectively was published by Kruse and Thibault **(10).**

X1.6 *Cyanate Compounds:*

X1.6.1 As discussed in X1.5, the cyanogen chloride that is formed due to the reaction of OCl^- with cyanide ions and HCN during the chlorination reaction will hydrolyze to cyanate (CNO^-). The reported toxicity of cyanate in water is >100 mg/L. The reversion of cyanate to cyanide was attempted with photodecomposition and reduction, but could not be accomplished **(30).** Theoretical calculations also indicate that cyanate cannot be reduced to cyanide.

X1.6.2 Acidification and dilution of the cyanate leads to hydrolysis of cyanate to the ammonium ion (NH_4^+). Ammonia toxicity was reported in the 2 to 2.5 mg/L range in hard water **(17).** Doudoroff reports toxic effects at even lower levels (<1 mg/L), **(25).** It can be assumed therefore that the toxicity of cyanate is mainly due to the fact that it will yield ammonia. Since chlorination is conducted at high pH, and the treated waste normally then neutralized, further pH reduction may occur due to the lower pH condition of natural waters. Therefore, we may assume that harmful concentrations of cyanate will not be easily encountered in a natural environment. A cyanate determination within ASTM has not yet been formalized. Recommended analytical procedures are available from the literature **(30–33).**

X1.7 *Thiocyanate Compounds:*

X1.7.1 The relatively nontoxic thiocyanate compounds **(17)**may become extremely toxic due to conversion to cyanogen chloride (see X1.5) when a waste stream containing the thiocyanate ion undergoes chlorination for disinfection **(25,26).** The probable reaction is: $KCNS + 4Cl_2 + 4H_2O \rightarrow CNCl + KCl + H_2SO_4 + 6\ HCl$.

X1.7.2 According to Doudoroff, this reaction will occur even if the chlorine added to the waste stream is not sufficient to provide a residual **(25).** Thiosulfate, a common reducing chemical used to detoxify chloramines, is not as effective for cyanogen chloride unless a large excess is used **(26).**

X1.7.3 The determination for "cyanides amenable to chlorination" will also include the thiocyanate ion due to the conversion to cyanogen chloride by chloramine-T. A specific test for thiocyanates is contemplated.

X1.8 *Total Cyanide:*

X1.8.1 The distillation method, followed by the various analytical techniques to establish the quantitative cyanide content of the sample, has proven to be reliable. Extensive investigation and testing conducted in Germany has aided the evaluation of the recommended procedures **(34–40).** Cobalt cyanide is not recovered completely during the distillation. The explanation for this condition was given by Leschber **(37)** and referred to by original investigations by Bassett and Corbet **(41).** Potassium cobalt cyanide, when boiled with dilute sulfuric acid, partially breaks down to carbon monoxide, carbon dioxide, and ammonium sulfate.

X1.8.2 The determination of total cyanide retains its significance. As discussed earlier in X1.2, iron cyanides will not be revealed by the Cyanides Amenable to Chlorination analysis methods. To a lesser extent, some of the nickel cyanide, cobalt cyanide, silver and gold cyanide will also not be completely recovered. Neither will the standard alkaline chlorination practices break down these complexes. It has been noted that the toxic effects of these compounds are also considerably less and of a different nature: photodecomposition for iron cyanides; slow dissociation for nickel-, cobalt-, silver-, and gold cyanides. At the same time, there are many waste treatment installations that are either not designed properly, or not operated properly; therefore, more cyanide compounds that could have been treated are discharged in the effluent. There are also some processes generating excessively large quantities of these complex cyanides, thereby producing a significant pollution hazard.

As examples, we should list:

(*a*) *Heat treating processes;*

(*b*) Coke and blast furnace operations;

(*c*) Cyanide-type processes used for stripping nickel and cobalt-nickel alloy deposits;

(*d*) Rinse waters from silver and gold plating operations;

(*e*) Accidentally mixed waste coming from nickel plating solutions and cyanide floor spill;

(*f*) Regeneration and backwash waters from ion exchange type waste treatment processes used for the removal of plating salts from rinse water waste. The treatment of these wastes consists usually of mixing, partially deliberately, partially due to the process, and partially accidentally, nickel and iron salts with cyanide compounds; and

(*g*) Some waste treatment processes still recommended the use of iron sulfate for the neutralization of cyanide salts, etc.

X1.8.3 The total cyanide determination therefore must be used to ensure good waste treatment practices. The mistaken belief that the enumerated cyanide compounds are not "toxic" must be avoided. The fact is that the toxicity is only of a lesser magnitude.

X1.9 *Cyanide in Solid Waste:*

X1.9.1 The waste treatment needs for soluble cyanide sludges is assumed, for example, sludges from plating solutions; cyanide salts removed from heat treat pots or in frozen condition as drag-out from heat treatment; or cyanide salts as residue from the evaporation of processing solutions or rinse waters. The treatment requirements for these highly toxic residues is obvious.

X1.9.2 Most of the metal cyanide complexes are insoluble and are made soluble in water only in the presence of excess alkali metal cyanides. Milne **(5)** quotes a few examples which, while not complete, should be sufficient to show the insolubility of some metallic cyanides.

X1.9.3 During waste treatment, if the process is not conducted carefully, as the breakdown of the alkali metal cyanide is progressing, the metal cyanide will become insoluble, and will precipitate as the slightly soluble cyanide compound of the particular metal originally present. As seen from Table X1.1, some sludges may contain high levels of relatively insoluble metallic cyanides having high potential toxicity. Lancy and Zabban have reported **(16)** the cyanide content in the precipitates when conducting slow chlorination and with no or minimal chlorine excesses. The complete treatment and removal of the cyanide concentration in the sludge can be accomplished only by either significant chlorine excess in the waste water, or by rapid chlorination to allow breakdown of the metal cyanide complex before it is precipitated and buried in the sludge. Some newer waste treatment processes, such as treatment with peroxygen compounds, will yield considerably higher available cyanide concentrations in the sludge.

TABLE X1.1 Solubility of Metal Cyanide Precipitates in Water

Precipitate	Solubility in Water, g/L	Temperature, °C
Silver cyanide	0.000028	18
Zinc cyanide	0.0058	18
Copper cyanide	0.014	20
Nickel cyanide	0.0592	18
Cadmium cyanide	17	15
Mercuric cyanide	93	14

X1.9.4 Iron cyanide is always present in electroplating solutions. The concentration is usually in the range from 20 to 25 g/L. Only a small quantity of this iron cyanide will appear in the rinse water effluent, and as it escapes chlorination, it may form insoluble iron cyanide compounds with other metals present, such as copper, zinc, iron, etc. The metal iron cyanide compounds may be considered insoluble and nontoxic, but can become soluble in the alkaline range (pH >9) if the solid waste is leached with alkaline waste. The resolubilized iron cyanide can undergo photodecomposition as discussed in X1.2. The insoluble iron cyanide content of solid waste may be a result of the best treatment that modern technology can do with regard to treatment and disposal of particular cyanide compounds. The usual disposal is burial or landfill where acid conditions are far more common than excessive alkalinity which would cause the redissolution.

X1.9.5 The insoluble cyanide content of a solid waste can be determined by placing a 500-mg sample with 500 mL of distilled water into the distillation flask and following the total cyanide distillation. The calculations should consider a multiplication by 1000 to give the cyanide content of the solid waste sample in ppm. Insoluble iron cyanides in the solid waste can be leached out before analysis by stirring a weighed sample for 12 to 16 h in a 10 % caustic soda solution. The leachate and wash waters of the solid waste will give the iron cyanide content of the sample using the distillation procedure. A previous chlorination will have eliminated all cyanide amenable to chlorination from the sample. The sample should not be exposed to sunlight. A method allowing differentiation between HCN, ferro- and ferricyanide, as mentioned earlier, is referenced **(10,21)**.

X2. DETECTION AND ELIMINATION OF THE INTERFERENCE CAUSED BY ALDEHYDES

X2.1 Introductory Comments

X2.1.1 The inference caused by the presence of aldehydes, causing the conversion of cyanide to cyanohydrins has been explained in 11.3. Section 6.4 discusses the cyanohydrin formation when aldose is present in the sample. The same interference removal technique developed for the removal of the complexation caused by aldehydes may also be useful for the demasking of the complexes caused by the reaction with aldose. The aim is to recover the cyanide that is in a labile complex which also depends on the relative concentrations of the cyanide and complexing organics, the time past since the reacting chemical mixtures occurred, the temperature of the solution, and the organics present forming the various cyanohydrins.

X2.2 Summary of Methods

X2.2.1 *Silver Nitrate Method*—Formaldehyde present in the sample in excess of 0.5 mg/L noticeably interferes with the CN^- determination (0.02 mg CN^-/L). The cyanohydrin that is formed by the interaction of the cyanide and aldehyde in the sample is in equilibrium. This equilibrium is upset by the addition of silver nitrate which oxidizes the aldehyde to the noninterfering carboxylic acid prior to the cyanide determination. The EDTA solution complexes the iron, if present in the sample, to avoid the formation of iron cyanide.

X2.2.2 *Ethylene Diamine Method*—Ethylene diamine is a suitable demasking agent for the recovery of cyanide from labile cyanohydrins.

X2.3 Description of Spot Test

X2.3.1 E. Sawicki, et al, have developed a suitable colorimetric method for the detection and estimation of aliphatic aldehydes in water **(42–44).** This method has been adapted for a spot test procedure.

X2.4 Apparatus

X2.4.1 *Spot Plate*, white, with 6 to 12 cavities.

X2.5 Reagents and Materials

X2.5.1 *Ethylene Diamine Solution* (3.5 %)—Dilute 3.5 mL of pharmaceutical grade anhydrous $NH_2CH_2NH_2$ to 100 mL with water.

X2.5.2 *EDTA Solution* (0.1 *N*)—Dissolve 37.2 g of sodium-ethylenediamine-tetraacetate, dihydrated, in water and dilute to 1 L.

X2.5.3 *Ferric Chloride Oxidizing Solution*—Dissolve 1.6 g of sulfamic acid and 1 g of $FeCl_3 \cdot 6H_2O$ in 100 mL of water.

X2.5.4 *MBTH Indicator Solution*—Dissolve 0.05 g of 3-methyl, 2-benzothiazolone hydrochloride in 100 mL of water. Filter if turbid.

X2.5.5 *Silver Nitrate Solution* (17 g/L)—Dissolve 17 g of silver nitrate ($AgNO_3$) crystals in water and dilute to 1 L.

X2.6 Procedure

X2.6.1 If the sample is alkaline, add sulfuric acid (1 + 1) dropwise to 10 mL of the sample to adjust the pH to less than 8.0. Place 1 drop of sample and 1 drop of water for a blank in separate cavities of the spot plate. Add 1 drop of MBTH solution and then 1 drop of $FeCl_3$ oxidizing solution to each spot. Allow 10 min for color development. The color change will be from a fruit green-yellow to a deeper green with blue-green to blue at high concentrations of aldehyde. The blank should remain yellow. The sensitivity of the test is approximately 0.2 mg/L CH_2O.

X2.6.2 *Silver Nitrate Method*:

X2.6.2.1 Add $AgNO_3$ solution dropwise to the sample and retest on the spot plate. For each drop of $AgNO_3$ add also 2 drops of EDTA solution. One milligram CH_2O/100 mL of sample will require approximately 2 drops of $AgNO_3$ solution and 4 drops of EDTA solution.

X2.6.2.2 The silver nitrate may also precipitate some of the thiocyanate if present in the sample. If this should be avoided, add a few drops of concentrated ammonium hydroxide to the sample. In case $AgNO_3$ solution has been added in excess and it is found that AgCN has precipitated, ammonium hydroxide can be added subsequent to the CH_2O removal to resolubilize the CN^- and Ag^+. The dark precipitate that has formed is metallic silver and can be filtered off if turbidity interferes with the test method.

X2.6.3 *Ethylene Diamine Method*:

X2.6.3.1 Add 2 mL of the ethylene diamine solution for each 100 mL of sample to be used for the cyanide determination. It has been found that this quantity of ethylene diamine addition is suitable to overcome the interference caused by up to 50 mg/L CH_2O present.

X2.6.4 When applying a spike in testing or evaluation of the methods do not expect necessarily 100 % recovery of the CN^-. Recovery will depend on CH_2O excess that has been present, time of contact, and temperature of the sample.

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Standard Test Method for Analysis of Liquefied Petroleum (LP) Gases and Propene Concentrates by Gas Chromatography[1]

This standard is issued under the fixed designation D 2163; 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 composition of liquefied petroleum (LP) gases. It is applicable to analysis of propane, propene, and butane in all concentration ranges 0.1 % and above.

1.2 *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.*

1.3 The values stated in SI units are to be regarded as standard.

2. Referenced Documents

2.1 *ASTM Standards:*

D 2421 Practice for Interconversion of Analysis of C_5 and Lighter Hydrocarbons to Gas-Volume, Liquid-Volume, or Weight Basis[2]

D 2598 Practice for Calculation of Certain Physical Properties of Liquified Petroleum (LP) Gases from Compositional Analysis[3]

D 3700 Practice for Containing Hydrocarbon Fluid Samples Using a Floating Piston Cylinder[3]

3. Terminology

3.1 *Definitions:*

3.1.1 *propene concentrate*—concentrate containing more than 50 % propene.

4. Summary of Test Method

4.1 Components in a sample of LP gas are physically separated by gas chromatography and compared to corresponding components separated under identical operating conditions from a reference standard mixture of known composition or from use of pure hydrocarbons. The chromatogram of the sample is interpreted by comparing peak heights or areas with those obtained on the reference standard mixture of pure hydrocarbons.

5. Significance and Use

5.1 The component distribution of liquefied petroleum gases and propene concentrates is often required as a specification analysis for end-use sale of this material. Its wide use as chemical feedstocks or as fuel, require precise compositional data to ensure uniform quality of the desired reaction products.

5.2 The component distribution data of liquefied petroleum gases and propene concentrates can be used to calculate physical properties such as relative density, vapor pressure, and motor octane (see Practice D 2598). Precision and accuracy of compositional data are extremely important when these data are used to calculate various properties of these petroleum products.

6. Gas Chromatograph System

6.1 *Detector*—The detector shall be a thermal conductivity type or its equivalent in sensitivity and stability. The system shall be capable of detecting 0.1 % concentration of any component of interest. For calculation techniques utilizing a recorder, the signal for the concentration shall be at least 5 chart divisions above the noise level on a 0 to 100 scale chart. Noise level must be restricted to a maximum of 1 chart division. When electronic integration is employed the signal for 0.1 % concentration must be at least twice the noise level.

6.2 *Recorder*—A strip-chart recorder and integrator with a full-scale range of 10 mV or less shall be required. A maximum full-scale balance time of 2 s and a minimum chart speed of ½ in. (12.7 mm)/min shall be required.

6.3 *Attenuator*—A multistep attenuator for the detector output signal shall be necessary to maintain maximum peaks within the recorder chart range. The attenuator system must be accurate to 0.5 % in any position.

6.4 *Sample Inlet System*—Provision shall be made to introduce up to 0.50 mL of the sample. The sample volume must be repeatable such that successive runs agree within 1 mm or 1 % (whichever is larger) on each component peak height.

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[1] This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricantsand is the direct responsibility of Subcommittee D02.D0.03on C4 Test Methods Liquefied Petroleum Gas.

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

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

6.5 *Temperature Control*—The analyzer columns shall be maintained at a temperature constant to 0.3°C during the course of the sample and corresponding reference standard runs.

6.6 *Carrier Gas*—The instrument shall be equipped with suitable facilities to provide a flow of carrier gas through the analyzer column at a flow rate that is constant to 1.0 % throughout the analysis.

6.7 *Columns*—Any column may be used provided all component peaks for compounds present in concentration of more than 5 % are resolved so that the ratio *A*/*B* shall not be less than 0.8, Fig. 1

where:

A = depth of the valley on either side of peak B, and

B = height above the baseline of the smaller of any two adjacent peaks (see Fig. 1).

For compounds present in concentrations of 5 % or less, the ratio of *A*/*B* shall not be less than 0.4. In case the small-component peak is adjacent to a large one, it may be necessary to construct the baseline of the small peak tangent to the curve as shown in Fig. 2.

7. Calibration Standard

7.1 Pure components or calibration standard mixtures[4] may be used for calibration. If pure components are used, identical volumes of each component are injected into the chromatograph and relative area response factors are determined. These factors are valid for a given instrument and operating conditions and should be redetermined periodically. If pure components are used for calibration, the calculation should be made in mole percent and converted to liquid volume percent (Note 1). Factors repeatable to within 1 % are required. The concentration of each component in the calibration standard mixtures shall be known to within 0.1 %. The concentration of the major component in the calibration standard mixture shall not differ from that of the like component in the sample to be analyzed by more than 10 % if the peak height method of calculation is used. On propene concentrates, the calibration standard mixtures shall not differ from that of like component in the sample to be analyzed by more than 5 %. Typical composition ranges of suitable calibration standard mixtures are given in Table 1.

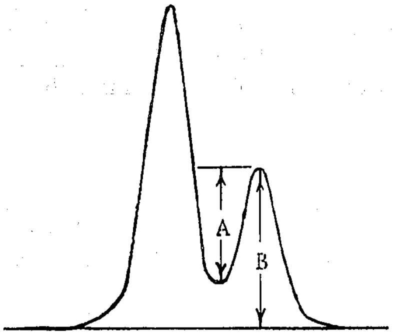

FIG. 1 Illustration of *A*/*B* Ratio

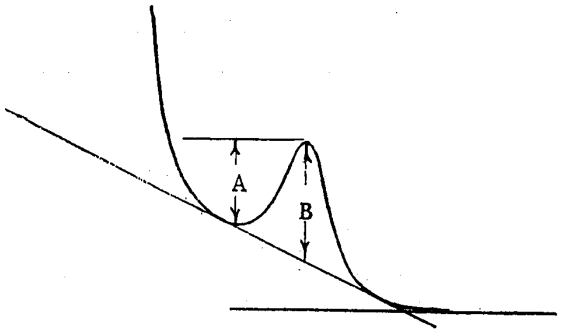

FIG. 2 Illustration of *A*/*B* Ratio for Small-Component Peak

NOTE 1—Test Method D 2421 may be used whenever a need exists for such translations.

8. Procedure

8.1 *Apparatus Preparation*—Mount the column suitable for the analysis desired (see Appendix X1) in the chromatograph and adjust the conditions to optimum for the column selected (Table 2). Allow sufficient time for the instrument to reach equilibrium as indicated by a stable base line.

8.1.1 The test method allows the user a wide latitude in choice of instrumentation to make the analysis, and most commercial instrumentation easily meets the requirements defined in the test method. However, only by strict adherence to the calibration procedures outlined in the method can reproducibility between instruments expect to be achieved.

8.1.2 Proper maintenance of instrumentation is critical to continued satisfactory performance of this analysis. Clean sample containers, clean sample inlet systems and clean detectors are mandatory to achieve the precision and accuracy capabilities of this method.

NOTE 2—**Warning:** Samples and reference mixtures are extremely flammable. Keep away from heat, sparks, and flames. Use with adequate ventilation. Cylinders must by supported at all times. Hydrocarbon vapors that may be vented must be controlled to assure compliance with applicable safety and environmental regulations. Vapor reduces oxygen available for breathing. Liquid causes cold burns.

8.2 *Preparation and Introduction of Sample*—Attach the cylinder containing the gas mixture to the sampling valve of the chromatograph so that a liquid phase sample is withdrawn. Adjust the flow rate from the sample cylinder so that complete vaporization of the liquid occurs at the cylinder valve. (An alternative technique is to trap a sample of only liquid phase in a short section of tubing, and then permit the entire sample to vaporize into an evacuated container). Adjust the ratio of the two volumes so that a gage pressure of 69 to 138 kPa (10 to 20 psi) is obtained in the final container. Then use this sample for the analysis. Flush the sample loop for 1 to 2 min at a flow rate of 5 to 10 mL/min before introducing the sample into the carrier gas stream.

8.2.1 On propene concentrates, the sample may be introduced as a liquid by means of a liquid sample valve or by vaporization of the liquid as above. On propene concentrates having a propene content of less than 80 %, only the alternative technique of trapping a sample of liquid and vaporizing the entire sample into an evacuated container shall be used.

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[4] Suitable reference standard mixtures of pure hydrocarbons are available from Scott Specialty Gases, Inc., Plumsteadville, PA.

TABLE 1 Reference Standard Mixtures, Liquid Volume Percent[A]

Component	Propane with No Unsaturates	Propane with Low Propene	Propane with High Propene	Butane	Propane-Butane Mixtures	Propene with Low Propane	Propene with High Propane
Ethane	4	4	3	...	2	0.2	0.1
Propane	93	87	57	3	45	4.8	22.6
Propene	...	4	35	...	6	94.9	76.6
n-Butane	1	1	1	64	30	0.1	0.5
Isobutane	1	3	3	25	15	...	...
Butene	...	...	...	6	...	...	0.2
Isopentane	1	1	1	2	2	...	...

[A] The composition values recorded in this table are offered as a guide to laboratories preparing their own mixtures from pure hydrocarbons or to commercial suppliers of standards. In either case, an accurate composition of the standards must be known to analyst.

TABLE 2 Instrument Conditions

	Column Length, m	Column Diameter, mm, OD	Substrate, Mass, %	Temperature, °C	Flow Rate, mL/min	Carrier G
Silicon 200/500	4	6.4	27	90	60 to 70	helium
Benzyl cyanide—silver nitrate	9	6.4	36	40	45 to 55	helium
Hexamethylphosphoramide	9	6.4	17	30	60 to 70	helium
Dimethylsulfolane plus benzyl cyanide and silver nitrate	7	6.4	36	35	60 to 70	helium
Dimethylsulfolane	15	6.4	30	25	30	helium
Hexamethyl phosphoramide	6	3.2	25	28	12	helium
Di-*n*-butyl maleate	4	6.4	25	28	60	helium
Tricresyl phosphate plus silicone, 550	9	6.4	30	35	70	helium
Methoxy ethoxy ethyl ether	9	6.4	30	30	60	helium

8.2.2 Sampling at the sample source and at the chromatograph must always be done in a manner that ensures that a representative sample is being analyzed. Lack of precision and accuracy in using this method can most often be attributed to improper sampling procedures. (See Test Method D 3700.)

8.3 *Preparation of the Chromatogram*—Obtain duplicate chromatograms of the sample. Adjust the attenuator at each peak for maximum peak height within the recorder chart range. Peak heights of like components shall agree within 1 mm or 1 % (whichever is larger). If a reference standard mixture is used for calibration, obtain duplicate chromatograms of the proper reference standard in a similar manner. Use the same sample size for all runs.

9. Calculation

9.1 *Peak Height Method*—Measure the peak height of each component and adjust this value to the attenuation of the same component in the reference standard mixture. Calculate the percentage by mole or liquid volume of each component as follows:

$$\text{Concentration, liquid volume or mol percent} = (P_s/P_o) \times S \quad (1)$$

where:

P_s = peak height of component in the sample,

P_o = peak height of component in reference standard mixture, and

S = percentage of mole or liquid volume of component in reference standard mixture.

9.2 *Area Method*—Measure the area of each component by multiplying the height of the peak by the width at half height. The width should be measured with the aid of a magnifying glass (Note 3). Adjust the area to the attenuation of the same component in the reference standard mixture.

Note 3—The use of planimeters or integrators is permissible provided their repeatability has been established and the resulting repeatability does not adversely affect the repeatability and reproducibility limits of the method given in Section 10.

9.2.1 Calculate the percentage by mole or liquid volume of each component as follows:

$$\text{Concentration, liquid volume or mol percent} = (A_s/A_o) \times S \quad (2)$$

where:

A_s = area of component in sample,

A_o = area of component in reference standard mixture, and

S = percentage by mole or liquid volume of component in reference standard mixture.

9.2.2 If pure components are used for calibration, calculate the composition as follows:

$$\text{Concentration, mol percent} = A_s/A_p \quad (3)$$

where:

A_s = area of component in sample, mm^2, and

A_p = area sensitivity of component, mm^2 per percent.

9.2.3 Total the results and normalize to 100 %.

9.3 *Normalization*—Normalize the mole or liquid volume percent values obtained in 9.1 or 9.2 by multiplying each value by 100 and dividing by the sum of the original values. The sum of the original values should not differ from 100.0 % by more than 2.0 %.

10. Precision and Bias[5]

10.1 The data in Table 3 and Fig. 3 shall be used for judging the acceptability of results (95 % confidence) on samples containing less than 50 % propene. The data in Table 4 shall be

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[5] The data from which this precision statement is based are not available.

TABLE 3 Precision Data for LPG Containing Less Than 50 % Propene

Concentration Range of Components, mol %	Repeatability	Reproducibility
0 to 70	use repeatability curve in Fig. 3	use reproducibility curve in Fig. 3
Above 70	0.2	1 % of amount present

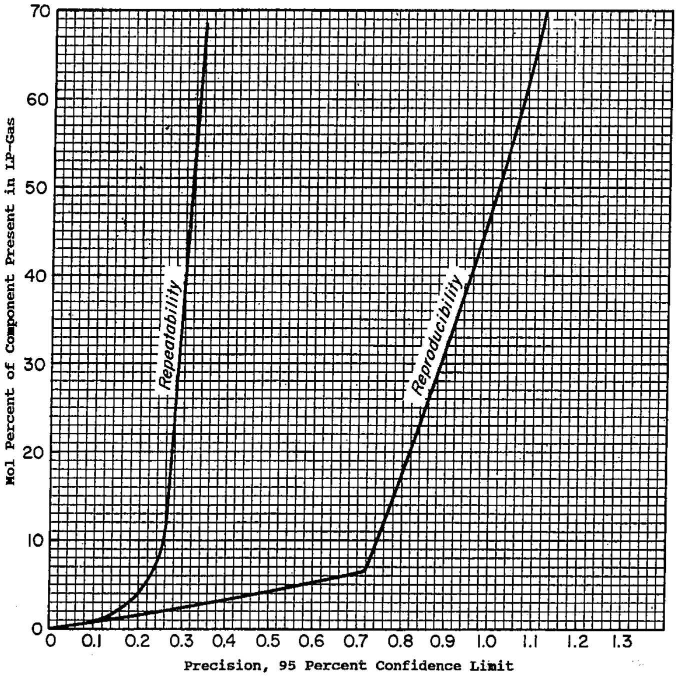

FIG. 3 Precision Curves

used for judging the acceptability of results on samples containing more than 50 % propene.

10.1.1 *Repeatability*—The difference between successive test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method exceed the values shown in Table 3 or Fig. 3 and Table 4 in only one case in twenty.

10.1.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators working in different laboratories on identical test material, in the normal and correct operation of the test method, exceed the values shown in Table 3 or Fig. 3 and Table 4 in only one case in twenty.

10.2 *Bias*—Since there is no accepted reference material suitable for determining the bias for the procedure in this test method, no statement on bias is being made.

TABLE 4 Precision Data for Propene Concentrates

Compound	Concentration, mol %	Repeatability	Reproducibility
Ethane	0.0 to 0.1	0.02	0.04
	0.2	0.05	0.06
Propene	70 to 77	0.38	1.5
	93 to 95	0.34	1.0
Propane	5 to 7	0.33	1.0
	22 to 29	1.0	1.7
Butanes	0.0 to 0.1	0.04	0.08
	0.5	0.04	0.2
	0.6	0.1	0.3
	1	0.1	0.5
Butenes	0.2	0.07	0.2

11. Keywords

11.1 analysis; liquified petroleum gas

APPENDIX

(Nonmandatory Information)

X1. PARTITION COLUMNS

X1.1 The following four partition columns have been cooperatively tested and found suitable for use with materials given in the scope of this test method.

X1.1.1 *Silicone 200/500 Column*—This column separates ethane, propane, *n*-butane, isobutane, *n*-pentane, and isopentane and is therefore suitable for analyzing LP gases free from unsaturated hydrocarbons.

X1.1.2 *Benzyl Cyanide-Silver Nitrate Column*—This column separates isobutane, *n*-butane, the butenes, *n*-pentane and isopentane, and accordingly is best suited for use with LP gas butane containing unsaturated C_4 hydrocarbons.

X1.1.3 *Hexamethylphosphoramide (HMPA) Column*—This column separates ethane, propane, propene, isobutane,*n*-butane, the butenes, *n*-pentane, and isopentane, and accordingly is suitable for use with all types of LP gases.

X1.1.4 *Dimethylsufolane (DMS)-Benzyl Cyanide-Silver Nitrate Column*—This column separates all components in commercial LP gases.

NOTE X1.1—There are commercial suppliers of gas chromatography equipment and columns who can make (and guarantee) that the columns they provide will meet the specifications (see 6.7 Columns) of this test method.

NOTE X1.2—**Warning:** toxic. **Precaution**—See the product safety bulletins from the supplier of the chemicals used in preparing these columns or before Benzyl Cyanide-Silver Nitrate Column; X1.1.3 Hexamethylphosphoramide (HMPA) column, and X1.1.4 Dimethylsufolane (DMS) Benzyl Cyanide-Silver Nitrate Column.

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Standard Test Method for
Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass[1]

This standard is issued under the fixed designation D 2216; 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 laboratory determination of the water (moisture) content by mass of soil, rock, and similar materials where the reduction in mass by drying is due to loss of water except as noted in 1.4, 1.5, and 1.7. For simplicity, the word "material" hereinafter also refers to either soil or rock, whichever is most applicable.

1.2 Some disciplines, such as soil science, need to determine water content on the basis of volume. Such determinations are beyond the scope of this test method.

1.3 The water content of a material is defined in 3.2.1.

1.4 The term "solid material" as used in geotechnical engineering is typically assumed to mean naturally occurring mineral particles of soil and rock that are not readily soluble in water. Therefore, the water content of materials containing extraneous matter (such as cement, and the like) may require special treatment or a qualified definition of water content. In addition, some organic materials may be decomposed by oven drying at the standard drying temperature for this method (110°C). Materials containing gypsum (calcium sulfate dihydrate or other compounds having significant amounts of hydrated water) may present a special problem as this material slowly dehydrates at the standard drying temperature (110°C) and at very low relative humidities, forming a compound (calcium sulfate hemihydrate) which is not normally present in natural materials except in some desert soils. In order to reduce the degree of dehydration of gypsum in those materials containing gypsum, or to reduce decomposition in highly organic soils, it may be desirable to dry these materials at 60°C or in a desiccator at room temperature. Thus, when a drying temperature is used which is different from the standard drying temperature as defined by this test method, the resulting water content may be different from standard water content determined at the standard drying temperature.

NOTE 1—Test Methods D 2974 provides an alternate procedure for determining water content of peat materials.

1.5 Materials containing water with substantial amounts of soluble solids (such as salt in the case of marine sediments) when tested by this method will give a mass of solids which includes the previously soluble solids. These materials require special treatment to remove or account for the presence of precipitated solids in the dry mass of the specimen, or a qualified definition of water content must be used. For example, see Noorany[2] regarding information on marine soils.

1.6 This test method requires several hours for proper drying of the water content specimen. Test Method D 4643 provides for drying of the test specimen in a microwave oven which is a shorter process. Also see Gilbert[3] for details on the background of this test method.

1.7 This standard requires the drying of material in an oven at high temperatures. If the material being dried is contaminated with certain chemicals, health and safety hazards can exist. Therefore, this standard should not be used in determining the water content of contaminated soils unless adequate health and safety precautions are taken.

1.8 *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 653 Terminology Relating to Soil, Rock, and Contained Fluids[4]

D 2974 Test Methods for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils[4]

D 4220 Practice for Preserving and Transporting Soil Samples[4]

D 4318 Test Method for Liquid Limit, Plastic Limit, and Plasticity Index of Soils[4]

D 4643 Test Method for Determination of Water (Moisture)

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[1] This test method is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.03 on Texture, Plasticity and Density Characteristics of Soils.

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[2] Noorany, I., "Phase Relations in Marine Soils", Journal of Geotechnical Engineering, ASCE, Vol. 110, No. 4, April 1984, pp. 539–543.

[3] Gilbert, P.A., "Computer Controlled Microwave Oven System for Rapid Water Content Determination", Tech. Report GL-88-21, Department of the Army, Waterways Experiment Station, Corps of Engineers, Vicksburg, MS, November 1988.

[4] *Annual Book of ASTM Standards*, Vol 04.08.

***A Summary of Changes section appears at the end of this standard.**

Content of Soil by the Microwave Oven Method[4]

D 4753 Specification for Evaluating, Selecting, and Specifying Balances and Scales for Use in Soil and Rock Testing[4]

D 6026 Guide for Using Significant Digits in Calculating and Reporting Geotechnical Test Data[5]

E 145 Specification for Gravity-Convection And Forced-Ventilation Ovens[6]

3. Terminology

3.1 Refer to Terminology D 653 for standard definitions of terms.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *water content (of a material)*—the ratio expressed as a percent of the mass of "pore" or "free" water in a given mass of material to the mass of the solid material. A standard temperature of 110° ± 5°C is used to determine these masses.

4. Summary of Test Method

4.1 A test specimen is dried in an oven at a temperature of 110° ± 5°C to a constant mass. The loss of mass due to drying is considered to be water. The water content is calculated using the mass of water and the mass of the dry specimen.

5. Significance and Use

5.1 For many materials, the water content is one of the most significant index properties used in establishing a correlation between soil behavior and its index properties.

5.2 The water content of a material is used in expressing the phase relationships of air, water, and solids in a given volume of material.

5.3 In fine-grained (cohesive) soils, the consistency of a given soil type depends on its water content. The water content of a soil, along with its liquid and plastic limits as determined by Test Method D 4318, is used to express its relative consistency or liquidity index.

6. Apparatus

6.1 *Drying Oven*, thermostatically-controlled, preferably of the forced-draft type, meeting the requirements of Specification E 145 and capable of maintaining a uniform temperature of 110 ± 5°C throughout the drying chamber.

6.2 *Balances*—All balances must meet the requirements of Specification D 4753 and this section. A Class GP1 balance of 0.01g readability is required for specimens having a mass of up to 200 g (excluding mass of specimen container) and a Class GP2 balance of 0.1g readability is required for specimens having a mass over 200 g. However, the balance used may be controlled by the number of significant digits needed (see 8.2.1 and 12.1.2).

6.3 *Specimen Containers*—Suitable containers made of material resistant to corrosion and change in mass upon repeated heating, cooling, exposure to materials of varying pH, and cleaning. Unless a dessicator is used, containers with close-fitting lids shall be used for testing specimens having a mass of less than about 200 g; while for specimens having a mass greater than about 200 g, containers without lids may be used (see Note 7). One container is needed for each water content determination.

NOTE 2—The purpose of close-fitting lids is to prevent loss of moisture from specimens before initial mass determination and to prevent absorption of moisture from the atmosphere following drying and before final mass determination.

6.4 *Desiccator*—A desiccator cabinet or large desiccator jar of suitable size containing silica gel or anhydrous calcium sulfate. It is preferable to use a desiccant which changes color to indicate it needs reconstitution. See 10.5.

NOTE 3—Anhydrous calcium sulfate is sold under the trade name Drierite.

6.5 *Container Handling Apparatus*, gloves, tongs, or suitable holder for moving and handling hot containers after drying.

6.6 *Miscellaneous*, knives, spatulas, scoops, quartering cloth, sample splitters, etc, as required.

7. Samples

7.1 Samples shall be preserved and transported in accordance with Practice 4220 Groups B, C, or D soils. Keep the samples that are stored prior to testing in noncorrodible airtight containers at a temperature between approximately 3 and 30°C and in an area that prevents direct contact with sunlight. Disturbed samples in jars or other containers shall be stored in such a way as to prevent or minimize moisture condensation on the insides of the containers.

7.2 The water content determination should be done as soon as practicable after sampling, especially if potentially corrodible containers (such as thin-walled steel tubes, paint cans, etc.) or plastic sample bags are used.

8. Test Specimen

8.1 For water contents being determined in conjunction with another ASTM method, the specimen mass requirement stated in that method shall be used if one is provided. If no minimum specimen mass is provided in that method then the values given below shall apply. See Howard[7] for background data for the values listed.

8.2 The minimum mass of moist material selected to be representative of the total sample shall be in accordance with the following:

Maximum particle size (100 % passing)	Standard Sieve Size	Recommended minimum mass of moist test specimen for water content reported to ±0.1 %	Recommended minimum mass of moist test specimen for water content reported to ±1 %
2 mm or less	No. 10	20 g	20 g^A
4.75 mm	No. 4	100 g	20 g^A
9.5 mm	⅜-in.	500 g	50 g
19.0 mm	¾-in.	2.5 kg	250 g
37.5 mm	1½ in.	10 kg	1 kg

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[5] *Annual Book of ASTM Standards,* Vol 04.09.

[6] *Annual Book of ASTM Standards,* Vol 14.02.

[7] Howard, A. K., "Minimum Test Specimen Mass for Moisture Content Determination", *Geotechnical Testing Journal,* A.S.T.M., Vol. 12, No. 1, March 1989, pp. 39-44.

75.0 mm	3-in.	50 kg	5 kg

[A]To be representative not less than 20 g shall be used.

8.2.1 The minimum mass used may have to be increased to obtain the needed significant digits for the mass of water when reporting water contents to the nearest 0.1 % or as indicated in 12.1.2.

8.3 Using a test specimen smaller than the minimum indicated in 8.2 requires discretion, though it may be adequate for the purposes of the test. Any specimen used not meeting these requirements shall be noted on the test data forms or test data sheets.

8.4 When working with a small (less than 200g) specimen containing a relatively large gravel particle, it is appropriate not to include this particle in the test specimen. However, any discarded material shall be described and noted on the test data forms or test data sheets.

8.5 For those samples consisting entirely of intact rock, the minimum specimen mass shall be 500 g. Representative portions of the sample may be broken into smaller particles, depending on the sample's size, the container and balance being used and to facilitate drying to constant mass, see 10.4. Specimen sizes as small as 200 g may be tested if water contents of only two significant digits are acceptable.

9. Test Specimen Selection

9.1 When the test specimen is a portion of a larger amount of material, the specimen must be selected to be representative of the water condition of the entire amount of material. The manner in which the test specimen is selected depends on the purpose and application of the test, type of material being tested, the water condition, and the type of sample (from another test, bag, block, and the likes.)

9.2 For disturbed samples such as trimmings, bag samples, and the like, obtain the test specimen by one of the following methods (listed in order of preference):

9.2.1 If the material is such that it can be manipulated and handled without significant moisture loss and segregation, the material should be mixed thoroughly and then select a representative portion using a scoop of a size that no more than a few scoopfuls are required to obtain the proper size of specimen defined in 8.2.

9.2.2 If the material is such that it cannot be thoroughly mixed or mixed and sampled by a scoop, form a stockpile of the material, mixing as much as possible. Take at least five portions of material at random locations using a sampling tube, shovel, scoop, trowel, or similar device appropriate to the maximum particle size present in the material. Combine all the portions for the test specimen.

9.2.3 If the material or conditions are such that a stockpile cannot be formed, take as many portions of the material as practical, using random locations that will best represent the moisture condition. Combine all the portions for the test specimen.

9.3 Intact samples such as block, tube, split barrel, and the like, obtain the test specimen by one of the following methods depending on the purpose and potential use of the sample.

9.3.1 Using a knife, wire saw, or other sharp cutting device, trim the outside portion of the sample a sufficient distance to see if the material is layered and to remove material that appears more dry or more wet than the main portion of the sample. If the existence of layering is questionable, slice the sample in half. If the material is layered, see 9.3.3.

9.3.2 If the material is not layered, obtain the specimen meeting the mass requirements in 8.2 by: (1) taking all or one-half of the interval being tested; (2) trimming a representative slice from the interval being tested; or (3) trimming the exposed surface of one-half or from the interval being tested.

NOTE 4—Migration of moisture in some cohesionless soils may require that the full section be sampled.

9.3.3 If a layered material (or more than one material type is encountered), select an average specimen, or individual specimens, or both. Specimens must be properly identified as to location, or what they represent, and appropriate remarks entered on the test data forms or test data sheets.

10. Procedure

10.1 Determine and record the mass of the clean and dry specimen container (and its lid, if used).

10.2 Select representative test specimens in accordance with Section 9.

10.3 Place the moist test specimen in the container and, if used, set the lid securely in position. Determine the mass of the container and moist material using a balance (see 6.2) selected on the basis of the specimen mass. Record this value.

NOTE 5—To prevent mixing of specimens and yielding of incorrect results, all containers, and lids if used, should be numbered and the container numbers shall be recorded on the laboratory data sheets. The lid numbers should match the container numbers to eliminate confusion.

NOTE 6—To assist in the oven-drying of large test specimens, they should be placed in containers having a large surface area (such as pans) and the material broken up into smaller aggregations.

10.4 Remove the lid (if used) and place the container with moist material in the drying oven. Dry the material to a constant mass. Maintain the drying oven at 110 ± 5°C unless otherwise specified (see 1.4). The time required to obtain constant mass will vary depending on the type of material, size of specimen, oven type and capacity, and other factors. The influence of these factors generally can be established by good judgment, and experience with the materials being tested and the apparatus being used.

NOTE 7—In most cases, drying a test specimen overnight (about 12 to 16 h) is sufficient. In cases where there is doubt concerning the adequacy of drying, drying should be continued until the change in mass after two successive periods (greater than 1 h) of drying is an insignificant amount (less than about 0.1 %). Specimens of sand may often be dried to constant mass in a period of about 4 h, when a forced-draft oven is used.

NOTE 8—Since some dry materials may absorb moisture from moist specimens, dried specimens should be removed before placing moist specimens in the same oven. However, this would not be applicable if the previously dried specimens will remain in the drying oven for an additional time period of about 16 h.

10.5 After the material has dried to constant mass remove the container from the oven (and replace the lid if used). Allow the material and container to cool to room temperature or until the container can be handled comfortably with bare hands and the operation of the balance will not be affected by convection currents and/or its being heated. Determine the mass of the container and oven-dried material using the same type/capacity balance used in 10.3. Record this value. Tight fitting lids shall be used if it appears that the specimen is absorbing moisture from the air prior to determination of its dry mass.

NOTE 9—Cooling in a desiccator is acceptable in place of tight fitting lids since it greatly reduces absorption of moisture from the atmosphere during cooling especially for containers without tight fitting lids.

11. Calculation

11.1 Calculate the water content of the material as follows:

$$w = [(M_{cws} - M_{cs})/(M_{cs} - M_c)] \times 100 = \frac{M_w}{M_s} \times 100 \qquad (1)$$

where:

w = water content, %,
M_{cws} = mass of container and wet specimen, g,
M_{cs} = mass of container and oven dry specimen, g,
M_c = mass of container, g,
M_w = mass of water ($M_w = M_{cws} - M_{cds}$), g, and
M_s = mass of solid particles ($M_s = M_{cds} - M_c$), g.

12. Report

12.1 Test data forms or test data sheets shall include the following:

12.1.1 Identification of the sample (material) being tested, such as boring number, sample number, test number, container number etc.

12.1.2 Water content of the specimen to the nearest 1 % or 0.1 %, as appropriate based on the minimum sample used. If this method is used in concert with another method, the water content of the specimen should be reported to the value required by the test method for which the water content is being determined. Refer to Guide D 6026 for guidance concerning significant digits, especially if the value obtained from this test method is to be used to calculate other relationships such as unit weight or density. For instance, if it is desired to express dry unit weight to the nearest 0.1 lbf/f^3(0.02 kN/m^3), it may be necessary to use a balance with a greater readability or use a larger specimen mass to obtain the required significant digits the mass of water so that the water content can be determined to the required significant digits. Also, the significant digits in Guide D 6026 may need to be increased when calculating phase relationships requiring four significant digits.

12.1.3 Indicate if test specimen had a mass less than the minimum indicated in 8.2.

12.1.4 Indicate if test specimen contained more than one material type (layered, etc.).

12.1.5 Indicate the temperature of drying if different from 110 ± 5°C.

12.1.6 Indicate if any material (size and amount) was excluded from the test specimen.

12.2 When reporting water content in tables, figures, etc., any data not meeting the requirements of this test method shall be noted, such as not meeting the mass, balance, or temperature requirements or a portion of the material is excluded from the test specimen.

13. Precision and Bias

13.1 *Statement on Bias*—There is no accepted reference value for this test method; therefore, bias cannot be determined.

13.2 *Statements on Precision*:

13.2.1 *Single-Operator Precision (Repeatability)*—The single-operator coefficient of variation has been found to be 2.7 percent. Therefore, results of two properly conducted tests by the same operator with the same equipment should not be considered suspect unless they differ by more than 7.8 percent of their mean.[8]

13.2.2 *Multilaboratory Precision (Reproducibility)*[9]—The multilaboratory coefficient of variation has been found to be 5.0 percent. Therefore, results of two properly conducted tests by different operators using different equipment should not be considered suspect unless they differ by more than 14.0 percent of their mean.

14. Keywords

14.1 consistency; index property; laboratory; moisture analysis; moisture content; soil aggregate; water content

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[8] These numbers represent the (1s) and (d2s) limits as described in Practice C 670.

[9] These numbers represent the (1s %) and (d2s %) limits as described in Practice C 670.

SUMMARY OF CHANGES

Committee D-18 has identified the location of selected changes to this standard since the last issue. (D 2216-92) that may impact the use of this standard.

(*1*) Title was changed to emphasize that mass is the basis for the standard.
(*2*) Section 1.1 was revised to clarify "similar materials".
(*3*) New 1.2 was added to explain a limitation in scope. The other sections were renumbered as appropriate.
(*4*) An information reference was included in 1.5.
(*5*) An information reference was included in 1.6
(*6*) A new ASTM referenced document was included in 2.1.
(*7*) New Footnotes 2, 3, and 5 were added and identified. Other footnotes were renumbered where necessary for sequential identification.
(*8*) Information concerning balances was added in 6.2
(*9*) Section 6.3 was revised to clarify the use of close-fitting lids, and a reference to Note 8 was added.

(*10*) In 6.4, "anhydrous calcium phosphate" was changed to "anyhydrous calcium sulfate" to correct an error and to agree with Note 3.
(*11*) A typo in 8.1 was corrected from "before" to "below" and a footnoted reference was added for information.
(*12*) A portion of 8.2 was deleted for clarity.
(*13*) A new 8.2.1 was added to clarify minimum mass requirements.
(*14*) Sections 8.3, 8.4, 9.3.3, and 12.1 were changed to substitute "test data form/sheet" for "report".
(*15*) Footnote seven was identified.
(*16*) Section 9.2.1 was revised to improve clarity and intent.
(*17*) The word "possible" was changed to "practical" in 9.2.3.
(*18*) Section 9.3.1 and 9.3.2 were revised to improve clarity and for practicality.
(*19*) A reference to Guide D 6026 was added in 12.1.2.
(*20*) Footnotes 8 and 9 were added to 13.2.1 and 13.2.2, respectively. These were inadvertently omitted from the 1992 version. These explanations provide clarity and information to the user.
(*21*) A Summary of Changes was added to reflect D-18's policy.

CERTIFICATE

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Standard Practice for Collection of a Gross Sample of Coal[1]

This standard is issued under the fixed designation D 2234; 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.

INTRODUCTION

Data obtained from coal samples are used in establishing price, controlling mine and cleaning plant operations, allocating production costs, and determining plant or component efficiency. The task of obtaining a sample of reasonable weight to represent an entire lot presents a number of problems and emphasizes the necessity for using standard sampling procedures.

Coal is one of the most difficult of materials to sample, varying in composition from noncombustible particles to those which can be burned completely, with all gradations in between. The task is further complicated by the use of the analytical results, the sampling equipment available, the quantity to be represented by the sample, and the degree of precision required.

This practice gives the overall requirements for the collection of coal samples. The wide varieties of coal-handling facilities preclude the publication of detailed procedures for every sampling situation. The proper collection of the sample involves an understanding and consideration of the physical character of the coal, the number and weight of increments, and the overall precision required.

1. Scope

1.1 This practice covers procedures for the collection of a sample under various conditions of sampling. The sample is to be crushed and further prepared for analysis in accordance with Method D 2013. However, the procedures for dividing large samples before any crushing are given in this practice.

1.2 This practice describes general and special purpose sampling procedures for coals *(1)* by size and condition of preparation (for example, mechanically cleaned coal or raw coal) and *(2)* by sampling characteristics.

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 121 Terminology of Coal and Coke

D 2013 Method of Preparing Coal Samples for Analysis[2]

E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods[3]

E 456 Terminology Relating to Quality and Statistics[2]

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *accuracy:*

3.1.1.1 *generally*—a term used to indicate the reliability of a sample, a measurement, or an observation.

3.1.1.2 *specifically*—a measure of closeness of agreement between an experimental result and the true value. Example: the observed and true sulfur content of a coal consignment. This measure is affected by chance errors as well as by bias.

3.1.2 *cross-belt sampler*—a sampling machine designed to extract an increment directly from a conveyor belt surface by taking a sweep through the material on the conveyor.

3.1.3 *falling-stream sampler*—a sampling machine designed to extract an increment from a falling stream of coal at the discharge end of a conveyor or chute by moving through the falling stream of material.

3.1.4 *gross sample*—a sample representing one lot of coal and composed of a number of increments on which neither reduction nor division has been performed.

3.1.5 *increment*—a small portion of the lot collected by one operation of a sampling device and normally combined with other increments from the lot to make a gross sample.

3.1.6 *representative sample*—a sample collected in such a manner that every particle in the lot to be sampled is equally represented in the gross or divided sample.

3.1.7 *sample*—a quantity of material taken from a larger quantity for the purpose of estimating properties or composition of the larger quantity.

3.1.8 *size consist*—the particle size distribution of a coal.

3.1.9 *random variance of increment collection (unit variance), S_r^2*—the theoretical variance calculated for a uniformly mixed lot and extrapolated to 0.5-kg (1-lb) increment size. For a method of estimating this variance, see Annex A1.

3.1.10 *segregation variance of increment collection, S_s^2*—the variance caused by nonrandom distribution of ash content or other constituent in the lot. For a method of estimating this variance, see Annex A1.

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[1] These methods are under the jurisdiction of ASTM Committee D-5 on Coal and Coke and are the direct responsibility of Subcommittee D05.23 on Sampling.

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

[3] *Annual Book of ASTM Standards,* Vol 14.02.

3.1.11 *total variance,* S_o^2—the overall variance resulting from collecting single increments, and including division and analysis of the single increments. For a method of estimating this variance, see Annex A2.

4. Summary of Practice

4.1 The general-purpose sampling procedures are intended to provide, in 19 of 20 cases, dry ash results that are within an interval of ±1⁄10 of the average dry ash results that would be obtained in hypothetical repeated sampling.

4.2 Special-purpose sampling procedures apply to the sampling of coal when other precision limits are required, or when other constituents are used to specify precision, or for performance tests.

4.3 For coals of known size and condition of preparation, tables are given for the determination of the number and weight of increments required for a gross sample for both general and special-purpose sampling. For coals having known sampling characteristics, as determined by the use of appropriate test and statistical procedures given in this practice, the number and weight of the increments required for either general purpose or special-purpose precision can be determined.

4.4 The procedures appear in the following order:

5. Significance and Use

5.1 It is intended that this practice be used to provide a representative sample of the coal from which it is collected. Because of the variability of coal and the wide variety of sampling equipment, caution should be used in all stages of sampling from system specifications and equipment procurement to equipment acceptance testing and actually taking the final sample.

5.2 After further processing (Method D 2013), the sample may be analyzed for a number of different parameters. These parameters may affect the lot's value, its ability to meet specifications, its environmental impact, as well as other properties.

6. Increment Collection Classification

6.1 The type of selection, the conditions under which individual increments are collected, and the method of spacing of increments from the coal consignment or lot are classified according to the following descriptions and Table 2. These designations are to be used for sampling specifications and for descriptions of sampling programs and sampling equipment.

6.2 *Types of Increments*—The types of selection of increments are based on whether or not there is human discretion in the selection of the pieces of coal or portions of the coal stream.

6.2.1 *Type I,* in which specific pieces or portions are not subject to selection on a discretionary basis. This includes that in which the increment is collected in precise accord with previously assigned rules on timing or location that are free of any bias. Type I selection increments generally yield more accurate results.

6.2.2 *Type II,* in which some measure of human discretion is exercised in the selection of specific pieces of coal or of specific portions of the stream, pile, or shipment.

6.3 *Conditions of Increment Collection*—The conditions under which individual increments are collected are the conditions of the main body of coal relative to the portion withdrawn. Four conditions are recognized:

6.3.1 *Condition A (Stopped-Belt Cut),* in which a loaded conveyor belt is stopped and a full cross-section cut with parallel sides is removed from the coal stream. The distance between the parallel faces shall not be less than three times the normal top size of the coal.

6.3.2 *Condition B (Full-Stream Cut),* in which a full cross-section cut is removed from a moving stream of coal.

6.3.3 *Condition C (Part-Stream Cut),* in which a portion, not a full cross section, is removed from a moving stream of coal.

6.3.4 *Condition D (Stationary Coal Sampling),* in which a portion of coal is collected from a pile, a rail car, a barge, or a shiphold.

6.4 *Spacing of Increments*—The spacing of increments pertains to the kind of intervals between increments. Two spacing methods are recognized: systematic and random. Systematic spacing is usually preferable.

6.4.1 *Systematic Spacing 1,* in which the movements of individual increment collection are spaced evenly in time or in position over the lot.

6.4.2 *Random Spacing 2,* in which the increments are spaced at random in time or in position over the lot.

7. Organization and Planning of Sampling Operations

7.1 *Precaution*—It is imperative that every gross sample be collected carefully and conscientiously and in strict accordance with the procedures prescribed in this practice; for if the sampling is done improperly, the sample will be in error, and it may be impossible or impracticable to take another sample. However, if the analysis is in error, another analysis can easily be made of the original sample, except for moisture.

7.2 *Selection of Appropriate Sampling Procedure*—

TABLE 1 Increment Types, Conditions, and Spacing

Condition of Increment Collection from the Main Body of Coal	Types of Increment: Type I, No Human Discretion Is Used; Spacing of Increments: 1. Systematic	Type I: 2. Random	Type II, Human Discretion Is Used; Spacing of Increments: 1. Systematic	Type II: 2. Random
Condition A, stopped belt cut	I-A-1	I-A-2	II-A-1	II-A-2
Condition B, full-stream cut	I-B-1	I-B-2	II-B-1	II-B-2
Condition C, part-stream cut	I-C-1	I-C-2	II-C-1	II-C-2
Condition D, stationary sampling	I-D-1	I-D-2	II-D-1	II-D-2

Variations in coal-handling facilities make it impossible to publish rigid rules covering every sampling situation in complete and exact details. Proper sampling involves an understanding and proper consideration of the minimum number and weight of increments, the size consist of the coal, the condition of preparation of the coal, the variability of the constituent sought, and the degree of precision required.

7.2.1 *Number and Weight of Increments*—The number and weight of increments required for a given degree of precision depends upon the variability of the coal. This variability increases with an increase in free impurity. A coal high in inherent impurity and with comparatively little free impurity may exhibit much less variability than a coal with a low inherent impurity and a relatively high proportion of free impurity. For most practical purposes, an increase in the ash content of a given coal usually indicates an increase in variability. It is imperative that not less than the minimum specified number of increments of not less than the minimum specified weight be collected from the lot. For Condition D, the increments shall be of equal weight.

7.2.2 *Increment Collection Method to Be Used*—To obtain complete representation of all sizes, it is most desirable that the sample increments be withdrawn from the full cross section of the stream. The best possible increment is a full cross-section cut removed from a stopped belt, Classification I-A-1 in Table 1. The best possible increment from a flowing stream of coal is one obtained by moving a cutter device entirely across the stream at a uniform speed, the same for each increment, into one side of the stream and out of the other, without allowing the receptacle to overflow (Classification I-B-1 in Table 1). Classification methods given in Table 1 are listed in order of decreasing reliability. The highest possible classification method, wherever feasible, should be used. Details of sampling procedures should be agreed upon in advance by all parties concerned. Whenever circumstances dictate utilization of increment collection classifications "Condition C" or "Condition D" or "Type II," details of sampling procedure shall be agreed upon in advance by all parties concerned.

7.3 *Distribution of Increments*—It is essential that the increments be distributed throughout the lot to be sampled. This distribution is related to the entire volume of the lot, not merely its surface or any linear direction through it or over it. If circumstances prevent the sampler from applying this principle, the lot is sampled only in part, and the gross sample is representative only of this part. The spacing of the increments shall be varied if the possibility exists that increment collection may get "in phase" with the sequence of coal variability. Example: routine sampling of commercial coal from a continuous stream (conveyor belt) in which increment collection is automatic and its sequence coincides with the "highs" or "lows" in the content of fines.

7.4 *Dimensions of Sampling Device*—The opening of the sampling device shall be no less than 2.5 times the nominal top size of the coal and no less than 31.8 mm (1.25 in.). The sampling device shall be of sufficient capacity to completely retain or entirely pass the increment without spillage at the maximum rate of coal flow.

7.5 *Characteristics and Movement of Sampling Device*—In sampling from moving streams of coal, the sampling device shall be designed to collect each increment with no selective rejection of material by size and with no contamination by nonsample material.

7.5.1 *Falling-Stream Sampler*—In collecting an increment, the falling-stream cutter should move at a constant velocity through the falling stream of coal. Falling-stream cutter speeds of 18 in./s (457 mm/s) or less have been found to produce acceptable results.

7.5.2 *Cross-Belt Sampler*—The cross-belt cutter should be designed and operated at a velocity across the conveyor surface that is high enough to prevent selective rejection of material by size. The velocity and design of the cutter should also prevent contamination of the sample with material not collected within the cutter. The sampling machine should be designed to assure a complete increment extraction, and the arc of travel of the sweep-arm cutter should closely fit the configuration of the conveyor belt.

7.6 *Preservation of Moisture*—The increments obtained during the sampling period shall be protected from changes in composition as a result of exposure to rain, snow, wind, sun, contact with absorbent materials, and extremes of temperature. The circulation of air through equipment must be reduced to a minimum to prevent both loss of fines and moisture. Samples in which moisture content is important shall be protected from excessive air flow and then shall be stored in moisture-tight containers. Metal cans with airtight lids, or heavy vapor-impervious bags, properly sealed, are satisfactory for this purpose.

7.7 *Contamination*—The sampling arrangement shall be planned so that contamination of the increments with foreign material or unrelated coal does not create bias of practical consequence.

7.8 *Mechanical System Features*—It is essential that mechanized systems as a whole, including sampling machines, chutes, feed conveyors, crushers and other devices, be self-cleaning and non-clogging and be designed and operated in a manner that will facilitate routine inspection and maintenance.

7.9 *Personnel*—Because of the many variations in the conditions under which coal must be sampled, and in the nature of the material being sampled, it is essential that the samples be collected under the direct supervision of a person qualified by training and experience for this responsibility. Where human labor is employed to collect the increments, it is essential that samples be collected by a trained and experienced sampler or under the direct personal observation of such a person. This includes sampling for the purpose of determining sampling characteristics of a coal or characteristics of a particular sampling apparatus.

7.10 *Criteria of Satisfactory Performance*—A satisfactory sampling arrangement is one that takes an unbiased sample at the desired degree of precision of the constituent for which the sample is to be analyzed. One fundamental characteristic of such an arrangement is that the size consist of the sample will adequately represent the true size consist of the coal. Sampling systems shall be tested initially and at regular intervals to determine whether the sample adequately represents the coal. In addition, sampling systems should be given a rough performance check as a matter of routine. This is done by comparing the weight or volume of collected sample with that of the total flow of coal to ensure a constant sampling ratio.

7.11 *Relative Location of Sampling and Weighing*—It is preferable that coal be weighed and sampled at the same time. If there is a lapse in time between these two events, consideration should be given by both the purchaser and the seller to changes in moisture during this interval and the consequent shift in relationship of moisture to the true quality of the coal at the instant when ownership of the coal transfers from one to the other.

8. Procedures

8.1 *Sampling of Coals Based on Size and Condition of Preparation:*

8.1.1 *General-Purpose Sampling:*

8.1.1.1 The general-purpose sampling procedures are intended to provide, in 19 of 20 cases, dry ash results that are within the interval of ±1⁄10 of the average dry ash results that would be obtained in hypothetical repeated sampling. Under some conditions, as detailed in 7.2.1 and 7.2.2, Conditions C and D and Type II, this precision may not be obtained.

8.1.1.2 *Number and Weight of Increments*—Obtain the number and weight of increments as specified in Table 2 except as provided in 8.1.1.5(*b*). Determine the minimum number of increments from the condition of preparation, and determine the minimum weight of each increment from the top size of the coal. Classify the coals to be sampled according to the general purpose procedure into three groups by top size. Further classify each of these groups into two subgroups in accordance with the condition of preparation. These classifications are shown in Table 2.

8.1.1.3 Variations in construction of the sampling device and flow, structure, or size consist of the coal may make it impracticable to collect increments as small as the minimum weight specified in Table 2. In such cases, collect an increment of greater weight. However, do not reduce the minimum number of increments, regardless of large excesses of individual increment weights. Table 2 lists the absolute minimum number of increments for general-purpose sampling which may not be reduced except as specified in 8.1.1.5(*b*). Other considerations may make it advisable or necessary to increase this number of increments.

8.1.1.4 *Number of Gross Samples*—Under the general-purpose sampling procedure, for quantities up to approximately 1000 tons [908 metric tons] [908 Mg] it is recommended that one gross sample represent the lot. Take this gross sample in accordance with the requirements prescribed in Table 2.

8.1.1.5 For quantities over 1000 tons [908 Mg], use any of the following alternatives:

(*a*) Take separate gross samples for each 1000-ton [908-Mg] lot of coal or fraction thereof.

(*b*) Use one gross sample to represent the total tonnage provided the number of increments, as stated in Table 2, are increased as follows:

$$N_2 = N_1 \sqrt{\frac{\text{total lot size (tons or Mg)}}{\text{1000 tons or 908 mg}}} \qquad (1)$$

where:

N_1 = number of increments specified in Table 2 and
N_2 = number of increments required.

For example, a 4000-ton [3632-Mg] lot will require twice the number of increments specified in Table 2. Using this technique, it is theoretically possible to collect one gross sample to represent a lot of infinite tonnage. Practical experience, however, indicates the maximum size of a lot of coal to

TABLE 2 Number and Weight of Increments for General-Purpose Sampling Procedure[A]

Top Size	5⁄8 in. [16 mm]	2 in. [50 mm]	6 in. [150 mm][B]
Mechanically Cleaned Coal[C]			
Minimum number of increments	15	15	15
Minimum weight of increments, lb	2	6	15
Minimum weight of increments, kg	1	3	7
Raw (Uncleaned Coal)[C]			
Minimum number of increments	35	35	35
Minimum weight of increments, lb	2	6	15
Minimum weight of increments, kg	1	3	7

[A] Under Conditions C and D, see 7.2.1 and 7.2.2.

[B] For coals above 6-in. [150-mm] top size, the sampling procedure should be mutually agreed upon in advance by all parties concerned.

[C] If there is any doubt as to the condition of preparation of the coal (for example, mechanically cleaned coal or raw coal) the number of increments for raw coal shall apply. Similarly, although a coal has been mechanically cleaned, it may still show great variation because of being a blend of two different portions of one seam or a blend of two different seams. In such cases, the number of increments should be as specified for raw (uncleaned) coal.

be represented by one gross sample should not exceed 10 000 tons [9080 Mg].

(*c*) Take separate gross samples for each 1000-ton [908-Mg] lot of coal or fraction thereof, and thoroughly mix their No. 60 sieve size analysis samples together in proportion to the tonnage represented by each sample. Make one analysis of the composite sample.

8.1.2 *Special-Purpose Sampling:*

8.1.2.1 This special-purpose sampling procedure shall apply to the sampling of coal when increased precision is required, and the only knowledge of the coal is its top size and conditions of preparation.

8.1.2.2 *Number and Weight of Increments*—Take the same number and weight of increments per gross sample as specified in Table 2, or as specified in 8.1.1.5(*b*).

8.1.2.3 *Number of Gross Samples*—To obtain increased precision for the final result for a given consignment, increase the number of gross samples collected from that consignment and analyze each gross sample separately, reporting the average of results. To reduce errors to one half, that is, to "double" the precision, take four times as many gross samples. Similarly, to reduce errors to one third, to "triple" the precision, take nine times as many gross samples.

8.2 *Sampling of Coals Based on Known Sampling Characteristics:*

8.2.1 *Principles of Sampling by Sampling Characteristics:*

8.2.1.1 The relationship between sampling characteristics (expressed as variances) and the number of increments which will give a desired precision (expressed as the specified variance of one gross sample) is shown as follows:

$$N_I = (s_s^2 + s_r^2/W)/(s_G^2 - s_{da}^2/P) \qquad (2)$$

where:

N_I = number of increments in one gross sample,
W = weight in pounds, of each increment; this is selected for convenience or by the limitations imposed by the particular mechanical sampling apparatus,
s_r^2 = random variance of a 0.5-kg (1-lb) increment; this value is obtained from the special sampling program given in Annex A1 (Note A1.1),
s_s^2 = segregation variance; this value is also obtained from the special sampling program given in Annex A1 (Note A1.1),
s_{da}^2 = variance of division and analysis. Procedures for calculating this quantity are given in Annex A2 of Method D 2013.
P = number of analysis samples (prepared independently from the same gross sample), and
s_G^2 = specified variance of one gross sample. The procedure for determining this variance is given in 8.2.1.2 and 8.2.1.3.

NOTE 2—The random variance and the segregation variance, s_r^2 and s_s^2, are each inflated by unknown amounts of variance due to division and analysis. Since this results in an increased numerator in Eq. 2, and consequently, a larger calculated number of increments, N_I, it can be

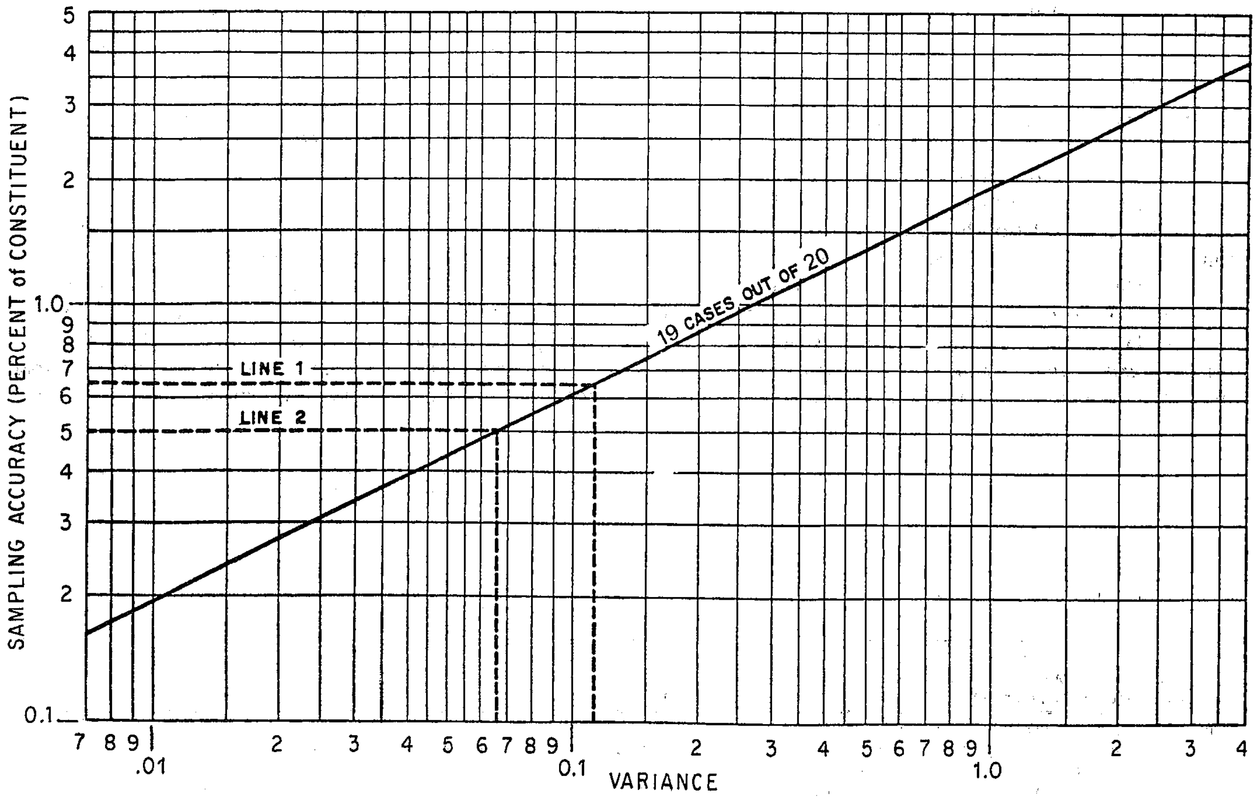

FIG. 1 Conversion of Sampling Accuracy to Variance

considered a "safety factor" for the sampling program. However, if too many large increments are taken for the evaluation of s_r^2 and s_s^2, the "safety factor" may become unreasonably large.

8.2.1.2 The relationship between the specified variance of one gross sample, s_G^2, and the precision for the result of several gross samples in one test period, expressed as the test period variance, s_T^2, is given as follows:

$$s_T^2 = s_G^2/N_G \qquad (3)$$

where:

s_T^2 = test period variance,
s_G^2 = specified variance of one gross sample, and
N_G = number of gross samples in the test period.

8.2.1.3 Figure 1 shows the relationship between variance and sampling precision (±10 % of a given constituent, 19 cases out of 20). The variance (Fig. 1) can be either the test period variance, s_T^2, or the specified variance of one gross sample, s_G^2. This choice will depend upon the sampling situation to be evaluated. The sampling precision (Fig. 1) can be based on any coal constituent, provided it is expressed as a percentage of that constituent. The following example is an illustration of the calculations necessary to determine the number of increments for one gross sample:

(*a*) *Accuracy Limits*—Assume a coal of 6.5 % average ash content. If the desired accuracy is ±1⁄10 of the ash content, the sampling accuracy can be expressed as ±0.65 % ash.

(*b*) *Test Period Variance*—The accuracy limits given in 8.2.1.3(*a*) correspond to a test period variance, s_T^2, of 0.112, from Fig. 1 (Line 1).

(*c*) *Specified Variance of One Gross Sample*—The specified variance of one gross sample is equal to the test period of variance, s_T^2, multiplied by the number of gross samples in the test period, N_G (Eq 3). Assuming seven gross samples in the period, the specified variance for one gross sample is then equal to 0.112 × 7 or 0.784.

(*d*) *Number of Increments*—Assume the following information was obtained from the special sampling procedures outlined in Annex A1 of this practice and Annex A2 of Method D 2013: $s_r^2 = 12.5$, $s_s^2 = 10.2$, and $s_{da}^2 = 0.06$ (one analysis sample per gross sample). The specified variance of one gross sample, s_G^2, as found previously, is 0.784. Further, the weight per increment for this sampling device, is found to be 23 kg (50 lb). Then, substituting into Eq 2:

$$N_I = (10.2 + 12.5/50)/(0.784 - 0.06/1)$$
$$= 14.4 \text{ or } 15 \text{ increments}$$

For this coal, 15 increments of 23 kg each would be required for each gross sample, and seven gross samples would constitute the sampling period. The weighted average for the test period will be within ±0.65 % ash, 19 cases out of 20.

8.2.1.4 The following variance relationship can be derived from Eq 2. It combines the random variance, s_r^2, and the segregation variance, s_s^2. This is applicable when the incremental weight is fixed by the characteristics of the sampling equipment:

$$s_T^2 = [(s_o^2 - s_{da}^2)/N_G N_I] + s_{da}^2/PN_G \qquad (4)$$

where:

s_o^2 = overall variance of single increments (including division and analysis), as determined by Annex A2.

Other terms are as defined in 8.2.1.1 and 8.2.1.2. The following example demonstrates the use of the overall variance for increments, s_o^2, in determining the number of increments for one gross sample:

(*a*) *Test Period Variance*—Assume a required accuracy of ±0.5 % ash. This corresponds to a test period variance, s_T^2, of 0.066 from Fig. 1 (Line 2).

(*b*) *Number of Increments*—Assume the following information was obtained from the special sampling procedures outlined in Annex A2 of Method D 2013, and Annex A2 of this practice: $s_o^2 = 3.5$ and $s_{da}^2 = 0.08$. If it is desired to take ten gross samples during the test period (N_G), with only one analysis (p) for each gross sample, the number of increments for each gross sample (N_I) can be determined by substitution into Eq 4:

$$0.066 = [(3.5 - 0.08)/10N_I] + [0.08/(10 \times 1)]$$

where:

N_I = 5.9 or 6 increments.

For this coal, six increments would be required for each of the ten gross samples. The weighted average for the test period will be within ±0.5 % ash, 19 cases out of 20.

8.2.1.5 For sampling mixed coals, the values of random variance, segregation variance, overall variance for increments, and the variance of division and analysis for use in Eqs 2 and 4 are those obtained from special sampling programs using the mixture which is the most difficult to sample.

8.2.2 *General-Purpose Sampling:*

8.2.2.1 This general-purpose sampling procedure is intended for the commercial sampling of coal where the level of precision as stated in 8.1.1.1 is satisfactory to all parties involved.

8.2.2.2 *Number of Gross Samples*—Select the number of gross samples for coals of known sampling characteristics to suit the parties concerned with results from the sampling, since the number of gross samples is directly related to the establishment of the required number of increments as outlined in 8.2.1.3 and 8.2.1.4. The following factors should be remembered in selecting the number of gross samples for the test period:

(*a*) Too few gross samples will result in additional preparation work because of the large number of increments per gross sample which will be required.

(*b*) The preparation of the samples for analysis purposes will be simplified by using samples of minimum weight.

8.2.3 *Special-Purpose Sampling:*

8.2.3.1 Apply this special-purpose sampling procedure to the sampling of coal when other precision limits are required or when other constituents are used to specify precision.

8.2.3.2 *Number and Weight of Increments and Number of Gross Samples*—For a precision of ±1⁄20 of the average of all the dry ash determinations in 19 out of 20 cases when gross samples are repeatedly taken from the same lot, use Fig. 1 to determine the test period variance, s_T^2. In this case, use the new sampling precision limitation of ±1⁄20 of the average dry ash in Fig. 1. Then determine the number of increments and number of gross samples as outlined in 8.2.1.3, 8.2.1.4, and 8.2.2.2.

8.2.3.3 For a precision of $\pm 1/30$ of the average ash, use Fig. 1 again to determine the test period variance, s_T^2. In this case, use the new sampling variance, s_T^2, precision limitations in Fig. 1.

8.2.3.4 Other precision limits may be used, or other constituents may be used to specify precision when agreed upon by the parties concerned. The principles outlined in this section will apply to all special precision limits.

8.2.3.5 Greater accuracy cannot be obtained by merely increasing the weight and number of increments if significant bias exists.

8.3 *Division of the Gross Sample Before Crushing:*

8.3.1 In the case of very large and unwieldy gross samples, it is permissible to divide the gross sample to reduce its weight, provided the following conditions are fulfilled:

8.3.1.1 If the entire gross sample is mixed in a suitable blender (double-cone or twin-shell tumbler) it is permissible to divide the sample using the schedule of Table 2. Test the divided sample for bias.

8.3.1.2 If each very large increment is reduced in quantity by secondary sampling, take at least six secondary increments from each primary increment. The method of collection of secondary increments must be proved to be free from bias. In no case shall the weight of a secondary increment be less than shown in the schedule of Table 2.

8.4 *Sampling of Coal for Total Moisture Determinations:*

8.4.1 *Types of Moisture Samples*—Moisture determinations as specified in the method to be used are to be made on the following kinds of samples.

8.4.1.1 *Entire Gross Sample*—For referee tests, air dry the entire gross sample and measure the weight loss from the entire gross sample during this drying. This procedure can be carried out on the entire gross sample as a single batch or on groups of primary increments or as separate operations on the individual primary increments; obtain, by one of these means, the total weight loss from the entire gross sample. After this air drying, the sample can be crushed or divided, or both, as required by the referee test for moisture.

8.4.1.2 *Special Moisture Subsample*—For moisture testing, a special subsample can be taken from a gross sample before any operations of air drying or crushing. Take this subsample from the gross sample in accordance with the requirements of 8.3.

8.4.1.3 *Other Subsamples for Moisture Testing*—For moisture testing, a subsample can be used that is collected after the initial crushing and dividing of a gross sample. The procedures for the crushing and dividing, and for this subsequent subsampling for moisture, are given in Method D 2013.

8.4.2 *Special Precautions*—Collect samples and subsamples for moisture in such a manner that there is no unmeasured loss of moisture of significant amount. Make adequate weighings before and after drying or other operations to measure all significant weight losses.

8.4.3 *Weight of Increments*—The minimum weight of each increment must be that which is sufficient as to be free of bias. This depends on the top size of the coal in the stream being sampled, the dimensions of the collection device, and other factors of the withdrawal of the increment. Since much of the moisture tends to be distributed uniformly across the surface, moisture bias is present when the size consist of the sample is not the same as the size consist of the lot sampled. In addition, when there is no knowledge of the sampling characteristics for moisture, each increment shall not weigh less than the values in Table 2.

8.4.4 *Number of Increments*—The number of increments required for a given degree of precision depends on the weight of the increments, the distribution of the moisture, and the total amount of moisture. The distribution of moisture, however, is not easily evaluated independent of total moisture; consequently, the combined effects can be measured by determining the sampling characteristics for moisture.

8.4.4.1 *Moisture Sampling Based on Known Sampling Characteristics*—When the sampling characteristics for moisture are known, calculate the number of increments required for a desired degree of precision. The procedures are those given in Section 7.

8.4.4.2 *Moisture Sampling Based Only on Size*—When there is no knowledge of the sampling characteristics for moisture, collect at least the number of increments from the lot of coal as those given in Table 2. When a special moisture subsample is taken from the gross sample before any drying or crushing operations, collect the number of increments for the subsample as specified in 8.3.

9. Precision and Bias

9.1 The precision of the general-purpose sampling procedure, based on size and condition of preparation, is stated in 8.1.1.1. If a different precision is required, reference 8.1.2. The precision of sampling coals of known sampling characteristics, either general purpose or special purpose, may be estimated by following the appropriate procedure of Section 8.

ANNEXES

(Mandatory Information)

A1. TEST METHOD FOR DETERMINING THE VARIANCE COMPONENTS OF A COAL

A1.1 Scope

A1.1.1 This test method covers a procedure for determining the following variance components of a coal:

A1.1.1.1 The random variance of a 0.5-kg (1-lb) increment, s_r^2, and

A1.1.1.2 The segregation variance, s_s^2, the variance caused by nonrandom distribution of the ash content in the lot or consignment.

A1.1.2 In this test method, each different coal will require a complete experiment, which involves the collection of two sets

TABLE A1.1 Schedule I: Sample Weights

Set Number	"A" Series, g	"B" Series, lb
1	89	117.4
2	126	117.5
3	152	123.4
4	109	90.7
5	149	101.7
6	87	89.6
7	110	107.7
8	142	110.8
9	123	123.0
10	111	106.2
11	140	116.4
12	121	96.7
13	112	109.0
14	122	106.9
15	158	99.8
16	160	87.6
17	55	88.6
18	76	92.3
19	105	93.0
20	132	99.8
21	108	106.6
22	86	124.2
23	142	127.8
24	123	111.3
25	133	111.6
26	261	107.2
27	129	106.0
28	150	102.8
29	108	97.7
30	99	107.4
Sum	3732	3180.7
Average	124.4 g, or 0.27 lb = w_1	106.0 lb or 48.1 kg = w_2

TABLE A1.2 Schedule II: Ash Results "A" Series

Set	Ash, %	Ash, %-squared
1	14.2	201.64
2	13.4	179.56
3	13.7	187.69
4	15.8	249.64
5	13.7	187.69
6	14.1	198.81
7	13.6	184.96
8	18.7	349.69
9	16.3	265.69
10	12.4	153.76
11	5.8	33.64
12	12.2	148.84
13	10.9	118.81
14	8.9	79.21
15	34.5	1190.25
16	8.7	75.69
17	7.5	56.25
18	15.7	246.49
19	21.8	475.24
20	11.8	139.24
21	12.2	148.84
22	11.8	139.24
23	7.1	50.41
24	12.8	163.84
25	14.0	196.00
26	6.3	39.69
27	12.3	151.29
28	7.2	51.84
29	13.1	171.61
30	11.3	127.69
Sum	391.8	5963.24

$s_A^2 = [5963.24 - (391.8)^2/30]/29 = 29.2$

of 30 samples from a stopped conveyor belt. The first set of samples includes 30 very small samples to furnish data for the random variance; the second set includes 30 large samples to furnish data for the segregation variance. Since one of the important components of variance is that due to segregation, it is essential that the 30 large samples be so distributed with respect to time that coverage of all subtypes of coal are represented.

A1.2 Apparatus

A1.2.1 The following equipment, in addition to that equipment normally provided for routine sampling, will be required:

A1.2.1.1 *Two-Section Belt Divider*—One of the sections should be approximately the width corresponding to three times the top size of the coal, and should trap a sample of between 2 and 9 kg (4 and 20 lb). The other section should be approximately the width corresponding to 20 times the top size of the coal and should trap a sample of between 36 and 68 kg (80 and 150 lb). The bottom edges of the divider should be shaped to conform to the surface of the conveyor belt.

A1.2.1.2 *Riffle Splitter,* with slots at least 2½ to 3 times as

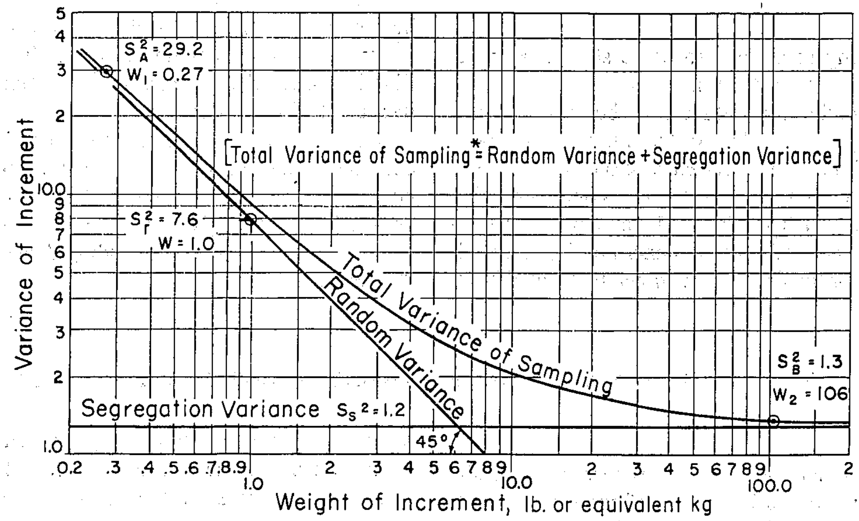

Fig. A1.1 Relation of Variance to Weight

TABLE A1.3 Schedule III: Ash Results "B" Series

Set	Ash, %	Ash, %-squared
1	13.6	184.96
2	13.2	174.24
3	14.3	204.49
4	15.3	234.09
5	15.0	225.00
6	14.3	204.49
7	13.6	184.96
8	14.7	216.09
9	14.2	201.64
10	12.5	156.25
11	13.0	169.00
12	14.3	204.49
13	13.7	187.69
14	12.8	163.84
15	13.2	174.24
16	14.0	196.00
17	10.5	110.25
18	13.5	182.25
19	15.4	237.16
20	15.0	225.00
21	14.4	207.36
22	12.8	163.84
23	13.0	169.00
24	13.0	169.00
25	12.3	151.29
26	13.1	171.61
27	14.2	201.64
28	11.6	134.56
29	13.1	171.61
30	11.4	129.96
Sum	405.0	5506.00

$$s_B^2 = \frac{[5506.00 - (405)^2/30]}{29} = 1.3$$

then:

$$S_r^2 = \frac{[0.27 \times 106\,(29.2 - 1.3)]}{106 - 0.27} = 7.6$$

and

$$s_s^2 = 1.3 - (7.6/106) = 1.2$$

wide as the maximum size of the particles, or a manual divider and canvas for subdividing the small samples by hand.

A1.3 Procedure

A1.3.1 The following sampling procedure should be used for each of the two required sets of samples:

A1.3.1.1 Stop the loaded belt and insert the belt divider with the division plates perpendicular to the direction of belt movement. Scrape off the coal from each section, and put each section into a separate completely labeled container. The container holding the coal from the small section of the belt divider should be labeled "A." The container holding the coal from the large section of the belt divider should be labeled "B."

A1.3.1.2 Collect a subsample from the "A" section by riffling or by manual subdivision after spreading the sample evenly on a smooth flat surface. Tag the subsample with a label "A," and weigh to the nearest gram. The weight of the subsample should be between 100 to 200 g.

A1.3.1.3 Dry the "A" subsample, grind to minus No. 60 sieve size, and determine the ash content to the nearest 0.1 %, dry basis.

A1.3.1.4 Weigh the entire "B" section, dry, and work down to an analysis sample. Determine the ash content to the nearest 0.1 %, dry basis.

A1.4 Calculation

A1.4.1 Calculate the variance of the "A" and "B" series (Note A1.1) as follows:

$$\text{Variance} = (\Sigma x^2 - (\Sigma x)^2/n)/(n - 1) \qquad (5)$$

where:

Σx^2 = sum of the squares of ash results,
$(\Sigma x)^2$ = square of the sum of ash results, and
n = number of individual ash results in the series.

A1.4.2 The random variance, s_r^2, is found from:

$$s_r^2 = [W_1 W_2 (s_A^2 - s_B^2)]/(W_2 - W_1) \qquad (6)$$

where:

W_1 = average weight of small samples, lb or equivalent kg,
W_2 = average weight of large samples, lb or equivalent kg,
s_A^2 = variance of small, "A" samples, and
s_B^2 = variance of large "B" samples.

A1.4.3 The segregation variance, s_s^2, is found from:

$$s_s^2 = s_B^2 - s_r^2/W_2 \qquad (7)$$

NOTE A1.1—An actual example illustrating the treatment of data from this sampling experiment is given in Tables A1.1 to A1.3 and in Fig. A1.1.

A1.4.3.1 Using log-log paper, plot the point corresponding to an increment weight w = 0.5 kg (1 lb) and variance s_r^2 = 7.6; draw a straight line through this point, downward at 45°. This line gives the random component of variance for an increment of any weight. Plot the point corresponding to an increment weight w_2 = 48 kg (106 lb) and variance s_s^2 = 1.2; draw a straight horizontal line through this point. This line gives the segregation component of variance for an increment of any weight.

A1.4.3.2 On Fig. A1.1, find the algebraic sum of the random component and the segregation component of variance for a number of increment weights; draw a curve through these points. This curve gives the total variance of sampling for increments of any weight, including those used in the "A" and "B" series.

A2. TEST METHOD FOR ESTIMATING THE OVERALL VARIANCE FOR INCREMENTS

A2.1 Scope

A2.1.1 This test method describes the procedure for estimating the overall variance for increments of one fixed weight of a given coal. It is applicable to mechanical sampling when there is no need to explore system and random variance components, but there is a need for obtaining the overall variance for increments (the size of increments is dictated by the sampling equipment).

TABLE A2.1 Variance Ratio Limit Values

1 Increment per Set	2 Variance Ratio Limit	3 "C" Factor
10	3.18	1.92
20	2.17	1.53
30	1.86	1.40
40	1.70	1.33
50	1.61	1.29

A2.2 Procedure

A2.2.1.1 The following procedure should be used to determine the overall variance of increments:

A2.2.1.1 Collect two series of individual increments at widely spaced intervals, for example, a series of ten increments, two each day for five days, followed by a second series of ten collected in similar fashion. Both series must be from the same coal.

A2.2.1.2 Collect each increment by using as much of the equipment and procedure used in routine sampling operations as possible. Remove the individual increment from the sampling system without mixing with or contaminating by any other increment. Where possible, allow it to pass through any mechanical crusher or subsampler, or both, which is located in the system before the point of blending with other increments.

A2.2.1.3 Then weigh the individual increment (if desired for record purposes) and reduce to a laboratory sample by procedures identical as possible to those used in the routine preparation and reduction of gross samples.

A2.2.1.4 Analyze the sample for the constituents for which the variance calculations are to be made. Usually sampling specifications are based on dry ash, but where total moisture or as-received Btu is of particular concern, the analyses should be made for these.

A2.3 Calculation

A2.3.1 For each series, compute a variance value from the analyses of the ten increments as follows:

$$s^2 = (\Sigma x^2 - (\Sigma x)^2/n)/(n - 1) \qquad (8)$$

where:

s^2 = variance value for series,
Σx^2 = sum of squares of ash results,
$(\Sigma x)^2$ = square of the sum of ash results, and
n = number of individual ash results in the series.

A2.3.2 For the two series, the ratio of the larger variance to the smaller should not exceed the value given in Table A2.1, Column 2. If they differ by less than this amount, the variances are combined to give the estimated overall increment variance for the coal as follows:

$$s_o^2 = C[(s_1^2 + s_2^2)/2] \qquad (9)$$

where:

s_o^2 = probable maximum value of the overall variance for increments,
C = factor from Table X2.2, Column 3, corresponding to the number of increments per set,
s_1^2 = s^2 from first series, and
s_2^2 = s^2 from second series.

A2.3.3 If the ratio of the larger variance to the smaller does give a greater value than the Table A2.1, Column 2 value, the two series are to be considered in a single set of increments, and another set equal to this enlarged set is to be taken. For

TABLE A2.2 Determination of the Overall Variance for Increments

Series 1			Series 2		
Increment Number, n	Dry Ash[B] (x)	(Dry Ash)^2 [B] (x)^2	Increment Number, n	Dry Ash[B] (x)	(Dry Ash)^2 [B] (x)^2
1	4.17	17.3889	11	3.07	9.4249
2	3.62	13.1044	12	4.88	23.8144
3	1.79	3.2041	13	5.14	26.4196
4	4.37	19.0969	14	3.63	13.1769
5	4.64	21.5296	15	3.17	10.0489
6	7.03	49.4209	16	7.20	51.8400
7	6.27	39.3129	17	3.52	12.3904
8	3.91	15.2881	18	0.87	0.7569
9	6.04	36.4816	19	0.72	0.5184
10	4.18	17.4724	20	4.78	22.8484
Sum	46.02	232.2998	Sum	36.98	171.2388

[A] This example involves increment weights in the approximate range from 45 to 90 kg (100 to 200 lb).

[B] 10 % ash was subtracted from each of the ash results to simplify the calculations.

$$s^2 = (\Sigma(x)^2 - (\Sigma x)^2/n)/(n - 1)$$

Series 1:

$s_1^2 = (232.2998 - (46.02)^2/10)/9$
$= 2.2795$

Series 2:

$s_2^2 = (171.2388 - (36.98)^2/10)/9$
$= 3.8319$

Variance ratio limit from Table A2.1 = 3.18
Variance ratio for two test series:

$$s_2^2/s_1^2 = 3.8319/2.2795 = 1.68 < 3.18$$

Since the computed value for the ratio is less than 3.18, variances are combined to give an estimate of the overall variance for increments, s_o^2:

$$s_o^2 = [1.92(2.2795 + 3.8319)]/2 = 5.867$$

example, if originally two sets of 10 increments were taken, these would be combined to give a set of 20. Then an additional set of 20 increments would be collected, giving two sets of 20 increments each. Variance values are computed for the two new series and the test is repeated using the appropriate factors given in Table A2.2. If these results have a ratio which is less than the appropriate value in Column 2 of Table A2.2, they are combined by using Eq 9 and used as the new variance for increments.

A2.3.4 *Example*—The example given in Table A2.2 illustrates the computation of the overall variance for increments, s_o^2. Two series of 10 increments each are used.

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Document Name: ASTM D2460: Standard Test Method for Alpha-Particle-Emitting Isotopes of Radium in Water

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

Standards Body: American Society for Testing and Materials

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Standard Test Method for Alpha-Particle-Emitting Isotopes of Radium in Water[1]

This standard is issued under the fixed designation D 2460; 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 separation of dissolved radium from water for the purpose of measuring its radioactivity. Although all radium isotopes are separated, the test method is limited to alpha-particle-emitting isotopes by choice of radiation detector. The most important of these radioisotopes are radium-223, radium-224, and radium-226. The lower limit of concentration to which this test method is applicable is 3.7×10^{-2} Bq/L (1 pCi/L).

1.2 This test method may be used for absolute measurements by calibrating with a suitable alpha-emitting radioisotope such as radium-226, or for relative methods by comparing measurements with each other. Mixtures of radium isotopes may be reported as equivalent radium-226. Information is also provided from which the relative contributions of radium isotopes may be calculated.

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 precautionary statement, see Section 9.

2. Referenced Documents

2.1 *ASTM Standards:*

C 859 Terminology Relating to Nuclear Materials[2]
D 1129 Terminology Relating to Water[3]
D 1193 Specification for Reagent Water[3]
D 1943 Test Method for Alpha Particle Radioactivity of Water[4]
D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water[3]
D 3370 Practices for Sampling Water[3]
D 3454 Test Method for Radium-226 in Water[4]
D 3648 Practices for the Measurement of Radioactivity[4]

3. Terminology

3.1 *Definition:*

3.1.1 For definitions of terms used in this standard, see Terminology C 859 and D 1129. For terms not included in these, reference may be made to other published glossaries (**1, 2**).[5]

4. Summary of Test Method

4.1 Radium is collected from the water by coprecipitation with mixed barium and lead sulfates. The barium and lead carriers are added to a solution containing alkaline citrate ion which prevents precipitation until interchange has taken place. Sulfuric acid is then used to precipitate the sulfates, which are purified by nitric acid washes. The precipitate is dissolved in ammoniacal EDTA. The barium and radium sulfates are reprecipitated by the addition of acetic acid, thereby separating them from lead and other radionuclides. The precipitate is dried on a planchet weighed to determine the chemical yield, and alpha-counted to determine the total disintegration rate of alpha-particle-emitting radium isotopes. This procedure is based upon published ones (**3, 4**).

5. Significance and Use

5.1 Radium is one of the most radiotoxic elements. Its isotope of mass 226 is the most hazardous because of its long half-life. The isotopes 223 and 224, although not as hazardous, are of some concern in appraising the quality of water.

5.2 The alpha-particle-emitting isotopes of radium other than that of mass 226 may be determined by difference if radium-226 is measured separately, such as by Test Method D 3454. Note that one finds radium-226 and -223 together in variable proportions (**5, 6**), but radium-224 does not normally occur with them. Thus, radium-223 often may be determined by simply subtracting the radium-226 content from the total: and if radium-226 and -223 are low, radium-224 may be determined directly. The determination of a single isotope in a mixture is less precise than if it occurred alone.

6. Interferences

6.1 A barium content in the sample exceeding 0.2 mg will cause a falsely high chemical yield.

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[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.

Current edition approved Aug 10, 1997. Published October 1997. Originally issued 1966. Replaces D 2460–66 T. Last previous edition D 2460–90.

[2] *Annual Book of ASTM Standards*, Vol 12.01.

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

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

[5] The boldface numbers in parentheses refer to a list of references at the end of this standard.

7. Apparatus

7.1 For suitable gas-flow proportional or alpha-scintillation counting equipment, refer to Test Method D 1943.

8. Reagents

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 of the Committee on Analytical 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 precision, or increasing the bias, 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 III.

8.3 *Radioactivity Purity Of Reagents*—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 *Acetic Acid, Glacial* (sp gr 1.05).

8.5 *Ammonium Hydroxide* (sp gr 0.90)—Concentrated ammonium hydroxide (NH_4OH).

8.6 *Ammonium Hydroxide* (1+1) Mix 1 volume of concentrated ammonium hydroxide (NH_4OH, sp gr 0.90) with 1 volume of water.

8.7 *Barium Nitrate Carrier Solution* (10 mg Ba/mL)—Dissolve 1.90 g of barium nitrate ($Ba(NO_3)_2$) in water and dilute to 100 mL.

8.8 *Citric Acid Solution* (350 g/L)—Dissolve 350 g of citric acid (anhydrous) in water and dilute to 1 L.

8.9 *Disodium Ethylendiamine Tetraacetate Solution* (93 g/L)—Dissolve 93 g of disodium ethylenediamine tetraacetate dihydrate in water and dilute to 1 L.

8.10 *Lead Nitrate Carrier Solution* (104 mg Pb/mL)—Dissolve 33.2 g of lead nitrate ($Pb(NO_3)_2$) in water and dilute to 200 mL.

8.11 *Methyl Orange Indicator Solution*—Dissolve 1.0 g of methyl orange in water and dilute to 1 L.

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

8.13 *Sulfuric Acid* (1 + 1)—Cautiously add with stirring 1 volume of concentrated sulfuric acid (H_2SO_4, sp gr 1.84) to 1 volume of water.

9. Safety Precautions

9.1 When diluting concentrated acids, always use safety glasses and protective clothing, and add the acid to the water.

10. Sampling

10.1 Collect the sample in accordance with Practices D 3370 as applicable.

TABLE 1 Growth of Alpha Activity into Initially Pure Radium-226

Time, h	Correction, *F*
0	1.0000
1	1.0160
2	1.0363
3	1.0580
4	1.0798
5	1.1021
6	1.1238
24	1.4892
48	1.9054
72	2.2525

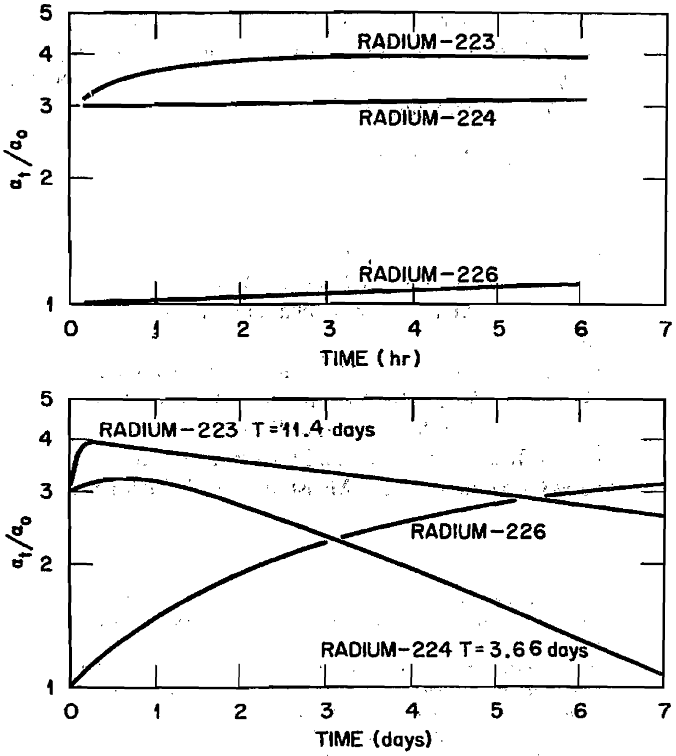
10.2 Sample 1 L, or a smaller volume, provided that it is estimated to contain from 3.7 to 370 Bq (100 to 10 00 pCi) of radium. Add 10 mL of HNO_3/L of sample.

11. Calibration and Standardization

11.1 For absolute counting, the alpha-particle detector must be calibrated to obtain the ratio of count rate to disintegration rate. Use NIST traceable radium-226 standards. Analyze two or more portions of such solution, containing known disintegration rates, in accordance with Section 12. After counting, correct the measured activity for chemical yield, and calculate the efficiency, *E* (see Section 13), as the ratio of the observed counting rate to the known disintegration rate.

12. Procedure

12.1 Add to a measured volume of sample 5 mL of citric acid and make alkaline (pH > 7.0) with NH_4OH. Confirm the



NOTE 1—Vertical scale is ratio of radioactivity, *a*, at later time, t, to radioactivity at initial time of separation. T is half-life.

FIG. 1 Growth and Decay of Alpha Activity into Initially Pure Radium Isotopes

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[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*, BDN Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacuetical Convention, Inc. (USPC), Rockville, MD.

TABLE 2 Important Alpha-Particle-Emitting Isotopes of Radium and their Descendents[A]

Nuclide		Radiation		Half-Life
Parent	Descendents	Type[B]	Energy, MeV[C]	
^{226}Ra		α	4.784 (94.5 %) 4.601 (5.5 %)	1.60 × 10^3 years
	^{222}Rn	α	5.490 (99.9 %)	3.83 days
	^{218}Po	α	6.003 (100.0 %)	3.11 min
	^{214}Pb	β (γ)		27 min
	^{214}Bi	β (γ)		19.9 min
	^{214}Po		7.687 (99.9 %)	1.64 × 10^{-4} s
^{224}Ra		α	5.686 (95.1 %) 5.449 (4.9 %)	3.66 days
	^{220}Rn	α	6.288 (99.9 %)	55.6 s
	^{216}Po	α	6.779 (100.0 %)	0.15 s
	^{212}Po	β (γ)		10.6 h
	^{212}Bi	β (64.1 %) (γ) α (35.9 %)	 6.090 (9.6 %) 6.051 (25.2 %) others	1.01 h
	^{212}Po	α	8.784	0.30 µs
	^{208}Ti	β (γ)		3.05 min
^{223}Ra		α (γ)	5.716 (52.5 %) 5.607 (24.2 %) 5.747 (9.5 %) 5.540 (9.2 %) others	11.4 days
	^{219}Rn	α (γ)	6.819 (81 %) 6.553 (12 %) 6.425 (7.5 %)	3.96 s
	^{215}Po	α	7.386 (100.0 %)	1.8 ms
	^{211}Pb	β (γ)		36.1 min
	^{211}Bi	α (γ)	6.623 (83.8 %) 6.279 (16.0 %)	2.14 min
	^{207}Ti	β		4.77 min

[A] Descendents with half-lives of less than 30 days.

[B] Gamma ray indicated only when emission probability per decay is more than 5 % and energy is greater than 0.1 MeV.

[C] Energy indicated for alpha radiation only. Emission probability per decay in parentheses.

alkalinity with pH-indicating paper or strip. Add 2 mL of lead carrier and 1.00 mL of barium carrier, and mix.

12.2 Heat to boiling and add 10 drops of methyl orange pH-indicator solution. With stirring, add H_2SO_4 (1 + 1) until the solution becomes pink, then add 5 drops more.

12.3 Digest the precipitate with continued heating for 10 min. Let cool and collect the precipitate in a centrifuge tube. When large volumes are handled, collection will be facilitated by first letting the precipitate settle, and then decanting most of the clear liquid. Centrifuge then discard the supernatant liquid.

12.4 Wash the precipitate with 10 mL of HNO_3, centrifuge, and discard the washings. Repeat this wash the precipitate.

12.5 Dissolve the precipitate in 10 mL of water, 10 mL of EDTA solution, and 4 mL of NH_4OH (1 + 1). Warm if necessary to effect dissolution.

12.6 Reprecipitate barium sulfate ($BaSO_4$) by the dropwise addition of acetic acid, then add 3 drops more. Record the time. Centrifuge, then discard the supernatant liquid. Add 10 mL of water, mix well, centrifuge, and discard the supernatant liquid.

12.7 Clean, flame, cool, and weigh a stainless steel planchet that fits the alpha-particle counter being used. Transfer the precipitate to the planchet with a minimum of water. Dry, flame, and weigh the precipitate to determine the chemical yield.

12.8 Promptly count the planchet in an appropriate alpha-particle counter, recording the time. Reserve the planchet for additional measurements, if desired (see 13.4).

12.9 Measure the background count rate of the detector by counting an empty, cleaned and flamed planchet for at least as long as the precipitate was counted.

13. Calculation

13.1 Calculate the fractional radium recovery (chemical yield of the carrier) as follows:

$$Y = (M_B - M_P) / 0.01699 \tag{1}$$

where:

M_B = mass of planchet with the dried barium sulfate precipitate, g,

M_P = mass of planchet only, g, and

0.01699 = mass of barium sulfate precipitate if all of the added barium carrier were recovered, g.

13.2 Calculate the concentration D of alpha-emitting radium radionuclides as radium-226 in becquerels (Bq) of radium per litre as follows:

$$D = C/EVYF \tag{2}$$

TABLE 3 Precision Data

Bq/L	s(o)	s(t)
0.455	0.057	0.149
4.588	0.303	0.577
45.51	5.996	7.588

where:

C = alpha counting rate, net counts/s, (sample counts/s minus background counts/s)
E = detection efficiency of the counter for alpha particles, counts/disintegration,
V = sample volume, L
Y = fractional chemical yield for the separation, and
F = correction for the ingrowth of descendents between the time of separation (see 12.6 and Table 1) and the time of counting.

13.3 See section 10 of Practices D 3648 concerning the overall uncertainty in a measurement.

13.4 The total propagated uncertainty (1 σ) for the concentration of alpha-emitting radium isotopes is calculated as follows:

$$\sigma_D\,(Bq)/L = D(Bq/L) * [(\sigma_N/N)^2 + (\sigma_E/E)^2 + (\sigma_v/V)^2 + (\sigma_y/Y)^2]^{1/2} \qquad (3)$$

where:

σ_N = one sigma uncertainty of the net sample counting rate,
σ_E = one sigma uncertainty of the detection efficiency of the alpha counter,
σ_V = one sigma uncertainty of the sample volume, and
σ_Y = one sigma uncertainty in the fractional radium recovery.

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

$$\sigma_N = (G/T_G{}^2 + B/t_B{}^2)^{1/2} \qquad (4)$$

where:

G = the sample gross counting rate, (s^{-1}) (5^{-1})
B = the background counting rate, (s^{-1}) (5^{-1}),
t_G = the sample counting time, s, and
t_B = the background counting time, s.

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

$$MDC\,(Bq/L) = \frac{2.71 + 4.65 * (t_G * B)^{1/2}}{t_G * E * Y * V * I} \qquad (5)$$

where:

t_G = the counting duration, s, and other terms are as defined earlier.

13.6 The relative contribution of various radium isotopes, if desired, may be obtained by alpha-particle spectroscopy (**7**). Otherwise, repeated measurements of the activity permit estimation of the isotopic composition. Table 2 lists radioactive properties of radium-226, radium-224, radium-223, and their descendents (**8**). Fig. 1 shows characteristic growth and decay curves for the three important isotopes, and equations and tables have been published (**9**).

14. Precision and Bias [7]

14.1 A limited collaborative test of this test method was conducted. Seven laboratories participated by processing samples at three levels. The results from one laboratory were rejected as outliers according to the statistical tests outlined in Practice D 2777. These collaborative data were obtained on distilled water without chemical interferences. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

14.2 *Precision*—The overall precision of this test method within its designated range varies with the quantity being tested. See Table 3 for the precision data obtained.

14.3 *Bias*—The limited collaborative study of this test method indicated that there was no statistically significant observed bias in the test method for any level. See Table 4 for the bias data obtained.

15. Quality Control

15.1 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.

16. Keywords

16.1 alpha particles; radioactivity; radium isotopes; water

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[7] Supporting data for this test method have been filed at ASTM Headquarters. Request RR D19-1003.

TABLE 4 Determination of Bias

Amount Added Bq/L	Mean	Bias, ±	Bias, %
0.455	0.522	0.067	14.7
4.588	4.67	0.082	1.7
45.51	47.49	1.98	4.3

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(8) Browne, E., and Firestone, R.B.; Shirley, V.S., ed., *Table of Radioactive Isotopes,* John Wiley & Sons, Inc., New York, NY, 1986.

(9) Kirby, H.W., "Decay and Growth Tables for the Naturally Occurring Radioactive Series," *Analytical Chemistry*, Vol 26, 1954, p 1064.

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Designation: D 2502 – 92 (Reapproved 1996)

An American National Standard

Standard Test Method for Estimation of Molecular Weight (Relative Molecular Mass) of Petroleum Oils From Viscosity Measurements [1]

This standard is issued under the fixed designation D 2502; 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 estimation of the mean molecular weight (relative molecular mass) of petroleum oils from kinematic viscosity measurements at 100 and 210°F (37.78 and 98.89°C).[2] It is applicable to samples with molecular weights in the range from 250 to 700 and is intended for use with average petroleum fractions. It should not be applied indiscriminately to oils that represent extremes of composition or possess an exceptionally narrow molecular weight (relative molecular mass) range.

1.2 Values stated in inch-pound units are to be regarded as the standard. The values given 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.*

2. Referenced Documents

2.1 *ASTM Standard:*

D 445 Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity)[3]

2.2 *Adjunct:*

Molecular Weight of Petroleum Oils from Viscosity Measurements (D 2502)[4]

3. Summary of Test Method

3.1 The kinematic viscosity of the oil is determined at 100 and 210°F (37.78 and 98.89°C). A function "*H*" of the 100°F viscosity is established by reference to a tabulation of *H* function versus 100°F viscosity. The *H* value and the 210°F viscosity are then used to estimate the molecular weight from a correlation chart.

4. Significance and Use

4.1 This test method provides a means of calculating the mean molecular weight (relative molecular mass) of petroleum oils from another physical measurement.

4.2 Molecular weight (relative molecular mass) is a fundamental physical constant that can be used in conjunction with other physical properties to characterize hydrocarbon mixtures.

5. Procedure

5.1 Determine the kinematic viscosity of the oil at 100 and 210°F (37.78 and 98.89°C) as described in Test Method D 445.

5.2 Look in Table 1 for 100°F (37.78°C) viscosity and read the value of *H* that corresponds to the measured viscosity. Linear interpolation between adjacent columns may be required.

5.3 Read the viscosity - molecular weight chart for *H* and 210°F (98.89°C) viscosity. A simplified version of this chart is shown in Fig. 1 for illustration purposes only (Note). Interpolate where necessary between adjacent lines of 210°F viscosity. After locating the point corresponding to the value of *H* (ordinate) and the 210°F viscosity (superimposed lines), read the molecular weight along the abscissa.

Example:

Measured viscosity, cSt:

100°F (37.78°C) = 179

210°F (98.89°C) = 9.72

Look in Table 1 for 179 and read the corresponding value $H = 461$.

Using $H = 461$ and 210°F viscosity = 9.72 in conjunction with chart gives molecular weight (relative molecular mass) = 360 (see Fig. 1).

Note 1—A 22 by 28-in. (559 by 711-mm) chart available as an adjunct to this test method was used in cooperative testing of the method. If other charts are used, the precision statements given in the Precision Section will not apply.

5.4 Report the molecular weight to the nearest whole number.

6. Precision and Bias

6.1 The precision of this test method as obtained by statistical examination of interlaboratory test results is as follows:

6.1.1 *Repeatability*—The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the value 3 g/mol only in one case in twenty.

6.1.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators,

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[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 D02.04 on Hydrocarbon Analysis.

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[2] Hirschler, A. E., *Journal of the Institute of Petroleum*, JIPEA, Vol 32, 1946, p. 133.

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

[4] Available from ASTM Headquarters. Order PCN 12-425020-00.

working in different laboratories on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the value 25 g/mol only in one case in twenty.

6.2 *Bias*—Since there is no accepted reference material suitable for determining bias for this test method, no statement of bias can be made.

6.3 The precision for this test method was not obtained in accordance with RR:D02-1007, "Manual on Determining Precision Data for ASTM Methods on Petroleum Products and Lubricants."[5]

7. Keywords

7.1 kinematic viscosity; molecular weight; petroleum oils; relative molecular mass

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

TABLE 1 Tabulation of *H* Function

Kinematic Viscosity, cSt, at 100°F (37.78°C)	*H*				
	0	0.2	0.4	0.6	0.8
2	−178	−151	−126	−104	−85
3	−67	−52	−38	−25	−13
4	−1	9	19	28	36
5	44	52	59	66	73
6	79	85	90	96	101
7	106	111	116	120	124
8	128	132	136	140	144
9	147	151	154	157	160
10	163	166	169	172	175
11	178	180	183	185	188
12	190	192	195	197	199
13	201	203	206	208	210
14	211	213	215	217	219
15	221	222	224	226	227
16	229	231	232	234	235
17	237	238	240	241	243
18	244	245	247	248	249
19	251	252	253	255	256
20	257	258	259	261	262
21	263	264	265	266	267
22	269	270	271	272	273
23	274	275	276	277	278
24	279	280	281	281	282
25	283	284	285	286	287
26	288	289	289	290	291
27	292	293	294	294	295
28	296	297	298	298	299
29	300	301	301	302	303
30	304	304	305	306	306
31	307	308	308	309	310
32	310	311	312	312	313
33	314	314	315	316	316
34	317	317	318	319	319
35	320	320	321	322	322
36	323	323	324	325	325
37	326	326	327	327	328
38	328	329	329	330	331
39	331	332	332	333	333

	H									
	0	1	2	3	4	5	6	7	8	9
40	334	336	339	341	343	345	347	349	352	354
50	355	357	359	361	363	364	366	368	369	371
60	372	374	375	377	378	380	381	382	384	385
70	386	387	388	390	391	392	393	394	395	397
80	398	399	400	401	402	403	404	405	406	407
90	408	409	410	410	411	412	413	414	415	415
100	416	417	418	419	420	420	421	422	423	423
110	424	425	425	426	427	428	428	429	430	430
120	431	432	432	433	433	434	435	435	436	437
130	437	438	438	439	439	440	441	441	442	442
140	443	443	444	444	445	446	446	447	447	448
150	448	449	449	450	450	450	451	451	452	452
160	453	453	454	454	455	455	456	456	456	457
170	457	458	458	459	459	460	460	460	461	461
180	461	462	462	463	463	463	464	464	465	465
190	465	466	466	466	467	467	468	468	468	469

TABLE 1 *Continued*

Kinematic Viscosity, cSt at 100°F (37.78°C)	H									
	0	10	20	30	40	50	60	70	80	90
200	469	473	476	479	482	485	487	490	492	495
300	497	499	501	503	505	507	509	511	512	514
400	515	517	518	520	521	523	524	525	527	528
500	529	530	531	533	534	535	536	537	538	539
600	540	541	542	543	544	545	546	547	547	548
700	549	550	551	551	552	553	554	554	555	556
800	557	557	558	559	559	560	561	562	562	563
900	563	564	565	565	566	566	567	567	568	569
	0	100	200	300	400	500	600	700	800	900
1 000	569	574	578	583	587	591	594	597	600	603
2 000	605	608	610	612	614	616	618	620	621	623
3 000	625	626	628	629	631	632	633	634	636	637
4 000	638	639	640	641	642	643	644	645	646	647
5 000	648	649	650	651	652	652	653	654	655	656
6 000	656	657	658	658	659	660	660	661	662	662
7 000	663	664	664	665	665	666	666	667	667	668
8 000	668	669	670	670	671	671	671	672	672	673
9 000	673	674	674	675	675	676	676	677	677	677
	0	1000	2000	3000	4000	5000	6000	7000	8000	9000
10 000	678	681	684	688	691	694	696	699	701	703
20 000	705	707	709	711	712	714	715	717	718	719
30 000	720	722	723	724	725	726	727	728	729	730
40 000	731	732	732	733	734	735	736	736	737	738
50 000	739	739	740	741	741	742	743	743	744	744
60 000	745	746	746	747	747	748	748	749	749	750
70 000	750	751	751	752	752	753	753	753	754	754
80 000	755	755	756	756	756	757	757	758	758	758
90 000	759	759	759	760	760	760	761	761	761	762
100 000	762	762	763	763	763	764	764	764	764	765

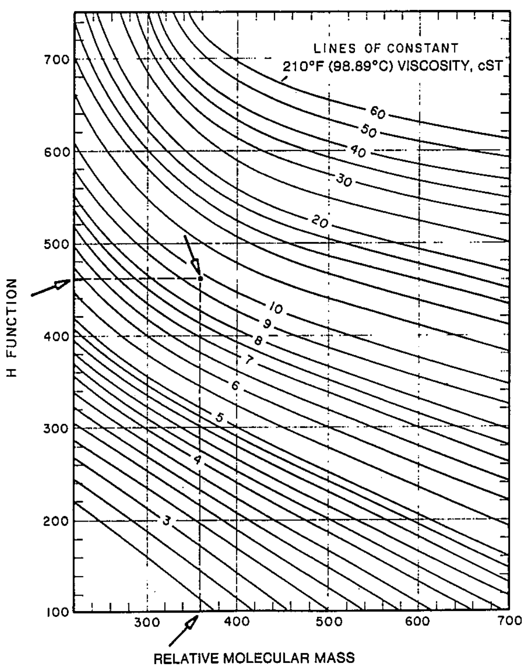

FIG. 1 Viscosity-Molecular Weight Chart

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Document Name: ASTM D2503: Standard Method of Test for Molecular Weight of Hydrocarbons by Thermoelectric Measurement of Vapor Pressure

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THE EXECUTIVE DIRECTOR
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Designation: D 2503 – 92 (Reapproved 1997)

An American National Standard

Standard Test Method for Relative Molecular Mass (Molecular Weight) of Hydrocarbons by Thermoelectric Measurement of Vapor Pressure[1]

This standard is issued under the fixed designation D 2503; 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 test method covers the determination of the average relative molecular mass (molecular weight) of hydrocarbon oils. It can be applied to petroleum fractions with molecular weights (relative molecular mass) up to 3000; however, the precision of the method has not been established above 800 molecular weight (relative molecular mass). The method should not be applied to oils having initial boiling points lower than 220°C.

1.2 Values stated in SI units are to be regarded as the standard. The values given 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.* For specific hazard statements, 5.2.1, 5.2.3, and 5.2.3.

2. Summary of Test Method

2.1 A weighed portion of the sample is dissolved in a known quantity of appropriate solvent. A drop of this solution and a drop of solvent are suspended, side by side, on separate thermistors in a closed chamber saturated with solvent vapor. Since the vapor pressure of the solution is lower than that of the solvent, solvent condenses on the sample drop and causes a temperature difference between the two drops. The resultant change in temperature is measured and used to determine the relative molecular mass (molecular weight) of the sample by reference to a previously prepared calibration curve.

3. Significance and Use

3.1 Relative molecular mass (molecular weight) is a fundamental physical constant that can be used in conjunction with other physical properties to characterize pure hydrocarbons and their mixtures.

3.2 A knowledge of the relative molecular mass (molecular weight) is required for the application of a number of correlative methods that are useful in determining the gross composition of the heavier fractions of petroleum.

4. Apparatus

4.1 *Vapor Pressure Osmometer*, with operating diagram.[2]

5. Reagents and Materials

5.1 *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.[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 *Solvents*—Solvents that do not react with the sample must be used. Since many organic materials exhibit a tendency to associate or dissociate in solution, it is desirable to use polar solvents for polar samples and nonpolar solvents for nonpolar samples. The solvents listed have been found suitable for hydrocarbons and petroleum fractions.

5.2.1 *Benzene*

NOTE 1—**Warning:** Poison. Carcinogen. Harmful if swallowed. Extremely flammable. Vapors may cause flash fire. Vapor harmful, may be absorbed through skin.

5.2.2 *Chloroform*

NOTE 2—**Warning:** May be fatal if swallowed. Harmful if inhaled. May produce toxic vapors if burned.

5.2.3 *1,1,1-Trichloroethane*

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[1] This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricantsand is the direct responsibility of Subcommittee D02.04on Hydrocarbon Analysis.

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[2] A vapor pressure osmometer is available from H. Knauer and Co., Berlin, West Germany. The manufacture of the Mechrolab instrument previously referred to in this footnote has been discontinued. However, some models may be available from stocks on hand at laboratory supply houses, or as used equipment from laboratory instrument exchanges.

[3] "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."

NOTE 3—**Warning:** Harmful if inhaled. High concentrations may cause unconsciousness or death. Contact may cause skin irritation and dermatitis.

NOTE 4—The precision data given in 10.1 and 10.2 will apply only when benzene is used as the solvent. There is also some evidence that determinations on the same oil sample carried out in different solvents will produce results that differ somewhat in absolute magnitude of apparent molecular weight (relative molecular mass).

5.3 *Reference Standards*—A calibration curve must be constructed for each new lot of solvent using a pure compound whose relative molecular mass (molecular weight) is accurately known. Compounds that have been used successfully include benzil (210.2), *n*-octadecane (254.5), and squalane (422.8).

6. Sampling

6.1 The sample must be completely soluble in the selected solvent at concentrations of at least 0.10 *M*, and it must not have an appreciable vapor pressure at the test temperature.

7. Preparation and Calibration of Apparatus

7.1 Prepare standard 0.01, 0.02, 0.04, 0.06, 0.08, and 0.1 *M* solutions of the calibrating compound in the solvent selected.

7.2 Remove the upper sample chamber assembly. Rinse the solvent cap with the solvent to be used. Install a vapor wick in the cup and fill with solvent to the bottom of the notches in the inner wick. Place the cup in the chamber base recess, align the vapor wick openings with the viewing tubes, and replace the upper assembly. Take care that the guide pins properly engage matching holes in the thermal block and that the matching surfaces of the base and block are clean. Be careful not to allow the thermistor beads to touch the cup or wicks as they may be bent out of alignment. Turn on the thermostat and allow the temperature of the sample chamber to reach equilibrium at 37°C.

NOTE 5—If the block is at room temperature, 2 to 3 h will be required. To avoid such delay, it is desirable to always leave the thermostat switch in the "on" position. If the chamber is at equilibrium and is opened briefly, 30 to 45 min will generally be required before temperature stabilization is regained. The exchange or refilling of syringes does not necessitate any waiting period.

7.3 Thoroughly rinse all syringes with the solvent being used and allow to dry.

7.4 Fill the syringes from guide tubes "5" and "6" with the solvent. Fill the syringes for guide tubes "1" through "4" with the standard solutions in order of increasing concentration.

7.5 Insert the syringes into the thermal block, keeping the guide pins pointed away from the probe. Turn on the "Null Detector" switch (Note 6). Set the sensitivity control to sufficient gain so that a 1.0-Ω shift in the "Dekastat" produces one major division shift of the meter needle.

NOTE 6—No measurements should be attempted until the "Null Detector" switch has been on for at least 30 min.

7.6 Turn on the "Bridge" switch and turn the "T-ΔT" switch to "T". Approximately zero the meter with the "T" potentiometer and observe the drift of the needle. If the solvent chamber is at equilibrium, the needle should not drift more than 1 to 2 mm during one complete heating cycle; a steady drift to the right indicates that the chamber is still warming up; if "T" is stable, switch the selector to the "ΔT" position.

7.7 While observing the thermistors in the viewing mirror, lower the syringe in position "5", by rotating the knurled collar of the holder fully clockwise. With the end of the needle directly above the reference thermistor, turn the feed screw and rinse the thermistor with about 4 drops of solvent. Finally, deposit a drop of solvent on the thermistor bead and raise the syringe by rotating the knurled collar in a counterclockwise direction. Rinse the sample thermistor with solvent from syringe "6" and apply a drop approximately the size of the drop on the reference thermistor. Depress the zero button, and zero the meter with the "Zero" control. Set the decade resistance to zero, and balance the bridge using the "Balance" control. Repeat the balancing of the bridge with fresh drops of solvent on each thermistor to assure a good reference zero.

7.8 Lower syringe "1" and rinse the sample thermistor with 3 to 4 drops of solution, finally applying one drop to the bead. Start the stop watch. Center the meter by means of the decade dials and take readings at 1-min intervals until two successive readings do not differ by more than 0.01 ohm. Record the Δ*R* value, estimating to the nearest 0.01 Ω from the meter. Record the time required to reach this steady state, and use this time for all subsequent readings for the solvent used.

7.9 Upon completing each series of sample readings, rinse the sample thermistor with solvent, deposit a drop, and recheck the zero point. The meter should reproduce the original indication within 0.5 mm. If the needle shows a negative deflection, the sample thermistor should be rinsed again. If it shows a positive deflection, the drop on the reference thermistor should be replaced.

7.10 Plot the Δ*R* values for each concentration of standard against the molarity of the standard for the solvent used.

NOTE 7—The calibration must be repeated for each of the solvents to be employed and separate working curves constructed. Recalibration is necessary each time a new batch of solvent is put into use.

8. Procedure

8.1 Select the solvent to be used and fill the solvent cup as described in 7.2. Weigh into a 25-mL volumetric flask the amount of sample suggested in the following table (Note 5):

Estimated Relative Molecular Mass	Sample Size, g
Less than 200	0.3
200 to 500	0.3 to 0.6
500 to 700	0.6 to 0.9
700 to 1000	0.9 to 1.3

Record the weight to the nearest 0.1 mg and dilute to volume with solvent.

NOTE 8—If the amount of sample is limited, weigh the sample into a 5 or 1-mL volumetric flask, using one-fifth or one twenty-fifth respectively of the amount indicated in the table. Weigh to the nearest 0.001 mg using a microbalance.

8.2 Fill syringes "5" and "6" with solvent and fill one of the remaining syringes with the sample solution. With the sample chamber at thermal equilibrium, balance the bridge to establish the reference zero as described in 7.6 and 7.7.

8.3 Rinse the sample thermistor with 3 or 4 drops of the sample solution and deposit 1 drop on the thermistor. Start the stop watch. Center the meter with the decade dials and record

ΔR at the time interval determined during the standardization for the solvent being employed (7.8). When running a series of samples, check the zero point frequently as described in 7.9.

8.4 Using the appropriate calibration curve, obtain the molarity corresponding to the observed ΔR value.

9. Calculation

9.1 Calculate the relative molecular mass (molecular weight) of the sample as follows:

$$\text{Relative Molecular Mass (molecular weight)} = c/m \qquad (1)$$

where:

c = concentration of sample solution, g/L and
m = molarity of solution, as determined in 8.4.

10. Report

10.1 Report the result to the nearest whole number.

11. Precision and Bias

11.1 **Precision**—The precision of this test method as obtained by statistical examination of interlaboratory test results is as follows:

11.1.1 Repeatability—The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the values shown in Table 1 only in one case in twenty.

11.1.2 *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, in the normal and correct operation of the test method, exceed the values shown in Table 1 only in one case in twenty.

11.1.3 The precision was not obtained in accordance with Committee D-2 Research Report RR-D-2-1007, "Manual on Determining Precision Data for ASTM Methods on Petroleum Products and Lubricants."[4]

11.2 *Bias*—Bias for this method has not been determined.

12. Keywords

12.1 hydrocarbons; molecular weight; osmometer; relative molecular mass; thermoelectric measurement; vapor pressure

TABLE 1 Precision Data (Benzene Solvent)

Relative Molecular Mass (Molecular Weight) Range	Repeatability, g/mol	Reproducibility, g/mol
245 to 399	5	14
400 to 599	12	32
600 to 800	30	94

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

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Document Name: ASTM D2597: Standard Test Method for Analysis of Demethanized Hydrocarbon Liquid Mixtures Containing Nitrogen and Carbon Dioxide by Gas Chromatography

CFR Section(s): 40 CFR 60.335(b)(9)(i)

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An American National Standard

Standard Test Method for Analysis of Demethanized Hydrocarbon Liquid Mixtures Containing Nitrogen and Carbon Dioxide by Gas Chromatography[1]

This standard is issued under the fixed designation D 2597; 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 analysis of demethanized liquid hydrocarbon streams containing nitrogen/air and carbon dioxide, and purity products such as an ethane/propane mix that fall within the compositional ranges listed in Table 1. This test method is limited to mixtures containing less than 5 mol % of heptanes and heavier fractions.

1.2 The heptanes and heavier fraction, when present in the sample, is analyzed by either (*1*) reverse flow of carrier gas after *n*-hexane and peak grouping or (*2*) precut column to elute heptanes and heavier first as a single peak. For purity mixes without heptanes and heavier no reverse of carrier flow is required.

NOTE 1—**Caution:** In the case of unknown samples with a relatively large C_6 plus or C_7 plus fraction and where precise results are important, it is desirable to determine the molecular weight (or other pertinent physical properties) of these fractions. Since this test method makes no provision for determining physical properties, the physical properties needed can be determined by an extended analysis or agreed to by the contracting parties.

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

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 hazard statements see Annex A3.

2. Referenced Documents

2.1 *ASTM Standards:*

D 3700 Practice for Containing Hydrocarbon Fluid Samples Using a Floating Piston Cylinder[2]

2.2 *Other Standard:*

GPA Standard 2177 Analysis of Demethanized Hydrocarbon Liquid Mixtures Containing Nitrogen and Carbon Dioxide by Gas Chromatography[3]

TABLE 1 Components and Compositional Ranges Allowed

Components	Concentration Range, Mol %
Nitrogen	0.01–5.0
Carbon Dioxide	0.01–5.0
Methane	0.01–5.0
Ethane	0.01–95.0
Propane	0.01–100.0
Isobutane	0.01–100.0
n-Butane and 2,2-Dimethylpropane	0.01–100.0
Isopentane	0.01–15.0
n-Pentane	0.01–15.0
2,2-Dimethylbutane	0.01–0.5
2,3-Dimethylbutane and 2-Methylpentane	
3-Methylpentane and Cyclopentane	0.01–15.0
n-Hexane	
Heptanes and Heavier	0.01–5.0

3. Summary of Test Method

3.1 Components to be determined in a demethanized hydrocarbon liquid mixture are physically separated by gas chromatography and compared to calibration data obtained under identical operating conditions. A fixed volume of sample in the liquid phase is isolated in a suitable sample inlet system and entered onto the chromatographic column.

3.1.1 Components nitrogen/air through *n*-hexane are individually separated with the carrier flow in the forward direction. The numerous heavy end components are grouped into an irregular shape peak by reversing direction of carrier gas through the column by means of a switching valve immediately following the elution of normal hexane. (See Fig. 1.) Samples that contain no heptanes plus fraction are analyzed until the final component has eluted with no reverse of carrier flow.

3.1.2 An alternative to the single column backflush method is the use of a precut column which is backflushed to obtain the heptanes plus as a single peak at the beginning of the chromatogram. Two advantages of the alternate method are as follows: (*1*) better precision in measuring the C_7 plus portion of the sample and (*2*) reduction in analysis time over the single column approach by approximately 40 %.

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[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.H on Liquefied Petroleum Gas.

Current edition approved July 15, 1994. Published September 1994. Originally published as D 2597 – 67T. Last previous edition D 2597 – 88.

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

[3] Available from Gas Processors Assn., 6526 E. 60th St., Tulsa, OK 74145.

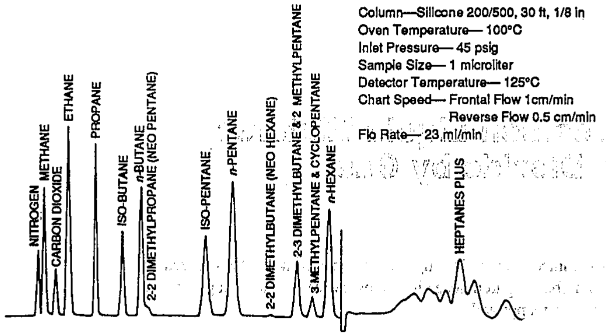

FIG. 1 Chromatogram of Demethanized Hydrocarbon Liquid Mixture (Frontal Carrier Gas Flow Through N-Hexane, Reverse Grouping Heptanes Plus)

3.2 The chromatogram is interpreted by comparing the areas of component peaks obtained from the unknown sample with corresponding areas obtained from a run of a selected reference standard. Any component in the unknown suspected to be outside the linearity range of the detector, with reference to the known amount of that component in the reference standard, must be determined by a response curve. Peak height method of integration can be used only if the chromatograph is operating in the linear range for all components analyzed. Linearity must be proved by peak height for all components when using peak height method. (See Section 6 for further explanation of instrument linearity check procedures.)

4. Significance and Use

4.1 The component distribution of hydrocarbon liquid mixtures is often required as a specification analysis for these materials. Wide use of these hydrocarbon mixtures as chemical feedstocks or as fuel require precise compositional data to ensure uniform quality of the reaction product. In addition, custody transfer of these products is often made on the basis of component analyses of liquid mixtures.

4.2 The component distribution data of hydrocarbon mixtures can be used to calculate physical properties such as specific gravity, vapor pressure, molecular weight, and other important properties. Precision and accuracy of compositional data are extremely important when these data are used to calculate physical properties of these products.

5. Apparatus

5.1 Any gas chromatograph can be used that meets the following specifications.

5.1.1 *Detector*—The detector shall be a thermal-conductivity type. It must be sufficiently sensitive to produce a deflection of at least 0.5 mv for 1 mol % of *n*-butane in a 1.0-μL sample.

5.1.2 *Sample Inlet System, Liquid*—A liquid sampling valve shall be provided, capable of entrapping a fixed volume of sample at a pressure at least 200 psi (1379 kPa) above the vapor pressure of the sample at valve temperature, and introducing this fixed volume into the carrier gas stream ahead of the analyzing column. The fixed sample volume should not exceed 1.0 μL and should be reproducible such that successive runs agree within ±2 % on each component peak area. The liquid sampling valve is mounted exterior of any type heated compartment and thus can operate at laboratory ambient conditions.

5.1.3 *Sample Inlet System, Gas (Instrument Linearity)*—Provision is to be made to introduce a gas phase sample into the carrier gas stream ahead of the chromatographic column so that linearity of the instrument can be estimated from response curves. The fixed volume loop in the gas sample valve shall be sized to deliver a total molar volume approximately equal to that delivered by the liquid sample valve in accordance with 5.1.2. (See Section 6 for further explanation of instrument linearity check procedures.)

5.1.4 *Chromatographic Columns*:

5.1.4.1 *Column No. 1*—A partition column shall be provided capable of separating nitrogen/air, carbon dioxide, and the hydrocarbons methane through normal hexane. (See Fig. 1 and Fig. 2.) Separation of carbon dioxide shall be sufficient so that a 1-μL sample containing 0.01 mol % carbon dioxide will produce a measurable peak on the chromatogram. (The silicone 200/500 column, containing a 27 to 30 weight % liquid phase load, has proven satisfactory for this type of analysis.)

5.1.4.2 *Column No. 2*—A partition column similar to Column No. 1. It shall be of the same diameter as Column No. 1. The column shall be of an appropriate length to clearly separate the heptanes plus fraction from the hexanes and lighter components.

5.1.5 *Attenuator*—A multistep device shall be included in the detector output circuitry to attenuate the signal from the detector to the recorder when using manual calculation methods. The attenuation between steps shall be accurate to ±0.5 %.

5.1.6 *Temperature Control*—The chromatographic column(s) and the detector shall be maintained at their respective temperatures, constant to ±0.3°C during the course of the sample and corresponding reference standard runs.

5.2 *Carrier Gas*—Pressure-reducing and control devices to

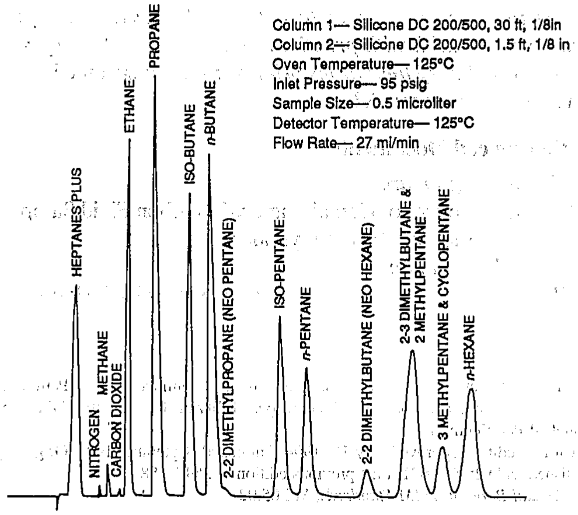

FIG. 2 Chromatogram of Demethanized Hydrocarbon Liquid Mixture (Precut Column Grouping Heptanes Plus, Frontal Carrier Gas Flow Remaining Components)

give repeatable flow rates.

5.3 *Recorder*—A strip chart recorder with a full-scale range of 1 mv shall be required when using manual calculation methods. A maximum pen response time of 1 s and a minimum chart speed of 1 cm/min (0.5 in./min accepted) shall be required. Faster speeds up to 10 cm/min (3 in./min accepted) are required if the chromatogram is to be interpreted using manual methods to obtain areas.

NOTE 2—A strip chart recorder is recommended for monitoring the progress of the analysis if an electronic digital integrator without plotting capability is in service.

5.4 *Electronic Digital Integrator*—A strongly preferred and recommended device for determining peak areas. This device offers the highest degree of precision and operator convenience.

NOTE 3—**Caution:** Electronic digital integrators are able to integrate peak areas by means of several different methods employing various correction adjustments. The operator should be well versed in integrator operation, preventing improper handling and manipulation of data—ultimately resulting in false information.

5.5 *Ball and Disk Integrator*—An alternative device in the absence of an electronic digital integrator for determining peak areas. This device gives more precise areas than manual methods and saves operator time in interpreting the chromatogram.

5.6 *Manometer*—Well type, equipped with an accurately graduated and easily readable scale covering the range from 0 to 900 mm of mercury. The manometer is required in order to charge partial pressure samples of pure hydrocarbons when determining response curves for linearity checks when using the gas sampling valve.

5.7 *Vacuum Pump*—Shall have the capability of producing a vacuum of 0.1 mm of mercury absolute or less. Required for linearity checks when using the gas sampling valve.

5.8 *Sample Filter*—An optional device to protect the liquid sampling valve from scoring due to the presence of foreign contaminates such as metal shavings, dirt, and so forth, in a natural gas liquid (NGL) sample. The filter can be of a small total volume, or an in-line type design and contain a replaceable/disposable element.

NOTE 4—**Caution:** A filter can introduce error if not handled properly. The filter should be clean and free of any residual product from previous samples so that a buildup of heavy end hydrocarbon components does not result. (Can be accomplished by a heating/cooling process or inert gas purge, etc.) The filter element should be 15-μm size or larger so that during the purging process NGL is not flashed, preventing fractionation and bubble formation.

5.9 *Sample Containers*:

5.9.1 *Floating Piston Cylinder*—A strongly preferred and recommended device suitable for securing, containing, and transferring samples into a liquid sample valve and which preserves the integrity of the sample. (See Fig. 3 and Test Method D 3700.)

5.9.2 *Double-Valve Displacement Cylinder*—An alternate device used in the absence of a floating piston cylinder suitable for securing, containing, and transferring samples into a liquid sample valve. (See Fig. 4 and Fig. 5.)

NOTE 5—**Caution:** This container is acceptable when the displacement liquid does not appreciably affect the composition of the sample of interest. Specifically, components such as CO_2 or aromatic hydrocarbons are partially soluble in many displacement liquids and thus can compromise the final analysis. This caution is of the utmost importance and should be investigated prior to utilizing this technique.

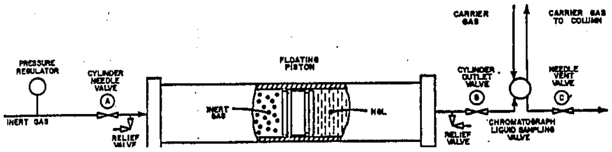

FIG. 3 Repressuring System and Chromatographic Valving with Floating Piston Cylinder

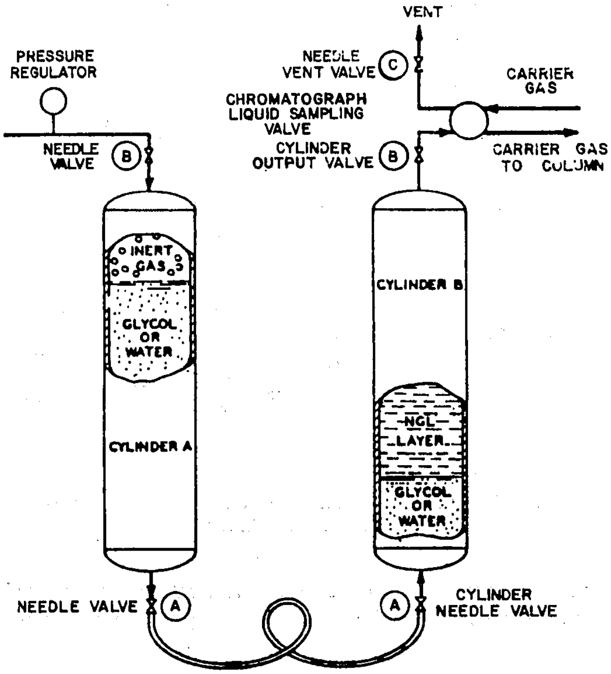

FIG. 4 Repressuring System and Chromatographic Valving with Double-Valve Displacement Cylinder

6. Calibration

6.1 In conjunction with a calibration on any specific chromatography, the linear range of the components of interest shall be determined. The linearity is established for any new chromatograph and reestablished whenever the instrument has undergone a major change (that is, replaced detectors, increased sample size, switched column size, or dramatically modified run parameters).

6.1.1 The preferred and more exacting procedure is to prepare response curves. The procedure for developing the data necessary to construct these response curves for all components nitrogen through *n*-pentane is set forth in Annex A2.

6.1.2 A second procedure utilizes gravimetrically constructed standards of a higher concentration than is contained in the unknown. A set of response factors are first determined for all components by means of a blend mix. (See 6.3.) A second (or third) gravimetrically determined standard (either purity or blend) can then be run, using the originally obtained

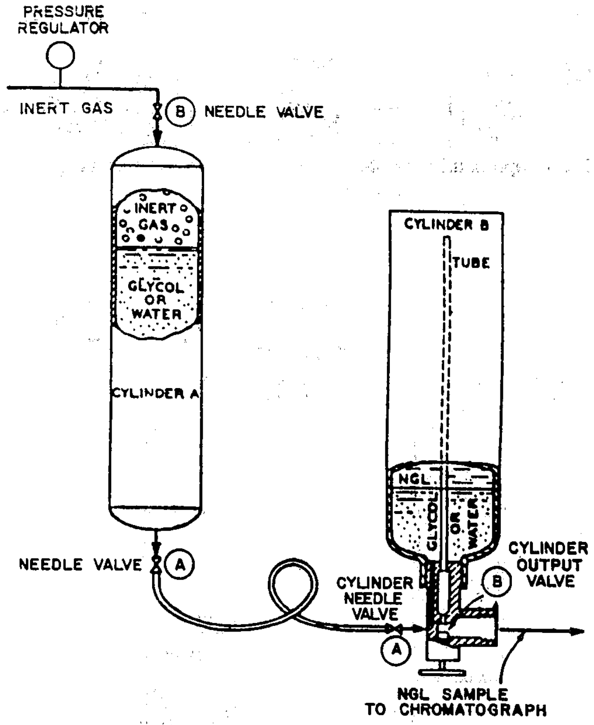

FIG. 5 Alternate Repressuring System with Double-Valve Displacement Cylinder

response factors, which contain a concentration of individual components exceeding the expected amounts in the unknowns. When both (or all three) runs match their respective standards within the precision guidelines allowed in Section 10, then the instrument can be considered linear within that range.

NOTE 6—This test method omits the need of a gas sample valve on the chromatographic instrument. However, several accurate primary NGL standards are required and the exact point at which nonlinearity occurs is not determined.

6.2 For routine analysis using this procedure it is intended that calibration be accomplished by use of a selected reference standard containing known amounts of all components of interest. It is recommended that the reference standard composition be similar to the one shown in Table 2, or closely resemble the composition of expected unknowns. This approach is valid for all components that lie within the proven linear range for a specific gas chromatograph.

NOTE 7—Check the reference standard for validity when received and periodically thereafter. Annex A1 details one procedure for making the validity check.

6.3 Using the selected liquid reference standard, obtain a chromatogram as outlined in Section 7.

6.3.1 Determine peak areas (or peak heights) from the chromatogram for all components. These data shall be used to calculate response factors in accordance with 9.1.

6.3.2 Repeat 6.3 through 6.3.1 until a satisfactory check is obtained. Usually two runs will suffice.

7. Procedure

7.1 *General*—In the routine analysis of samples described in the scope of this procedure, it is possible to obtain all components of interest from a single run. Response factors,

TABLE 2 Example of Response Factors Determined from Reference Standard

Component	Mol % in Referenced Standard	Peak Area Referenced Standard Run	Mol % Response Factors (×10 000)	Relative Response Factor (C_3 Reference Peak)
Nitrogen/air	0.10	311	$\frac{0.10}{311} = 3.2154$	$\frac{0.10}{311} \times \frac{122825}{28.05} = 1.4080$
Methane	1.49	3552	$\frac{1.49}{3552} = 4.1948$	$\frac{1.49}{3552} \times \frac{122825}{28.05} = 1.8368$
Carbon dioxide	0.50	1568	$\frac{0.50}{1568} = 3.1888$	$\frac{0.50}{1568} \times \frac{122825}{28.05} = 1.3963$
Ethane	53.90	182108	$\frac{53.90}{182108} = 2.9598$	$\frac{53.90}{182108} \times \frac{122825}{28.05} = 1.2960$
Propane	28.05	122825	$\frac{28,05}{122825} = 2.2837$	$\frac{28.05}{122825} \times \frac{122825}{28.05} = 1.0000$
Isobutane	3.05	15306	$\frac{3.05}{15306} = 1.9927$	$\frac{3.05}{15306} \times \frac{122825}{28.05} = 0.8726$
n-Butane 2,2-Dimethylpropane	6.01	30834	$\frac{6.01}{30834} = 1.9491$	$\frac{6.01}{30834} \times \frac{122825}{28.05} = 0.8535$
Isopentane	1.00	5856	$\frac{1.00}{5856} = 1.7077$	$\frac{1.00}{5856} \times \frac{122825}{28.05} = 0.7478$
n-Pentane	2.00	12280	$\frac{2.00}{12280} = 1.6287$	$\frac{2.00}{12280} \times \frac{122825}{28.05} = 0.7132$
2,2-Dimethylbutane	0.02	132	$\frac{0.02}{132} = 1.5152$	$\frac{0.02}{132} \times \frac{122825}{28.05} = 0.6635$
2,3-Dimethylbutane 2-Methylbutane	0.64	4513	$\frac{0.64}{4513} = 1.4181$	$\frac{0.64}{4513} \times \frac{122825}{28.05} = 0.6210$
3-Methylpentane Cyclopentane	0.41	2401	$\frac{0.41}{2401} = 1.7076$	$\frac{0.41}{2401} \times \frac{122825}{28.05} = 0.7477$
N-Hexane	0.74	5064	$\frac{0.74}{5064} = 1.4613$	$\frac{0.74}{5064} \times \frac{122825}{28.05} = 0.6399$
Heptanes Plus	2.09	14851	$\frac{2.09}{14851} = 1.4073$	$\frac{2.09}{14851} \times \frac{122825}{28.05} = 0.6162$

determined in duplicate runs on a selected reference standard, are used to convert peak areas (or peak heights) of the unknown sample to mol percent.

7.2 *Apparatus Preparation*—With the proper column(s) and liquid sample valve in place, adjust operating conditions to optimize the resultant chromatogram. Using the reference standard, introduce the sample in the following manner.

7.3 *Introduction of Sample*:

7.3.1 *Floating Piston Cylinders*—For floating piston cylinders, refer to Fig. 3 and proceed as follows: connect a source of inert gas to Valve *A* so that pressure can be applied to the sample by means of the floating piston. Apply a pressure not less than 200 psi (1379 kPa) above the vapor pressure of the sample at the temperature of the sample injection valve.

7.3.2 Thoroughly mix the sample.

7.3.3 Connect the sample end of the cylinder, Valve *B*, to the inlet of the chromatograph liquid sample valve. All connections and tubing are to be made of material impervious to the sample composition and of as small diameter and shortest length of plumbing as is practical, thereby minimizing dead space. All tubing between sample cylinder and liquid sampling valve shall be the same diameter.

7.3.4 With Valve *C* closed, open Valve *B* to fill the sample valve and associated lines.

7.3.5 Slowly crack Valve *C* to purge the sample valve. When the purge is complete, close Valve *C*. **Caution**—Use extreme care to ensure that no flashing of sample occurs in the inlet sampling line and valve system. Always meter at sample purge Valve *C*, never at sample Valve *B*. The sample line and valve system should remain at 1379 kPa (200 psi) above the vapor pressure of the product.

7.3.6 Operate the liquid sample valve either manually or automatically to inject the liquid sample into the carrier gas flow immediately ahead of the chromatographic column. Actuate the sample valve quickly and smoothly to place the sample on the column all at once and to ensure continuous carrier gas flow through the column.

7.3.7 *Double-Valve Displacement Cylinders*—For doublevalve displacement cylinders refer to Fig. 4 and Fig. 5 and proceed as follows: Connect the sample Cylinder *B* to Cylinder *A* so repressurizing fluid can be entered into the bottom of Cylinder *B*. With this configuration the hydrocarbon sample is taken from the upper portion of the cylinder. Pressurize Cylinder *A* with an inert gas and maintain a pressure at least 200 psi (1379 kPa) above the vapor pressure of the hydrocarbon sample at operating conditions. Open the necessary valves to admit pressurizing fluid into the sample Cylinder *B*.

7.3.8 Mix the sample thoroughly by gently inverting Cylinder *B* several times. Fix the cylinder in a vertical position by means of a ringstand, or similar device.

7.3.9 Connect the sample outlet Valve *B* on Cylinder *B* to the inlet of the chromatograph liquid sample valve. All connections and tubing are to be made of material impervious to the sample composition and of as small diameter and shortest length of plumbing as is practical, thereby minimizing "dead space." All tubing between sample cylinder and liquid valve should be the same diameter.

7.3.10 With Valve *C* closed, open Valve *B* to fill the sample valve and associated lines.

7.3.11 Slowly crack Valve *C* to purge the sample valve. When the purge is complete close Valve *C*. **Caution**—Use extreme care to ensure that no flashing of sample occurs in the inlet sampling line and valve system. Always meter at sample purge Valve *C*, never at sample Valve *B*. The sample line and valve system should remain at 1379 kPa (200 psi) above the vapor pressure or the product.

7.3.12 Operate the liquid sample valve either manually or automatically to inject the liquid sample into the carrier gas flow immediately ahead of the chromatographic column. The liquid sample valve should be actuated quickly and smoothly to place the sample on the column all at once and to ensure continuous carrier gas flow through the column.

7.4 *Valve Switching*:

7.4.1 After the elution of *n*-hexane the carrier gas flow is reversed by means of a backflush valve operated manually or automatically. (An acceptable backflush valve configuration is shown in Fig. 6.) Reversing carrier flow causes severe baseline deviations (see Fig. 1). When using electronic digital integrators, exercise care to ensure integration does not occur until baseline is adequately reestablished. The resulting irregular shaped C_7 plus peak is eluted over a period of time equivalent to time on forward flow minus the retention time for the air peak. Only after baseline is reestablished should the run be terminated and carrier flow returned to original direction.

7.4.2 An alternative to backflushing after normal hexane is the use of a precut column to group the C_7 plus fraction at the beginning of the chromatogram as a single peak. (An acceptable valve configuration for the precut method is illustrated in Fig. 7.) The valve position is switched when normal hexane and lighter components have traveled through Column 2 and are in Column 1. At this point, heptanes and heavier components are retained in Column 2. When the valve is reversed, the heptanes plus fraction will elute from Column 2 first. Baseline must be clearly and distinctly established before elution of the C_7 plus peak so an accurate measurement of this peak can be obtained. After the elution of *n*-hexane, terminate the run and return the valve to the initial position.

8. Unknown Sample Run

8.1 Obtain a chromatogram of the unknown sample in accordance with instructions outlined in Section 7.

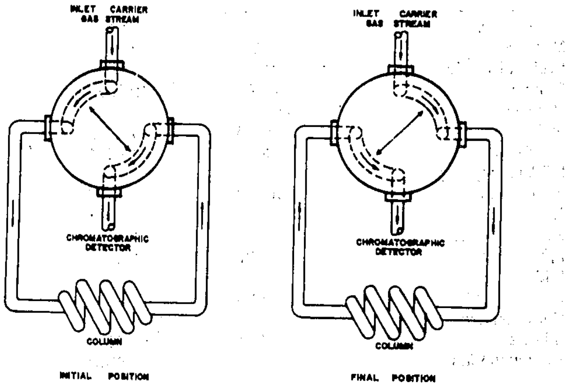

FIG. 6 Backflush Valve Configuration

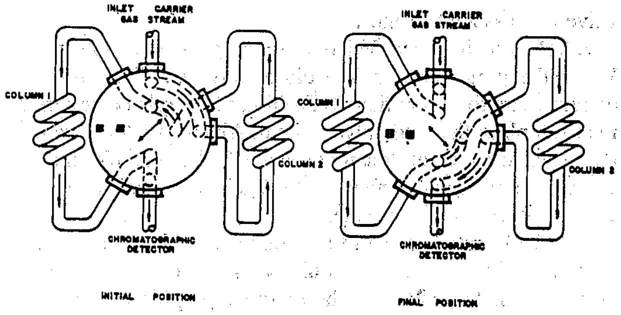

FIG. 7 Precut Valve Configuration

8.1.1 Determine peak areas (or peak heights) from the chromatogram for all components. These data shall be used to calculate composition of the unknown in accordance with instructions outlined in 9.2.

9. Calculation

9.1 *Calculation of Response Factors Using a Known Reference Standard*:

9.1.1 Determine the peak area (or peak height) of each component nitrogen/air through heptanes plus (if applicable) from the chromatogram of the known reference standard.

NOTE 8—The backflush peak (where applicable) for heptanes plus is considered to be a single component for the purpose of this calculation. In addition, the peak area method shall be used in calculating the heptanes plus fraction.

9.1.2 Calculate a response factor for each of the preceding components in accordance with the following equation (see Table 2):

$$K = \frac{M}{P} \quad (1)$$

where:

K = response factor,
M = mol percent of component in reference standard, and
P = peak area or peak height in arbitrary units (millimetres, square inches, counts, and so forth) corrected to maximum sensitivity.

9.1.3 An alternative method of determining response factors is the use of a single reference component in the standard. Calculate a relative response factor for each component in accordance with the following equation (see Table 2):

$$KF_i = \frac{M_i}{P_i} \times \frac{P_{RP}}{M_{RP}} \quad (2)$$

where:

KF_i = relative response factor for component i,
M_i = mol percent of component i in reference standard,
P_i = peak area (or peak height) in arbitrary units corrected to maximum sensitivity for component i,
P_{RP} = peak area (or peak height) of the component selected as the reference peak, and
M_{RP} = mol percent of the component in reference standard as the reference peak.

From the equation defining the relative response factor, the component chosen as the reference peak always has a response factor of 1.000.

9.2 *Calculation of Mol Percent of Components in Unknown Sample*:

9.2.1 Determine peak area (or peak height) of each component nitrogen/air through heptanes plus from the chromatogram of the unknown sample using the same arbitrary units as in 9.1.

9.2.2 Calculate the concentration in mol percent of each of these components in accordance with the following equation (see Table 3):

$$M = P \times K \quad (3)$$

where:

M = mol percent of component in unknown,
P = peak area (or peak height) of each component in unknown sample, and

TABLE 3 Calculation of Unknown Sample Using Response Factors from Table 2

Component	Peak Area	Mol % Response Factor (×10 000)	Unnormalized Mol %	Normalized Mol %	Relative Response Factor (C_3 Reference Peak)	Unnormalized Area × RRF	Normalized Mol %
Nitrogen/Air	91	3.2154	0.02926	0.04	1.4080	128	0.04
Methane	4720	4.1948	1.97995	2.85	1.8368	8670	2.85
Carbon Dioxide	2615	3.1888	0.83387	1.20	1.3963	3651	1.20
Ethane	64090	2.9598	18.96936	27.27	1.2960	83061	27.27
Propane	113346	2.2837	25.88483	37.21	1.0000	113346	37.21
Isobutane	31590	1.9927	6.29494	9.05	0.8726	27565	9.05
n-Butane	33672	1.9491	6.56301	9.44	0.8535	28739	9.44
2,2-Dimethylpropane							
Isopentane	16368	1.7077	2.79516	4.02	0.7478	12240	4.02
N-Pentane	17235	1.6287	2.80706	4.04	0.7132	12292	4.04
2,2-Dimethylbutane	75	1.5152	0.01136	0.02	0.6635	50	0.02
2,3-Dimethylbutane	4027	1.4181	0.57107	0.82	0.6210	2501	0.82
2-Methylpentane							
3-Methylpentane	1584	1.7076	0.27048	0.39	0.7477	1184	0.39
Cyclopentane							
n-Hexane	4521	1.4613	0.66065	0.95	0.6399	2893	0.95
Heptanes Plus	13335	1.4073	1.87663	2.70	0.6162	8217	2.70
			69.54763	100.00		304537	100.00

K = response factor as determined in 9.1.

9.2.2.1 Total the mol percent values and normalize to 100 %.

9.2.3 Using the relative response factors calculate the concentration in mol percent of each of these components in accordance with the following equation (see Table 3):

$$M_i = \frac{KF_i \times P_i}{\sum_{i=1}^{n} (KF_i \times P_i)} \times 100 \qquad (4)$$

where:

M_i = mol percent of component i in unknown,

KF_i = relative response factor for component i,

P_i = peak area (or peak height) of component i in unknown, and

$\sum_{i=1}^{n}(KF_i \times P_i)$ = summation of all relative response areas in the chromatogram.

9.2.3.1 Total mol percent values and normalize to 100 %.

10. Precision and Bias

10.1 The precision of this test method as determined by statistical examination of interlaboratory results is as follows:

10.1.1 *Repeatability*—The difference between two test 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:

Component	Mol % Range	Percent Relative Repeatability
Nitrogen	0.01–.89	9
Carbon Dioxide	0.01–2.3	4
Methane	1.6–4.5	4
Ethane	27.–54.	.5
Propane	28.–34.	.5
Isobutane	3.0–8.8	1
n-Butane	6.0–9.3	1
Isopentane	1.0–3.9	2
n-Pentane	2.0–3.8	2
C_6^+	3.6–5.7	2

10.1.2 *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, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

Component	Mol % Range	Percent Relative Reproducibility
Nitrogen	0.01–89	60
Carbon Dioxide	0.01–2.3	30
Methane	1.6–4.5	10
Ethane	27.–54.	2
Propane	38.–34.	2
Isobutane	3.0–8.8	4
n-Butane	6.0–9.3	4
Isopentane	1.0–3.9	6
n-Pentane	2.0–3.8	6
C_6^+	3.6–5.7	10

NOTE 9—The repeatability and reproducibility statements for this procedure are from the statistical data obtained in a GPA cooperative test program completed in 1986. The testing program included six samples analyzed in a round robin by eight laboratories.

10.2 *Bias*—The bias of the procedure in this test method has not been determined but is now under consideration.

11. Keywords

11.1 chromatography; demethanized hydrocarbons; liquefied petroleum gases; natural gas liquids

ANNEXES

(Mandatory Information)

A1. FIDELITY OF SELECTED REFERENCE STANDARDS

A1.1 Referring to Section on Summary of Test Method, it is noted that the test method is based on response factors calculated from a selected reference standard using peak area measurements. Liquid reference standards are difficult to prepare and are subject to change in composition during use. Hence it is virtually mandatory that the reference standard be authenticated in some manner when received and periodically during use. One simple approach is described as follows:

A1.1.1 Determine mol percent response factors for normal hydrocarbons using area measurements of peaks recorded on chromatogram of reference standard run (see 9.1.2).

A1.1.2 Determine molecular weight corresponding to each component hydrocarbon in A1.1.1.

A1.1.3 Using log/log paper plot the response factor on the vertical scale versus molecular weights on the horizontal scale (see Fig. A1.1).

A1.1.4 If all is in order the resultant plot will be essentially a straight line with a negative slope. For a specific instrument, the slope of the plot should remain essentially constant. A change in the angle usually indicates a change in blend composition.

A1.1.5 An example follows using data from Table 2 in this test method (see Table A1.1).

A1.2 It should be noted the relationship described in A1.1.1-A1.1.5 is valid for reference blends in the vapor state as well as the liquid state, so long as the following conditions are met.

A1.2.1 Chromatogram is obtained using a thermal conductivity detector.

A1.2.2 Peak areas in arbitrary units are used for peak measurements.

A1.2.3 Known concentrations of hydrocarbon components

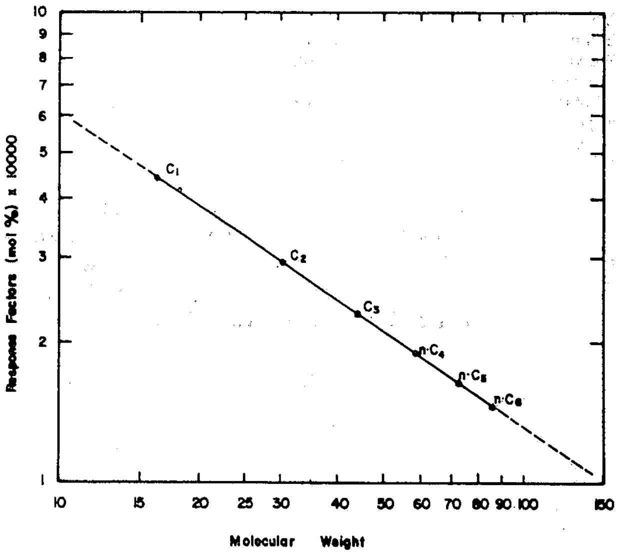

FIG. A1.1 Response Factors (mol %) Versus Molecular Weight

TABLE A1.1 Response Factors and Mol Weights Normal Hydrocarbon Components[A]

Component	Response Factor × 10^{-4}	Mol Weight
Methane	4.195	16.043
Ethane	2.960	30.070
Propane	2.284	44.097
n-Butane	1.949	58.123
n-Pentane	1.629	72.150
n-Hexane	1.461	86.177

[A] Initially with a new system and a new blend this check should be performed often, say once a day for the first week to satisfy the operator that the component analysis furnished with the blend is essentially correct. After this time the check should be performed each time a calibration run is made to verify the continued fidelity of the selected reference blend.

in the known reference blend are expressed in mol %.

A1.3 In addition to authentication of reported composition of a new blend and periodically verifying its validity, this plot can be used to:

A1.3.1 Reduce the frequency of calibrations required.

A1.3.2 Reveal calculation and interpretation errors in calibration runs.

A1.3.3 Pick off factors for components not in the standard by extrapolating the plot. A factor for the back flush peak can be picked off if the molecular weight can be satisfactorily estimated.

A2. DETERMINATION OF RESPONSE FACTORS

A2.1 Linearity Check

A2.1.1 In order to establish linearity of response for the thermal conductivity detector, it is necessary to carry out the procedure outlined as follows:

A2.1.2 The major component of interest (methane for natural gas) is charged to the chromatograph by means of the fixed-size sample loop at partial pressure of 100 to 700 mm of Hg in increments of 100 mm. The peak area of the methane is plotted versus partial pressure. Any deviation from linearity indicates the fixed volume sample loop is too large. The sample size should be reduced until the pure major component is linear over the concentration range expected in the samples.

A2.1.2.1 Connect the pure component source to the sample entry system. Evacuate the sample entry system and observe manometer for any leaks. (See Fig. A2.1 for a suggested manifold arrangement.) The sample entry system shall be vacuum tight.

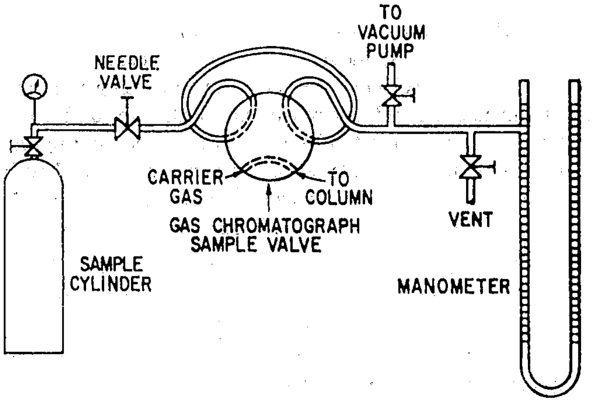

FIG. A2.1 Suggested Manifold Arrangement for Entering Vacuum Samples

A2.1.2.2 Carefully open the needle valve to admit the pure component up to 100 mm of partial pressure.

A2.1.2.3 Record exact partial pressure and actuate sample valve to place sample onto column. Record peak area of pure component.

A2.1.2.4 Repeat A2.2.3 for 200, 300, 400, 500, 600, and 700 mm of mercury. Record peak area obtained at each pressure.

A2.1.2.5 Plot the area data versus partial pressure on the *x* and *y* axes of linear graph paper as shown in Fig. A2.2.

NOTE A2.1—Experience has shown that if the major component is linear over the expected concentration range in the sample, the lesser components will also be linear. Methane and ethane exhibit less than 1 % compressibility at 760 mm Hg and are therefore the components of choice for linearity checks.

NOTE A2.2—**Caution:** *n*-Butane at atmospheric pressure exhibits 3.5 % compressibility, which, if the detector response is linear, will produce a nonlinear response opposite to detector non-linearity.

A2.2 Calibration Procedure

A2.2.1 Response factors of the components of interest can be established in two ways. The routine method is to use a gas reference standard of known composition to determine response factors, provided all components in the reference standard and in the unknown samples lie within the proven linear range for a specific chromatography instrument. An acceptable non-routine method of determining response factors is to charge the pure components to the chromatograph. The latter method is described in Annex A1.

A2.2.1.1 Connect the reference standard gas to the sample entry system. Evacuate the sample entry system and observe the manometer for any leaks.

A2.2.1.2 Carefully open the needle valve to admit reference standard gas up to some predetermined partial pressure.

NOTE A2.3—The use of some constant partial pressure below atmospheric pressure avoids variations in sample size due to changes in barometric pressure.

A2.2.1.3 Record the partial pressure and operate the gas sampling valve to place the sample onto the column. Record the chromatogram, integrator/computer peak areas, and peak retention times.

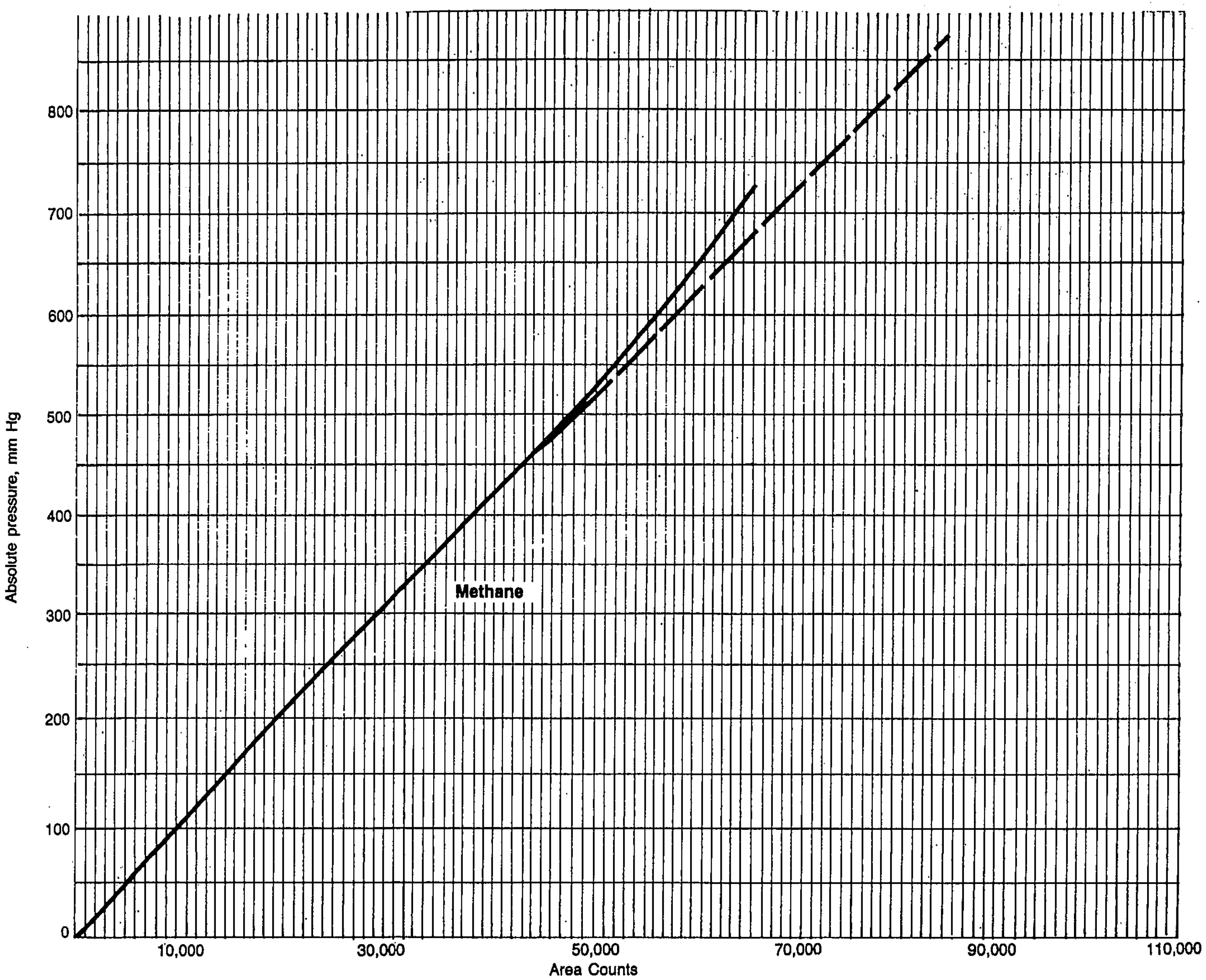

FIG. A2.2 Linearity of Detector Response

NOTE A2.4—It is recommended that the integrator/computer has the capability to print out retention times of peak maxima to aid in peak identification and to monitor instrument conditions for unknown changes.

A3. PRECAUTIONARY STATEMENTS

A3.1 Flammable Liquefied Gases

A3.1.1 Keep away from sparks and open flame.

A3.1.2 Keep container closed.

A3.1.3 Use with adequate ventilation.

A3.1.4 Avoid buildup of vapors and eliminate all sources of ignition, especially nonexplosive electrical devices and heaters.

A3.1.5 Avoid prolonged breathing of vapor or spray mist.

A3.1.6 Avoid prolonged or repeated skin contact.

A3.2 Compressed Gases (Helium, Nitrogen)

A3.2.1 Keep container closed.

A3.2.2 Use adequate ventilation.

A3.2.3 Do not enter storage areas unless adequately ventilated.

A3.2.4 Always use a pressure regulator.

A3.2.5 Release regulator tension before opening cylinder.

A3.2.6 Do not transfer to cylinder other than one in which gas is received.

A3.2.7 Do not mix gases in cylinders.

A3.2.8 Do not drop cylinders.

A3.2.9 Make sure cylinder is supported at all times.

A3.2.10 Stand away from cylinder outlet when opening cylinder valve.

A3.2.11 Keep cylinder out of sun and away from heat.

A3.2.12 Keep cylinder from corrosive environment.

A3.2.13 Do not use cylinder without label.

A3.2.14 Do not use dented or damaged cylinder.

A3.2.15 For technical use only. Do not use for inhalation purposes.

CERTIFICATE

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Document Name: ASTM D2622: Standard Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry

CFR Section(s): 40 CFR 80.46(a)(1)

Standards Body: American Society for Testing and Materials

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Designation: D 2622 – 98

Standard Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry[1]

This standard is issued under the fixed designation D 2622; 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 test method covers the determination of total sulfur in petroleum and petroleum products that are single-phase and either liquid at ambient conditions, liquifiable with moderate heat, or soluble in hydrocarbon solvents. These materials can include diesel fuel, jet fuel, kerosine, other distillate oil, naphtha, residual oil, lubricating base oil, hydraulic oil, crude oil, unleaded gasoline, M-85 and M-100.

1.2 The interlaboratory study on precision covered a variety of materials with sulfur concentrations ranging from approximately 3 mg/kg to 5.3 mass %. For a subset of these samples, with sulfur concentrations below 60 mg/kg, the repeatability standard deviation (S_r) was 1.5 mg/kg. An estimate of the limit of detection is 3 × S_r, and an estimate of the limit of quantitation[2] is 10 × S_r. However, because instrumentation covered by this test method can vary in sensitivity, the applicability of the test method at sulfur concentrations below approximately 20 mg/kg must be determined on an individual basis.

1.3 Samples containing more than 5.0 mass % sulfur can be diluted to bring the sulfur concentration of the diluted material within the scope of this test method.

1.4 Volatile samples (such as high vapor pressure gasolines or light hydrocarbons) may not meet the stated precision because of selective loss of light materials during the analysis.

1.5 A fundamental assumption in this test method is that the standard and sample matrix are well matched. Matrix mismatch can be caused by C/H ratio differences between samples and standards (see Tables 1 and 2) or by the presence of other heteroatoms (see Table 3).

1.6 The values stated in either SI units or angstrom units are to be regarded separately as standard.

1.7 *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 hazard information, see Note 1.

2. Referenced Documents

2.1 *ASTM Standards:*

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

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products[3]

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

D 4927 Test Methods for Elemental Analysis of Lubricant and Additive Components—Barium, Calcium, Phosphorus, Sulfur, and Zinc by Wavelength-Dispersive X-Ray Fluorescence Spectroscopy[4]

E 29 Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications[5]

3. Summary of Test Method

3.1 The sample is placed in the X-ray beam, and the peak intensity of the sulfur $K\alpha$ line at 5.373 Å is measured. The background intensity, measured at a recommended wavelength of 5.190 Å (5.437 Å for a Rh target tube) is subtracted from the peak intensity. The resultant net counting rate is then compared to a previously prepared calibration curve or equation to obtain the concentration of sulfur in mass %.

NOTE 1—**Warning:** Exposure to excessive quantities of X-radiation is injurious to health. The operator needs to take appropriate actions to avoid exposing any part of their body, not only to primary X-rays, but also to secondary or scattered radiation that might be present. The X-ray spectrometer should be operated in accordance with the regulations governing the use of ionizing radiation.

4. Significance and Use

4.1 This test method provides rapid and precise measurement of total sulfur in petroleum and petroleum products with a minimum of sample preparation. A typical analysis time is 1 to 2 min per sample.

4.2 The quality of many petroleum products is related to the amount of sulfur present. Knowledge of sulfur concentration is

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[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 D02.03.B on Spectrometric Methods.

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[2] *Analytical Chemistry*, Vol 55, 1983, pp. 2210–2218.

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

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

[5] *Annual Index of ASTM Standards*, Vol 14.02.

TABLE 1 Comparison of NIST and ASTM Interlaboratory Study (RR) Results

NIST SRM	Sulfur, mass %, NIST	Sulfur, mass %, ASTM RR Average	C/H mass ratio	Apparent Bias, % Sulfur	Relative Bias, %	Signif icant
1616a	0.0146	0.0148	5.205	0.0002	1.37	No
1617a	0.1731	0.1776	5.205	0.0045	2.60	Yes
2724a	0.0430	0.0417	5.986	-0.0013	-3.02	Yes
1623c	0.3806	0.3661	7.504	-0.0145	-3.81	Yes
2717	3.0220	2.948	8.229	-0.0736	-2.44	Yes
1621e	0.948	0.8973	8.553	-0.0507	-5.35	Yes
1624c		0.3918	6.511			
2723		0.0299	5.937			

TABLE 2 Comparison of NIST and ASTM Interlaboratory Study (RR) Corrected Results, Mass % Sulfur

NOTE—The correction factors were calculated from data determined with XRF-11. The correction formula, which is applicable when the base material used for the calibration standards is white oil, is:

$$S_{corrected} = S_{uncorrected} / (1.086 - 0.01511 \times C/H)$$

where

C/H = mass ratio of carbon to hydrogen for the sample

Application of these correction factors requires separate determination of the C/H mass ratio. The significance was determined based on a *t* test using a function of the NIST uncertainty at 1 sigma and the round robin reproducibility standard deviation.

SRM	RR ID	NIST	RR Corrected	Apparent Bias	Relative Bias, %	Signif icant
1616a	K2	0.0146	0.0147	0.0001	0.68	No
1617a	K1	0.1731	0.1763	0.0032	1.85	No
2724a	D2	0.0430	0.0419	-0.0011	-2.56	No
1623 c	R1	0.3806	0.3763	-0.0043	-1.13	No
2717	R4	3.0220	3.065	0.0430	1.42	No
1621 e	R3	0.948	0.9382	-0.0098	-1.03	No
1624c	D3		0.397			
2723	D4		0.0300			

TABLE 3 Concentration of Interfering Elements

Element	Mass % Tolerated
Phosphorus	0.3
Zinc	0.6
Barium	0.8
Lead	0.9
Calcium	1
Chlorine	3
Ethanol (Note 12)	8.6
Methanol (Note 12)	6

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 determining whether the sulfur content of petroleum or a petroleum product meets specification or regulatory limits.

4.4 When this test method is applied to petroleum materials with matrices significantly different from the white oil calibration materials specified in this test method, the cautions and recommendations in Section 5 should be observed when interpreting results.

NOTE 2—Compared to other test methods for sulfur determination, Test Method D 2622 has high throughput, minimal sample preparation, and excellent precision, and is capable of determining sulfur over a wide range of concentrations. The equipment specified for Test Method D 2622 tends to be more expensive than that required for alternative test methods, such as Test Method D 4294. Consult the Index to ASTM Standards[6] for alternative test methods.

5. Interferences

5.1 When the elemental composition (excluding sulfur) of samples differs significantly from the standards, errors in the sulfur determination can result. For example, differences in the carbon-hydrogen ratio of sample and calibration standards introduce errors in the determination. Some other interferences and action levels are listed in Table 3.

5.2 M-85 and M-100 are fuels containing 85 and 100 % methanol, respectively. They have a high oxygen content leading to significant absorption of sulfur Kα radiation. Such fuels can, however, be analyzed using this test method provided either that correction factors are applied to the results (when calibrating with white oils) or that the calibration standards are prepared to match the matrix of the sample.

5.3 In general, petroleum materials with compositions that vary from white oils as specified in 9.1 can 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 expected aromatic content of the samples to be analyzed. Standards made from this simulated gasoline can produce results that are more accurate than results obtained using white oil standards.

5.4 Test Method D 4927 is the recommended test method for determination of sulfur in lubricating oils and lubricating oil additives because Test Methods D 4927 implements interelement correction factors.

6. Apparatus

6.1 *Wavelength Dispersive X-Ray Fluorescence Spectrometer (WDXRF)*, equipped for X-ray detection in the 5.37 Å range. For optimum sensitivity to sulfur, the instrument should be equipped with the following.

6.1.1 *Optical Path*, of helium.

6.1.2 *Pulse-Height Analyzer*, or other means of energy discrimination.

6.1.3 *Detector*, designed for the detection of long wavelength X-rays.

6.1.4 *Analyzing Crystal*, suitable for the dispersion of sulfur Kα X-rays within the angular range of the spectrometer employed. Pentaerythritol and germanium are popular although other materials, such as EDDT, ADP, graphite, and quartz can be used.

6.1.5 *X-ray Tube*, capable of exciting sulfur Kα radiation. Tubes with anodes of rhodium, chromium, and scandium are most popular although other anodes can be used.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that

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[6] *Annual Book of ASTM Standards*, Vol 00.01.

all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[7] 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*, 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 (see 9.1).

NOTE 3—It is essential to know the concentration of sulfur in the di-*n*-butyl sulfide, not the purity, since impurities may also be sulfur containing compounds.

7.3 *Drift Correction Monitor(s) (Optional)*—Several different materials have been found to be suitable for use as drift correction monitors. Examples of sulfur containing materials that have been found to be suitable include a renewable liquid petroleum material, a semipermanent solid, a pressed powder sample, a metal alloy, or a fused glass disk. The monitor's count rate, in combination with count time, shall be sufficient to give a relative counting error of less than 1 %. The count rate for the monitor sample is determined during calibration (see 9.4) and again at the time of analysis (see 10.1). These counting rates are used to calculate a drift correction factor (see 11.1)

7.3.1 Drift correction is usually implemented automatically in software, although the calculation can readily be done manually. For X-ray instruments that are highly stable, the magnitude of the drift correction factor may not differ significantly from unity.

NOTE 4—Calibration standards may be used for this purpose. Because it is desirable to discard standards after each determination, a lower cost material is suggested for daily use.

7.4 *White Oil*, containing less than 2 mg/kg sulfur or other suitable base material containing less than 2 mg/kg sulfur. When low level (<200 mg/kg) measurements are anticipated, then the sulfur content, if any, of the base material needs to be included in the calculation of calibration standard concentration (see 9.1).

7.5 *X-ray transparent film*—Any film that resists attack by the sample, is free of sulfur, and is sufficiently X-ray transparent can be used. Films can include polyester, polypropylene, polycarbonate, and polyimide. However, samples of high aromatic content can dissolve polyester and polycarbonate films.

7.6 *Helium Gas*, minimum purity 99.9 %.

7.7 *Counting Gas*, for instruments equipped with flow proportional counters.

7.8 *Sample Cells*, compatible with the sample and the geometry requirements of the spectrometer. Disposable cells are preferred.

7.9 *Calibration Check Samples*, portions of one or more liquid petroleum or product standards of known sulfur content and not used in the generation of the calibration curve. The check samples shall be used to determine the accuracy of the initial calibration. (see 9.5)

7.10 *Quality Control Samples*, stable petroleum or product samples representative of the samples of interest that are run on a regular basis to verify that the system is in statistical control (Section 13).

NOTE 5—Verification of system control through the use of QC samples and control charting is highly recommended. It is recognized that QC procedures are the province of the individual laboratory.

NOTE 6—Suitable QC samples can often be prepared by combining retains of typical samples.

8. Sampling and Specimen Preparation

8.1 Samples shall be taken in accordance with the instructions in Practices D 4057 or D 4177 when applicable.

8.2 When reusable sample cells are used, clean and dry cells before each use. Disposable sample cells shall not be reused. For each sample, an unused piece of X-ray film is required for the sample cell. Avoid touching the inside of the sample cell, the portion of the window film in the cell, or the instrument window that is exposed to X-rays. Oil from fingerprints can affect the reading when analyzing for low levels of sulfur. Wrinkles in the film will affect the intensity of the sulfur X-rays transmitted. Therefore, it is essential that the film be taut and clean to ensure reliable results. The analyzer may need recalibration if the type or thickness of the window film is changed. After the sample cell is filled, a small vent hole is provided.

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 checked after starting each new roll or batch of film.

9. Calibration

9.1 Prepare calibration standards by careful mass dilution of the certified di-*n*-butyl sulfide with white oil or other suitable base material (see 5.3). The standards, with accurately known sulfur concentrations, shall approximate the nominal sulfur concentrations listed in Table 4 for the sulfur concentration ranges of interest. Take into account any sulfur in the base material when calculating the concentration of standards below 0.02 mass %.

NOTE 7—If desired, additional standards can be analyzed with concentrations between those listed in Table 4.

NOTE 8—Commercially available standards can be used provided their sulfur concentrations are accurately known and they approximate the

TABLE 4 Sulfur Standards

Sulfur Concentration, mass %	Sulfur Concentration, mass %	Sulfur Concentration, mass %
0.0000[A]	0.100	1.0
0.001	0.250	2.0
0.010	0.500	3.0
0.025		4.0
0.050		5.0
0.075		

[A] Base material

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

nominal concentrations listed in Table 4.

9.2 Establish calibration curve data by carefully measuring the net intensity of the emitted sulfur radiation from each of the standards by the procedure described in Section 10 and Section 11.

9.3 Construct a calibration model by either:

9.3.1 Using the software and algorithms supplied by instrument manufacturer,

9.3.2 Fitting the data to one of the following equations:

$$S\,\% = (D + ER)(1+\alpha S) \text{ or} \tag{1}$$

$$S\,\% = aR + bR^2 + c \tag{2}$$

where:

S = sulfur concentration in mass %,
D = intercept of the calibration curve,
E = slope of the calibration curve,
R = net intensity for the sulfur radiation, and
α = correction factor for the effect of sulfur on the sulfur result and a, b, and c are fitted constants.

NOTE 9—The factor α in Eq 1 can be determined empirically or theoretically. Equipment vendors can often supply theoretical alphas.

9.3.3 Plotting corrected net intensity in counts per second versus sulfur concentration. Plot the data in several small ranges to minimize non-linear effects.

NOTE 10—Calibration plots are linear to a minimum concentration of 0.10 mass % sulfur. The analyst should choose the other plotting ranges to match the testing requirements. Deviation from linearity can increase as sulfur concentration increases.

9.4 When using drift correction monitors, determine the intensity of the drift correction monitor sample(s) during the calibration procedure. The value determined corresponds to the factor A in Eq 4 in 11.1.

9.5 Immediately after completing the calibration, determine the sulfur concentration of one or more of the calibration check samples (7.9). The measured value shall be in the range defined by the certified concentration ± the repeatability of this test method. When 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.

10. Procedure

10.1 When using drift correction monitors, prior to analyzing samples on a given day, analyze the drift correction monitor(s) and determine the counting rate, using the same material as used at the time of calibration. The value determined corresponds to the factor B in Eq 4 in 11.1.

10.1.1 When the factor F' is used in Eq 5 (Section 11), regularly analyze a blank sample to determine the factor F' in Eq 5. On a sulfur free sample, such as the base material, determine the count rate at the appropriate sulfur peak and background angles.

10.2 Place the sample in an appropriate cell using techniques consistent with good practice for the particular instrument being used. Although sulfur radiation will penetrate only a small distance into the sample, scatter from the sample cell and the sample can vary. Laboratory personnel shall ensure that the sample cell is filled above a minimum depth, beyond which additional sample does not significantly affect the count rate. Generally, fill the sample cell to a minimum of three-fourths of the cell's capacity. Provide a small vent hole in the sample cell.

10.3 Place the sample in the X-ray beam and allow the X-ray optical path to come to equilibrium.

10.4 Determine the intensity of the sulfur Kα radiation at 5.373 Å by making counting rate measurements at the precise angular settings for this wavelength.

NOTE 11—It is suggested that a sufficient number of counts be taken to satisfy at least a 1.0 % expected coefficient of variation (% rsd) when practical. When sensitivity or concentration, or both, make it impractical to collect a sufficient number of counts to achieve a 1.0 % coefficient of variation, accepted techniques, which will allow the greatest statistical precision in the time allotted for each analysis, should be used. The coefficient of variation is calculated as follows:

$$\text{coefficient of variation, \%} = (100\sqrt{Ns + Nb})/(Ns - Nb) \tag{3}$$

where

N_s = number of counts collected at sulfur line, and
N_b = number of counts collected at background wavelength in the same time interval taken to collect N_s counts.

10.5 Measure background count-rate at a previously-selected, fixed, angular setting, adjacent to the sulfur Kα peak.

NOTE 12—Suitability of any background setting will depend on the X-ray tube anode employed. A wavelength of 5.190 Å is recommended where chromium or scandium is used whereas 5.437 Å has been found suitable for rhodium, 2θ, peak and background, angles for various crystals are listed in Table 5.

10.6 Determine the corrected counting rate and calculate the concentration of the sample as described in Section 11.

10.7 When, from the measurements made in accordance with 10.2-10.6, the counting rate is higher than that of the highest point of the calibration curve, dilute the sample with the base material used to prepare the calibration standards until the sulfur counting rate is within the limits of the calibration curve and repeat the procedure described in 10.3-10.6.

10.8 When the sample is known or believed to contain concentrations of interfering substances higher than those listed in Table 3, dilute the sample by mass with base material to concentrations below those listed.

NOTE 13—The concentrations of substances in Table 3 were determined by the calculation of the sum of the mass absorption coefficients times

TABLE 5 2θ Angles for Various Crystals

Crystal	2d (Å)	S Kα (5.373 Å)	Background (5.190 Å)	(5.437 Å)
NaCl (200)	5.6406	144.56	133.89	149.12
EDDT (020)	8.806	75.18	72.21	76.24
ADP (101)	10.640	60.65	58.39	61.46
Pentaerythritol (002)	8.742	75.85	72.84	76.92
Quartz (101)	6.5872	106.93	101.81	106.97
Ge (111)	6.532	110.68	105.23	112.68
Graphite (002)	6.706	106.45	101.38	106.29
Graphite (002) (PG)	6.74	105.72	100.71	107.55

mass fraction of each element present. This calculation was made for dilutions of representative samples containing approximately 3 % of interfering substances and 0.5 % sulfur.

10.8.1 The data collected showed reasonable X-ray results when the calculated sum of mass absorption coefficients times mass fractions for samples was not greater than 4 to 5 % above the sum of mass absorption coefficients times mass fractions for the calibration standards. Absorption interferences are additive, and they are only minimized by dilution, not completely eliminated. Table 3 is therefore to be used as a guide to concentrations that can be tolerated without significant error, not as an absolute quantity.

NOTE 14—The effect of matrix interferences can also be corrected on an empirical or theoretical basis. Except for gasohol, these corrections are not within the scope of this test method.

NOTE 15—The concentrations of ethanol and methanol were calculated using a theoretical mixture of hydrocarbons and di-butyl sulfide to which ethanol (or methanol) was added until the sum of the mass coefficients times mass fractions increased by 5 %. In other words, the amount of ethanol (or methanol) that caused a negative 5 % error in the sulfur measurement was calculated. This information is included in Table 3 to inform those who wish to use Test Method D 2622 for determining sulfur in gasohol (or M-85 and M-100) of the nature of the error involved.

10.8.2 Thoroughly mix the blend to ensure homogeneity, and transfer it to the instrument for measurement.

10.8.3 Determine the sulfur content of the blend in the normal manner as described in 10.2-10.6, and calculate the sulfur content of the original sample as described in Section 11.

11. Calculation

11.1 When using the drift correction monitor described in 7.3, calculate a correction factor for changes in daily instrument sensitivity as follows:

$$F = A/B \tag{4}$$

where:

A = counting rate of the drift correction monitor as determined at the time of calibration (see 9.4), and

B = counting rate of the drift correction monitor as determined at the time of analysis (see 10.1).

NOTE 16—The inclusion of this factor in Eq 5 may not be necessary or desirable with some instrumentation. In this case F is set to unity. It is recommended that the user chart the F factor and develop criteria for its application based on the stability of the instrumentation and standard SQC principles.

11.2 Determine the corrected net counting rate as follows:

$$R = [(C_K/S_1) - (C_B F'/S_2)]F \tag{5}$$

where:

C_K = total counts collected at 5.373 Å,

C_B = total counts collected at the background location chosen in 10.5,

S1 and S2 = seconds required to collect C counts,

R = corrected net counting rate, and

F' = (counts/s at 5.373 Å)/(counts/s) at background chosen in 10.5 on a sample containing no sulfur.

11.2.1 The use of the factor F in Eq 5 is optional. (Note 14)

11.2.2 The inclusion of the factor F' in Eq 5 is optional. In general it is needed for multichannel spectrometers, which use different spectrometer channels to measure peak and background intensities.

NOTE 17—Charting the F' factor, even if it is not used in Eq 5, will alert the user to changes in instrument operation due to contamination of system elements, such as crystals, collimators, and fixed windows.

11.3 Calculate the sulfur content of the sample by inserting the corrected net counting rate from Eq 5 in the chosen calibration model from Section 9. In many cases the instrument vendor will provide software or the required calculations.

11.4 Calculate the concentration of sulfur in samples, which have been diluted, as follows:

$$S\text{, mass \%} = S_b \times [(W_s + W_o)/W_s] \tag{6}$$

where:

S_b = mass % sulfur in diluted blend,

W_s = mass of original sample, g, and

W_o = mass of diluent, g.

The instrument vendor may have provided software to perform this calculation when required masses are input.

12. Reporting

12.1 For samples analyzed without dilution, report the result calculated in 11.3. For samples that have been diluted, report the result calculated in 11.4. Report the result as the total sulfur content, mass %, to three significant figures for concentrations greater than 0.0100 %, to two significant figures between 0.0010 % and 0.0099 % and to one significant figure below 0.0010 %. For guidance in properly rounding significant figures, refer to the rounding method in Practice E 29. State that the results were obtained according to Test Method D 2622.

12.2 When analyzing M-85 or M-100 fuels with a calibration determined with white oil based standards, divide the result obtained in 11.3 as follows (Note 13):

$$S\text{ (in M}-85\text{), mass \%} = S\text{, mass \%} / 0.59 \tag{7}$$

$$S\text{ (in M}-100\text{), mass \%} = S\text{, mass \%} / 0.55 \tag{8}$$

This correction is not required if the standards are prepared in the same matrix as the samples, as described in 5.2.

NOTE 18—One laboratory compared the sulfur sensitivity for M-85 and M-100 fuels to the sulfur sensitivity for paraffin oils (Test Method D 2622) by theoretical calculation.[8] This laboratory and one other found excellent agreement between the theoretical and measured factors, therefore creating these correction factors.

13. Quality Control

13.1 It is recommended that each laboratory establish a program to ensure that the measurement system described in this test method is in statistical control. One part of such a program might be the regular use and charting[9] of quality control samples (see7.10). It is recommended that at least one type of quality control sample be analyzed that is representative of typical laboratory samples.

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[8] XRF-11, Criss Software, Largo, MD.

[9] ASTM MNL 7, Manual on Presentation of Data and Control Chart Analysis, Section 3, Control Chart for Individuals.

14. Precision and Bias [10]

14.1 The precision of the test method was determined by statistical analysis of results obtained in two separate interlaboratory studies. The first interlaboratory study (Case I) covered distillates, kerosines, residual oils, and crude oils. The second interlaboratory study (Case II) covered a set of 21 gasolines. Neither M-85 nor M-100 was included. The ranges of sulfur concentrations represented by the sample sets, together with the precisions, are listed in 14.1.1 and 14.1.2.

14.1.1 *Repeatability*—The difference between successive test results obtained by the same operator with the same apparatus under constant operation 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:

Case	Range, Mass %	Repeatability
I	0.006 - 5.3	$0.02651\ X^{0.9}$
II	0.0003 - 0.093	$0.00736\ (X+0.0002)^{0.4}$

where X is the sulfur concentration, mass %.

14.1.2 *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, in the normal and correct operation of the test method exceed the following values only in one case in twenty:

Case	Range, Mass %	Reproducibility
I	0.006 - 5.3	$0.0913\ X^{0.9}$
II	0.0003 - 0.093	$0.0105\ (X+0.0002)^{0.4}$

where X is the sulfur concentration, mass %.

14.2 *Bias*—One interlaboratory study (Case I) included eight NIST reference materials. The certified sulfur value, interlaboratory round robin (RR) value, measured C/H, apparent bias, and relative bias are given in Table 1. Table 2 compares NIST value with sulfur concentrations corrected for C/H ratio. The white oil was assumed to have a C/H mass ratio of 5.698 ($C_{22}H_{46}$).

14.2.1 The variation in relative sulfur sensitivity as a function of C/H mass ratio is shown graphically in Fig. 1.

15. Keywords

15.1 analysis; diesel; gasoline; jet fuel; kerosine; petroleum; spectrometry; sulfur; X-ray

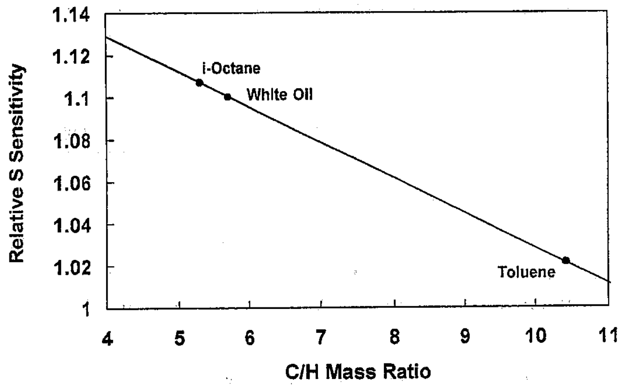

FIG. 1 Relative Sulfur Sensitivity

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[10] Support data are available from ASTM Headquarters. Request RR:D02-1428.

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Standard Test Methods for Bonded, Fused, and Laminated Apparel Fabrics[1]

This standard is issued under the fixed designation D 2724; 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 cover procedures for characterizing the delamination, strength of bond, appearance, and shrinkage propensity of bonded, fused, and laminated apparel fabrics after drycleaning and laundering.

1.2 The values stated in SI units are to be regarded as standard; the values in parentheses are provided as information only.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems 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 76 Specification for Tensile Testing Machines for Textiles[2]

D 123 Terminology Relating to Textiles[2]

E 337 Test Method for Measuring Humidity with a Psychrometer (the Measurement of Wet- and Dry-Bulb Temperatures)[3]

2.2 *AATCC Standard:*

124 Appearance of Durable Press Fabrics After Repeated Home Launderings[4]

2.3 *Federal Trade Commission Trade Regulation Rule:*

16 CFR 423 Care Labeling of Textile Wearing Apparel and Certain Piece Goods[5]

3. Terminology

3.1 *blister, n—in bonded, fused, or laminated fabrics,* a bulge, swelling, or similar surface condition on either the face fabric or the backing fabric characterized by the fabric being raised from the plane of the underlying component over a limited area to give a puffy appearance.

3.2 *bonded fabric, n*—a layered fabric structure wherein a face or shell fabric is joined to a backing fabric, such as tricot, with an adhesive that does not significantly add to the thickness of the combined fabrics.

3.2.1 *Discussion*—In this context a thin layer of foam is considered an adhesive when the cell structure is completely collapsed by a flame.

3.3 *bond strength, n— of bonded, fused, or laminated fabrics,* the tensile force expressed in ounces per 25 mm (1 in.) of width, required to separate the component layers under specified conditions.

3.4 *bubble*—See preferred term *blister.*

3.5 *crack mark, n—in bonded, fused, or laminated fabrics,* a sharp break or crease in the surface contour of either the face fabric or the backing fabric that becomes evident when the bonded, fused, or laminated composite is rolled, bent, draped, or folded.

3.5.1 *Discussion*—Crack marks are usually the result of combining tight fabric constructions at least one of which does not have sufficient residual stretch to allow the combined fabrics to be bent in an arc without producing crack marks on the concave side of the arc. Crack marks also occur when bonded fabrics are allowed to remain in a creased or wrinkled state before full adhesive cure has taken place. Other causes include the use of excessive adhesive in bonding, or excessive foam thicknesses and excessive foam collapse in flame lamination.

3.6 *foam tear, n*—a condition wherein the foam portion of a laminated fabric ruptures prior to the failure of the bond.

3.7 *fused fabric, n*—a type of bonded fabric made by adhering a fusible fabric to another fabric, such as for use as an interlining.

3.8 *fusible fabric, n*—a utilitarian fabric which has a thermoplastic adhesive applied to one side, sometimes in a pattern of dots, so that the surface can be bonded to another fabric surface by the use of heat and pressure.

3.9 *interlining, n*—any textile which is intended for incorporation into an article of wearing apparel as a layer between an outer shell and an inner lining.

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[1] These test methods are under the jurisdiction of ASTM Committee D13 on Textiles, and are the direct responsibility of Subcommittee D13.59 on Fabric Test Methods, General.

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[2] *Annual Book of ASTM Standards*, Vol 07.01.

[3] *Annual Book of ASTM Standards*, Vol 11.03.

[4] Available from American Association of Textile Chemists and Colorists, P.O. Box 12215, Research Triangle Park, NC 27709.

[5] As amended effective January 2, 1984, Section A236, available from U.S. Government Printing Office, North Capital and H Streets NW, Washington DC, 20401.

3.10 *laminated fabric, n*—a layered fabric structure wherein a face or outer fabric is joined to a continuous sheet material, such as polyurethane foam, in such a way that the identity of the continuous sheet material is retained, either by the flame method or by an adhesive, and this in turn normally but not always, is joined on the back with a backing fabric such as tricot.

3.11 *lot, n—in bonded, fused, or laminated fabric,* a single run on the bonding or laminating machine in which the processing is carried out without stopping or changing processing conditions, and consisting of either a single dye lot or a single gray goods lot.

3.12 *puckering, n— in bonded, fused, or laminated fabrics,* a wavy, three-dimensional effect typified by closely spaced wrinkles, on either the face fabric or the backing fabric or both.

3.12.1 *Discussion*—Puckering may be due to (*1*) differential shrinkage of the component layers, (*2*) differences in tension when the component layers are combined, or (*3*) selective lineal delamination.

3.13 *solvent relative humidity, n*—the humidity of air over a drycleaning bath and in equilibrium with the solvent and its small amount of water.

3.13.1 *Discussion*—Every drycleaning solvent bath containing detergent can require a different absolute water content to reach the Federal Trade Commission (FTC) specified level of solvent relative humidity for a normal drycleaning. The actual solvent relative humidity in the air over a solvent must be measured by an hygrometer after equilibrium has been reached between the water content of air and the solvent.

3.14 For definitions of other textile terms used in this test method, refer to Terminology D 123.

4. Summary of Test Methods

4.1 Bench marks are placed at specified distances on the fabrics, which are then measured, and subsequently drycleaned, or laundered and dried, or both, through a prescribed cycle that is repeated a specified number of times. The drycleaned or washed specimens are examined for appearance and delamination and measured to determine any accompanying shrinkage and, if desired, tested to determine the strength of the bond.

5. Uses and Significance

5.1 These test methods for the determination of properties of bonded, fused, or laminated apparel fabrics, are considered satisfactory for acceptance testing of commercial shipments of bonded and laminated apparel fabrics since the methods have been used extensively in the trade for acceptance testing.

5.1.1 In case of a dispute arising from differences in reported test results when using Test Methods D 2724 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 that are as homogeneous as possible and that 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 results from the two laboratories should be compared using Student's *t*-test for unpaired data and an acceptable probability level chosen by the two parties before the testing is begun. If a bias is found, either its cause must be found and corrected or the purchaser and the supplier must agree to interpret future test results in the light of the known bias.

6. Apparatus and Materials

6.1 *Drycleaning Machine,*[6] single-unit, coin-operated type, capable of providing a complete automatic dry-to-dry cycle using perchlorethylene. It shall consist of a commercial rotating cage type, totally enclosed machine. The diameter of the rotating cage shall be not less than 600 mm (24 in.) and not more than 1080 mm (42 in.). Its depth shall be not less than 300 mm (12 in.). It shall be fitted with two to four lifters. The speed shall be such as to give a *g*-factor between 0.5 and 0.9 for cleaning and between 35 and 120 for extraction. The machine shall be equipped with thermometers for the measurement of the solvent temperature and the air drying temperature.

NOTE 1—The *g*-factor is calculated using Eq 1 or Eq 2:

$$g = 1.42n^2D/100\ 000 \qquad (1)$$

$$g = 5.59n^2d/10\ 000\ 000 \qquad (2)$$

where:

n = revolutions per minute,
D = cage diameter, in., and
d = cage diameter, mm.

6.2 *Domestic Automatic Washer,*[7] top-loading, spin-extracting type.

6.3 *Domestic Automatic Tumble Dryer,*[7] front-loading type.

6.4 *Aspirated Psychrometer*, which meets the requirements of Test Method E 337.

6.5 *Marking Device*[8]—A thin sheet of stainless steel or other rigid flat material in which a square opening 254 by 254 mm (10 by 10 in.) has been cut.

6.6 *Rule*, 305-mm (12-in.) or longer, preferably divided into tenths of an inch. A premarked device calibrated to give the percentage of shrinkage or growth may also be used.

6.7 *Sewing Machine*, suitable for sewing a single row of stitching, preferably with No. 00 mercerized cotton thread, 25 mm (1 in.) from the edge of the fabric specimen.

6.8 *Steam Iron*, hand type.

6.9 *Steam Press,*[9] a press, 600 by 1250 mm (24 by 50 in.), or larger, provided with 60 to 70 psig steam pressure at the press. Any steam press large enough for pressing a specimen 380 mm (15 in.) square may be used.

6.10 *Tensile Testing Machine*, conforming to Specification

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[6] Sources of suitable equipment are: McGraw-Edison Co., Speed Queen Div., Ripon, Wis.; Philco-Bendix Corp., Fairfield, IO; American Permac, Inc., 175 Express St., Plainview, L. I.; Valley Industries Productions, Inc., 133 E. Jericho Turnpike, Mineola, NY; and Atlas Electric Devices, Chicago, IL.

[7] Kenmore Model 600 washer and dryer, available from Sears Roebuck and Co., are satisfactory for this purpose.

[8] Other suitable devices are available from Better Fabrics Testing Bureau, Inc., 101 W. 31 St., New York, NY, and from Cluett, Peabody and Co., Inc., Sanforized Div., Troy, NY.

[9] Sources of suitable equipment are: Hoffman Machine Co., Syracuse, NY; Pentax Co., Pawtucket, R. I.; Prosperity Co., Syracuse, NY; U. S. Testing Co., Hoboken, NJ.

D 76, either a constant rate of traverse type[10] or a constant rate of extension type, equipped with clamps having a width of 76.2 mm (3.00 in.) and preferably calibrated in kilograms with a range from 0 to 4.5 kg (0 to 160 oz). The constant rate of extension type machine is preferred because of the inherently lower machine-induced errors in this type of machine.

6.11 *Detergent*, home laundry type.

6.12 *Perchlorethylene*, commercial grade.

NOTE 2—**Warning:** Perchlorethylene is toxic, and the usual precautions for handling chlorinated solvents should be taken. It should be used only under well-ventilated conditions. The solvent is nonflammable.

6.13 *Drycleaning Detergent,*[11] anionic drycleaning detergent.

7. Sampling

7.1 *Lot Sample*—As a lot sample for acceptance testing, take at random the number of rolls of fabric directed in an applicable material specification or other agreement between the purchaser and the supplier. Consider rolls of fabric to be the primary sampling units.

NOTE 3—An adequate specification or other agreement between the purchaser and the supplier requires taking into account the variability between rolls of fabric and between specimens from a swatch from a roll of fabric so as to provide a sampling plan with a meaningful producer's risk, consumer's risk, acceptable quality level, and limiting quality level.

7.2 *Laboratory Sample*—As a laboratory sample for acceptance testing, take a full width swatch 1 m (1 yd) long from the end of each roll of fabric in the lot sample, after first discarding a minimum of 1 m (1 yd) of fabric from the very outside of the roll.

7.3 *Test Specimens*—Proceed as follows:

7.3.1 *Drycleaning and Laundering*—Cut four specimens from each swatch in the laboratory sample with each specimen being 380 by 380 mm (15 by 15 in.) in size, with the one side of the specimens from a single swatch parallel to the selvage. Locate two of the specimens from each swatch about ⅓ of the distance from one selvage and locate the other two specimens from each swatch about ⅓ of the distance from the other selvage. Locate each of the two specimens from one side of the swatch along a diagonal line on the swatch so that they will contain different warp ends and filling picks. Sew a straight line of stitching around each specimen 25 mm (1 in.) from each edge. Reserve the rest of the swatch for comparison with the drycleaned and laundered test specimens.

7.3.2 *Strength of Bond*—Prepare three test specimens, each measuring 76 mm (3 in.) wide, and 152 mm (6 in.) long, the length of the specimens corresponding to the length direction of the fabric. Do not take the test specimens closer to the selvage than a distance equal to 20 % of the fabric width.

NOTE 4—Samples that are 51 mm (2 in.) wide may be used as the minimum width.

8. Conditioning

8.1 Bring the samples from the prevailing atmosphere and condition them for at least 4 h in the standard atmosphere for testing textiles if shrinkage is to be determined. Preconditioning is not necessary.

9. Specimen Preparation

9.1 Using an indelible fineline marker, mark a 254 by 254 mm (10 by 10 in.) reference square centrally located on the face of each test specimen. Apply three sets of reference markings 254 ± 2 mm (10 ± 0.1 in.) apart, as measured with a rule, in the direction of the fabric length. Locate the markings within 25 mm (1 in.) of each end and at the midpoint of each side of the square. Similarly, apply three sets of markings in the direction of the fabric width. Any other method of accurately locating the 254-mm reference marks is satisfactory as long as the three marks on each side of the square are at least 105 mm (4 in.) apart.

10. Drycleaning Procedure

NOTE 5—Launderable fabrics are expected normally to be drycleanable, except where the face fabric is not drycleanable and is so labeled. For example, the fabric could contain a functional finish soluble in the solvent, or the fiber could be degraded by the solvent, which would be the case with poly(vinyl chloride) fiber.

10.1 *Solvent Preparation*—Prepare a standard detergent/drycleaning solvent mixture by adding sufficient detergent to the solvent to make a 1 % volume/volume solution. Add sufficient water to the solution to give a solvent relative humidity level of 75 % for the particular drycleaning detergent used. Put this solvent in the machine storage tank. The same solution can be used for repeated cleanings until it becomes dirty and needs replacing as long as the necessary water additions to maintain the solvent relative humidity constant are made prior to each test run. This is so because the specimens being run could conceivably alter the solvent relative humidity for succeeding test runs while the detergent level would remain constant.

10.2 *Sample and Dummy Load Preparation*— Prepare a load consisting of all specimens to be tested and made up to 3.6 kg (8 lb) total with dummy load of approximately 380 by 380-mm (15 by 15-in.) fabric pieces of similar material. Condition this load at least 4 h in the standard atmosphere for testing textiles. After the drycleaning operation, condition the load again before running through each additional drycleaning cycle. Conditioning before each drycleaning cycle is intended to minimize depletion of water from the drycleaning solution specified in 10.1.1 which may affect shrinkage results.

10.3 *Drycleaning Procedure*—Run through the complete dry-to-dry cycle in the machine. Run the solvent phase of the drycleaning cycle with the solvent no higher than 32°C (90°F). During the drying phase of the drycleaning cycle, either the air outlet temperature should not exceed 60°C (140°F) or the inlet air temperature should not exceed 80°C (175°F). If heat-sensitive fibers, for example, modacrylic fibers, are involved, the outlet air temperature should not exceed 40°C (105°F) or the inlet air temperature should not exceed 60°C (140°F). After the complete drycleaning cycle, remove the sample from machine for examination and reconditioning.

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[10] Model X-5, available from Edward H. Benz Co., 283 Whiteford Ave., Providence, RI 02908, has been found satisfactory.

[11] Formula 886, petroleum sulfonate type or staticol, amine sulforate type, available from R. R. Street, Inc., 561 W. Monroe St., Chicago, IL; or Perksheen 324, amine sulfonate type, available from Adco, Inc., 900 W. Main St., Sedalia, MO, have been found suitable for this purpose.

10.4 Repeat the drycleaning operation through two additional cycles. At the end of the third cycle remove the test specimens from the machine, lay on a flat surface, smooth the test specimens by hand, and examine. Press the test specimens using the steam press according to the following cycle:

10.4.1 Five seconds steam with head up.

10.4.2 Five seconds dry hot press with head down, 145 to 151°C (293 to 303°F) of steam pressure at the press.

10.4.3 Five seconds vacuum, steam off, head down.

10.4.4 Five seconds vacuum, steam off, head up.

10.4.5 Allow the pressed specimens to condition in the standard atmosphere for testing textiles for at least 4 h.

10.5 Measure the distance between each of the six sets of reference marks on each test specimen.

10.6 Lay the fabric flat on a table or board with a surface rough enough so that the fabric side touching the table will not readily slide. Examine each test specimen for any evidence of delamination. Place the fingers on the specimen and attempt to slide the upper fabric layer over the bottom or intermediary substrate. If in doubt, make a small cut through the specimen with scissors to determine if any separation of substrates has occurred. Turn the fabric over and make the same type of examination on the other side.

10.7 Examine the face fabric for any alteration in appearance as compared with the original sample. This may be done with conventional room lighting, or with "Lighting Equipment for Viewing Test Specimens," as described in Fig. 1 of AATCC Method 124 – 1984. Examine only the area of the test specimen bounded by the stitching.

11. Laundering Procedure

11.1 *Machine Laundering*—Wash the test specimens in the automatic home laundry machine, using 50 g of laundry detergent, or a sufficient amount to give a safe suds level, at the applicable domestic automatic temperature and procedure under which the fabric is to be marketed. In the absence of this information use the "normal" cycle and high water level settings and determine the washing temperature according to the fabric type and construction as follows:

11.1.1 Face fabrics containing 20 % or more of wool, acetate, modacrylic, or acrylic fibers, 41 ± 3°C (105 ± 5°F).

11.1.2 Face fabrics of tricots, circular knits, woven nylon, and print fabrics other than those described under 11.1.1, 49 ± 3°C (120 ± 5°F).

11.1.3 All other woven face fabrics, 60 ± 3°C (140 ± 5°F).

11.2 *Load for Machine Laundering*—Use a total load of 1.8 kg (4 lb) including test specimens plus a dummy load of approximately 380 by 380 mm (15 by 15 in.) fabrics of similar fabric construction. Load all fabrics in the flat position.

11.3 *Hand Laundering*—If the fabrics are to be designated "Hand Washable," dissolve 20 g of laundry detergent in 7.6 L (2 gal) of water at 41 ± 3°C (105 ± 5°F) in a 9.5-L (10-qt) pail and then add two test specimens. Wash by lifting each specimen out of the bath followed by immediate reimmersion at least ten times. Just before the final reimmersion, lightly rub by hand the center of each specimen separately for a period of 1 min. Rinse by transferring the specimens to 7.6 L of water at 41 ± 3°C (105 ± 5°F) and gently agitating the specimens by hand for a period of 2 min with no twisting or wringing. Remove the specimens and dry as directed in 11.6.

11.4 *Tumble Drying*—Immediately after the first wash cycle, as directed in 11.1, remove the test specimens and dummy load from the laundry machine and transfer to the tumble dryer. Run the dryer at the "moderate" setting and dry for the minimum time required for adequately drying the fabrics being tested. Remove the test specimens and dummy load immediately following the shut-off and examine.

11.5 Repeat the washing and drying cycles as directed in 11.1 and 11.4 four more times. After the fifth cycle, remove the test specimens, lay on a flat surface, smooth by hand, and examine. Press the face fabric side lightly with a sliding action using the hand steam iron, with no pressure other than the weight of the iron. If no ironing temperature is specified for the face fabric, use the safe ironing temperature guide appearing in Table 1. Allow the specimens to condition on a flat surface in the standard atmosphere for testing textiles for a minimum of 4 h before rating and measuring as directed in 10.5-10.7.

11.6 *Drip Drying*—Remove the specimens from the pail or from the automatic washer just before the water begins to drain for the final spin-dry cycle, squeeze by hand without wringing or twisting, and hang each specimen by two adjacent corners, with the fabric length in the vertical direction, in still air at room temperature until dry and examine.

11.7 Repeat the washing and drying cycles as directed in 11.2 or 11.3, and 11.6, four more times. After the fifth cycle, lay on a flat surface, smooth the test specimens by hand, and examine. Press the face fabric side lightly with a sliding action using a hand steam iron with no pressure other than the weight

TABLE 1 Safe Ironing Temperature Guide

Class 0	Class I	Class II	Class III	Class IV
Below 121°C (250°F)	121 to 135°C (250 to 275°F)	149 to 163°C (300 to 325°F)	177 to 191°C (350 to 375°F)	204°C (400°F) and Above
Modacrylic 93 to 121°C (200 to 250°F)	Acetate	Triacetate (unheat set)	Nylon 66	Cotton
	Olefin (polypropylene)	Acrylic	Polyester	Fluorocarbon Glass
Olefin (polyethylene) 79 to 121°C (175 to 250°F)	Silk	Azlon Nylon 6		Hemp, Jute Ramie
Rubber 82 to 93°C (180 to 200°F)		Spandex Wool		Linen Rayon, Viscose
Saran 66 to 93°C (150 to 200°F)				Triacetate (heat set)
Vinyon 54°C (130°F)				

TABLE 2 Components of Variance Shrinkage

		Single-Operator Component Percentage Points	DF	Between-Laboratory Component Percentage Points	DF
Drycleaning	length shrinkage	0.68	45	0.97	4
	width shrinkage	0.59	45	0.77	4
Hand wash-line dry	length shrinkage	1.00	20	1.48	4
	width shrinkage	0.33	20	1.11	4
Machine wash-tumble dry	length shrinkage	0.56	25	0.79	4
	width shrinkage	1.00	25	1.18	4

TABLE 3 Critical Differences, Percentage Points, Between Average Percentages for the Conditions Noted

	Number of Observations in Each Average	Length Shrinkage		Width Shrinkage	
		Single-Operator Precision	Between-Laboratory Precision	Single-Operator Precision	Between-Laboratory Precision
Drycleaning	2	1.4	4.2	1.2	3.6
	4	1.1	4.1	1.0	3.3
	6	0.8	4.0	0.7	3.2
Hand wash-line dry	2	2.1	6.3	0.6	4.4
	4	1.5	6.1	0.5	4.4
	6	1.2	6.0	0.4	4.3
Machine wash-tumble dry	2	1.2	3.4	2.1	5.2
	4	0.9	3.3	1.5	5.0
	6	0.7	3.2	1.2	4.9

of the iron. If no ironing temperature is specified for the face fabric, the safe ironing temperature guide appearing in Table 1 may be used. Allow the specimens to condition on a flat surface in the standard atmosphere for testing textiles for a minimum of 4 h before rating and measuring as directed in 10.5-10.7.

NOTE 6—All specimens hand washed as directed in 11.3 should be drip dried. Specimens machine washed as directed in 11.1.1 should be drip dried only when the fabrics are to be marketed as "Machine Wash, Drip Dry."

12. Calculation

12.1 Calculate the shrinkage or gain in each direction by averaging the three measurements in each direction on each test specimen and using these average measurements in accordance with Eq 3:

$$\text{Shrinkage, \%} = (A - B)100/A \qquad (3)$$

where:

A = average original distance between bench marks, and
B = average final distance between bench marks.

12.2 Calculate the average length shrinkage and the average width shrinkage of both test specimens separately fordrycleaning and for each laundering and drying procedure used.

13. Precision and Bias

13.1 *Interlaboratory Test Data*[12]—An interlaboratory test, in which nine different bonded and laminated fabrics were used, was run during 1969. Five laboratories participated and calculated the percent shrinkage in length and width as a result of drycleaning, hand washing followed by line drying, and machine washing followed by tumble drying. The calculated components of variance expressed as standard deviations and the degrees of freedom on which they are based are shown in Table 2.

NOTE 7—The within-laboratory (multioperator) component was not determined separately and is included in the between-laboratory component.

13.2 *Precision*—Based upon the components of variance stated in Table 2, the average test results should be considered significantly different at the 95 % probability level if the difference equals or exceeds the differences listed in Table 3.

NOTE 8—The critical differences listed in Table 3 were calculated using the values of t that correspond to the degrees of freedom listed in Table 2.

13.3 *Bias*—The procedure in Test Methods D 2724 for measuring dimensional stability during drycleaning or laundering has no bias because the value of this property can be defined only in terms of a test method.

STRENGTH OF BOND (OPTIONAL)

14. Test Conditions

14.1 Bond strength tests may be made on the fabric as bonded or laminated, or after the three specified drycleaning cycles or after the five specified laundering cycles. These tests also may be made on dry specimens (conditioned in the standard atmosphere for testing textiles for a minimum of 4 h), or on wet specimens (saturated with perchlorethylene at room temperature following the drycleaning tests or saturated with water at room temperature following the laundering tests).

14.2 Alternatively, following the drycleaning tests, wet strength-of-bond tests may be made on flame-laminated fabrics with the specimens saturated in water instead of perchlorethylene. An interlaboratory test run in 1975[9] showed no significant differences between perchlorethylene and water in wet tests on flamelaminated fabrics. However, there were significant differences on adhesive-bonded fabrics. Therefore, water is not a suitable substitute for perchlorethylene in wet tests on these fabrics.

15. Procedure for Bonded and Fused Fabrics

15.1 Manually separate the two layers of fabric along the

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[12] ASTM Research Report RR: D13-1003 is available on loan from ASTM Headquarters, 100 Barr Harbor Drive, West Conshohocken, PA 19428.

76.2 mm (3 in.) width of each test specimen for a distance of approximately 25 mm (1 in.) in the direction of the specimen length.

15.2 Set the lower clamp at a distance of 25 mm (1 in.) from the upper clamp. Secure the separated face fabric of a test specimen in the upper clamp of the tensile testing machine in such a way that the longitudinal axis of the specimen forms a right angle with the closed clamping surface. Secure the separated backing fabric in the lower clamp of the machine in such a way that the longitudinal axis of the specimen forms a right angle with the closed jaws of the lower clamp.

15.3 If the indicating scale on the machine is provided with a pawl and ratchet mechanism, disengage the mechanism to permit readings of variable force when the machine is placed in operation.

15.4 Operate the machine at a pulling speed of 5.1 ± 0.2 mm/s (12 ± 0.5 in./min).

15.5 Estimate the bond strength to the nearest 140 mN (0.5 ozf) as the average of at least the five highest and the five lowest peak loads of resistance per inch of width, registered for 100 mm (4 in.) of delamination.

15.6 Repeat the operations described in 15.2-15.5 for each of the remaining two test specimens.

15.7 Report the bond strength in ounces per inch of width as the average strength of the three test specimens.

16. Procedure for Laminated Fabrics

16.1 Manually separate the face fabric from the foam along the 76.2-mm (3-in.) width of each test specimen for a distance of approximately 25 mm (1 in.) in the direction of the specimen length.

16.2 Set the lower clamp at a distance of 25 mm (1 in.) from the upper clamp. Secure the separated face fabric of a test specimen in the upper clamp of the tensile testing machine in such a way that the longitudinal axis of the specimen forms a right angle with the closed clamping surface. Secure the separated foam or foam and backing fabric in the lower clamp of the machine in such a way that the longitudinal axis of the specimen forms a right angle with the closed jaws of the lower clamp.

16.3 Proceed as instructed in 15.3-15.7.

16.4 If foam is laminated to a backing fabric, retain each test specimen from 16.3 after the bond strength has been determined for face to foam. Manually separate the backing fabric from the foam as instructed in 16.1 except that the manual separation should be made at the opposite end of the test specimen separated for the face fabric-to-foam test.

16.5 Set the lower clamps at a distance of 25 mm (1 in.) from the upper clamp. Secure the separated foam or foam and face fabric of a test specimen in the upper clamp of the tensile testing machine in such a way that the longitudinal axis of the specimen forms a right angle with the closed clamping surface. Secure the separated backing fabric in the lower clamp of the machine in such a way that the longitudinal axis of the specimen forms a right angle with the closed jaws of the lower clamp.

16.6 Proceed as instructed in 15.3-15.7.

16.7 Examine both sides of the foam on the test specimens after testing for bond strength. Determine whether the foam portion ruptured during delamination allowing some foam to adhere to either fabric surface. If this has occurred, make the notation "foam tear" for that test specimen for the side or sides where "foam tear" occurred. If "foam tear" occurs on only one side of one test specimen, disregard this result and report the average bond strength for that side of the remaining two specimens. If "foam tear" occurs on the same side of two or three specimens, report the bond strength for that side as "foam tear."

16.8 In the event it is impossible to separate manually the foam from either the face or the backing fabric as instructed in 16.1 and 16.4 without rupturing the foam, report the bond strength for the side or sides where this occurs as "foam tear."

17. Report

17.1 State that the tests were made as directed in ASTM Test Methods D 2724. Describe the material or product sampled and the method of sampling used.

17.2 Report the following information:

17.2.1 The individual length and width dimensional changes to the nearest 0.5 % for each test specimen as well as the average length and width shrinkage for both test specimens and identify these results with the procedures used.

17.2.2 The absence or presence of any delamination in the drycleaned or laundered and dried specimens before pressing or ironing. Use the term "acceptable bond" for fabrics that have not delaminated and "unacceptable bond" for fabrics that have delaminated. In the case of three-layer laminated fabrics, report whether the delamination has occurred on the face or backing fabric or both. Rate the lot as "unacceptable" if either fabric has delaminated.

17.2.3 Any alteration in appearance or esthetic properties of the drycleaned or laundered and dried specimens when compared with the residual portion of the original sample. For example, report whether the specimens, identified by the drycleaning or laundering and drying procedures used, show:

17.2.3.1 Puckering,
17.2.3.2 Crack marks,
17.2.3.3 Bubbling or blisters,
17.2.3.4 Face fabric pilling,
17.2.3.5 Loss or gain of stiffness,
17.2.3.6 Color change, and
17.2.3.7 Wrinkles.

17.2.4 If strength of bond tests were run, report the following information along with the solvent used for wet specimens:

17.2.4.1 Whether the tests were run on the fabric as bonded or laminated, or after the three drycleaning cycles, or after the five laundering cycles.

17.2.4.2 Whether the tests were run on dry or wet specimens as described in Section 14.

17.2.4.3 Whether constant rate of transverse or constant rate of extension type tensile testing machine was used.

NOTE 9—While this method provides for three drycleaning cycles, five laundering and drying cycles, or both, the number of cycles can be decreased or increased for special purposes but in this case the report should state what cycles were used.

18. Precision and Bias

18.1 *Interlaboratory Test Data*[11]—An interlaboratory test, in which nine different bonded and laminated fabrics were used, was run during 1969. Five laboratories participated and recorded the average wet bond strength (sometimes called wet peel bond strength) for 76-mm (3-in.) wide specimens after drycleaning, hand washing, and machine washing the specified number of times. No data is reported for machine wash-tumble dry wet-bond strength because some of the fabrics delaminated before the five wash cycles were completed and some exhibited "foam tear." Of the participating laboratories, four used the constant rate of extension type tensile testing machine, and one used the constant rate of traverse type machine. The calculated components of variance expressed as standard deviations and the degrees of freedom on which they are based, are listed in Table 4.

18.2 *Precision*—Based upon the components of variance stated in 18.1, the average test results should be considered significantly different at the 95 % level if the difference equals or exceeds the differences listed in Table 5.

NOTE 10—The critical differences listed in Table 5 were calculated using the values of *t* that correspond to the degrees of freedom listed in Table 4.

18.3 *Bias*—The procedure in Test Methods D 2724 for measuring strength of bond has no bias because the value of this property can be defined only in terms of a test method.

NOTE 11—The nature of the bonding and laminating processes which involve the adhesion of two or three components with adhesive systems that apply the adhesive in discrete quantities in a discontinuous form on the textile surface, produces bonded and laminated fabrics that are nonuniform in their bond strength characteristics. Considerable variations in bond strength are commonly found at various points across the width of the fabric and from one end to the other in a single piece. Because of this, it is often desirable to report the bond strength value of the test specimen with the lowest bond strength in addition to reporting the average as specified in 15.7.

TABLE 4 Components of Variance, Wet Bond Strength

	Single-Operator Component, oz/in.	DF	Between-Laboratory Component, oz/in.	DF
Drycleaning	0.54	30	0.00	4
Hand wash-line dry	0.23	15	0.48	4

TABLE 5 Critical Differences, Wet Bond Strength

	Number of Observations in Each Average	Critical Differences oz/1 in. Wide Test Specimen	
		Single-Operator Precision	Between-Laboratory Precision
Drycleaning	2	1.1	1.1
	3	0.9	0.9
	4	0.8	0.8
Hand wash-line dry	2	0.6	2.0
	3	0.5	1.9
	4	0.4	1.9

19. Indexing Terms

19.1 This standard is indexed under the following terms: apparel, bonded fabric, and delamination strength.

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Standard Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D-19 on Water[1]

This standard is issued under the fixed designation D 2777; 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 establishes uniform standards for estimating and expressing the precision and bias of applicable test methods for Committee D-19 on Water.

1.2 Except as specified in 1.3, 1.4, and 1.5, this practice requires the task group proposing a new test method to carry out a collaborative study from which statements for precision (overall and single-operator standard deviation estimates) and bias can be developed. This practice provides general guidance to task groups in planning and conducting such determinations of precision and bias.

1.3 If a full-scale collaborative study is not technically feasible, due to the nature of the test method or instability of samples, the largest feasible scaled-down collaborative study shall be conducted to provide the best possible limited basis for estimating the overall and single-operator standard deviations.

1.3.1 Examples of acceptable scaled-down studies are the local-area studies conducted by Subcommittee D19.24 on microbiological methods because of inherent sample instability. These studies involve six or more completely independent local-area analysts who can begin analysis of uniform samples at an agreed upon time.

1.3.2 If uniform samples are not feasible under any circumstances, a statement of single-operator precision will meet the requirements of this practice. Whenever possible, this statement should be developed from data generated by independent multiple operators, each doing replicate analyses on independent samples of a specific matrix type, which generally fall within specified concentration ranges (see 7.2.5.2(*3*)).

1.3.3 This practice is not applicable to methodology involving continuous sampling or measurement, or both, of specific constituents and properties.

1.3.4 This practice is also not applicable to open-channel flow measurements.

1.4 A collaborative study that satisfied the requirements of the version of this practice in force when the study was conducted will continue to be considered an adequate basis for the precision and bias statement required in each test method. If the study does not satisfy the current minimum requirements for a collaborative study, a statement listing the study's deficiencies and a reference to this paragraph shall be included in the precision and bias statement as the basis for an exemption from the current requirements.

1.5 This paragraph relates to special exemptions not clearly acceptable under 1.3 or 1.4. With the approval of Committee D-19 on the recommendation of the Results Advisor and the Technical Operations Section of the Executive Subcommittee of Committee D-19, a statement giving a compelling reason why compliance with all or specific points of this practice cannot be achieved will meet both ASTM requirements **(1)**[2] and the related requirements of this practice. Precision and bias statements authorized by this paragraph shall include the date of approval by Committee D-19.

1.6 In principle, all test methods are covered by this practice.

1.7 In Section 11 this practice shows exemplary precision and bias statement formats for: (*1*) test methods yielding a numerical measure, (*2*) test methods yielding a non-numerical report of success or failure based on criteria specified in the procedure, and (*3*) test methods specifying that procedures in another ASTM test method are to be used with only insignificant modifications.

1.8 All studies, even those exempt from some requirements under 1.3 or 1.5, shall receive approval from the Results Advisor before being conducted (see Section 8) and after completion (see Section 12).

2. Referenced Documents

2.1 *ASTM Standards:*

D 1129 Terminology Relating to Water[3]
D 1141 Specification for Substitute Ocean Water[3]
D 1193 Specification for Reagent Water[3]
D 4375 Terminology for Basic Statistics in Committee D-19 on Water[3]
D 5790 Test Method for Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry[4]
D 5905 Specification for Substitute Wastewater[3]

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[1] This practice is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.02 on General Specifications, Technical Resources, and Statistical Methods.

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[2] The boldface numbers in parentheses refer to the list of standards at the end of this practice.

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

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

E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods[5]
E 178 Practice for Dealing with Outlying Observations[5]
E 456 Terminology Relating to Quality and Statistics[5]
E 1169 Guide for Conducting Ruggedness Tests[5]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this practice, refer to Terminologies D 1129, D 4375 and E 456, and Practice E 177.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *accuracy*—a measure of the degree of conformity of a single test result generated by a specific procedure to the assumed or accepted true value and includes both precision and bias.

3.2.2 *bias*—the persistent positive or negative deviation of the average value of a test method from the assumed or accepted true value.

3.2.3 *laboratory*—a single and completely independent analytical system with its own specific apparatus, source of reagents, set of internal standard operating procedures, etc. Different laboratories will differ from each other in all of these aspects, regardless of how physically or organizationally close they may be to each other.

3.2.4 *operator*—usually the individual analyst within each laboratory who performs the test method throughout the collaborative study. However, for complicated test methods, the operator may be a team of individuals, each performing a specific function throughout the study.

3.2.5 *precision*—the degree of agreement of repeated measurements of the same property, expressed in terms of dispersion of test results about the arithmetical mean result obtained by repetitive testing of a homogeneous sample under specified conditions. The precision of a test method is expressed quantitatively as the standard deviation computed from the results of a series of controlled determinations.

4. Summary of Practice

4.1 After the task group has assured itself that the test method has had all preliminary evaluation work completed, it should prepare the test method write-up in final form. The plan for collaborative study is developed in accordance with this practice and submitted along with the test method write-up to the Results Advisor for concurrence except as specified in 1.3, 1.4, and 1.5. Upon receipt of concurrence, the collaborative test is conducted, data analyzed, and precision and bias statements formulated by the task group. The final precision and bias statistics must be based on retained data from at least six independent laboratories. The statements, with backup data including the reported results summary, the calculations leading up to the statements, and the test method write-up with precision and bias statements included are submitted to the subcommittee vice-chairman who in turn sends a copy of it to the Results Advisor for concurrence before balloting. This assures having an acceptable copy of the collaborative study results to send to ASTM for items on the main committee ballot. In most instances, the collaborative study shall be complete before a subcommittee ballot. If the collaborative study is not complete, the test method may go on the ballot as a provisional test method rather than a standard test method. Copies of the test data, approved calculations, and statistical results shall be filed at ASTM Headquarters when the test method is submitted by the subcommittee chairman as an item for the main committee ballot.

4.1.1 The appendix shows an example of "Form A—Approval of Plans for Interlaboratory Testing," as Fig. X1.1.

4.1.2 For an example of a data reporting form, see Fig. X2.1.

4.1.3 In addition, the appendix shows a sample calculation of precision and bias from real collaborative test data, the related table of statistics, and the related precision and bias statement.

5. Significance and Use

5.1 Following this practice should result in precision and bias statements which can be achieved by any laboratory properly using the test method studied. These precision and bias statements provide the basis for generic limits for use in the Quality Control section of the test method.

5.2 The method specifies the media for which the test method is appropriate. The collaborative test corroborates the write-up within the limitations of the test design. An extensive test can only use representative media so that universal applicability cannot be implied from the results.

5.3 The fundamental assumption of the collaborative study is that the media tested, the concentrations tested, and the participating laboratories are a representative and fair evaluation of the scope and applicability of the test method as written.

6. Preliminary Studies

6.1 Considerable pilot work on a test method must precede the determination of its precision and bias **(2,3)**. This pilot work should explore such variables as preservation requirements, reaction time, concentration of reagents, interferences, calibration, and sample size. Potentially significant factors must be investigated and controlled in the written test method in advance of the collaborative test. Also, disregard of such factors may introduce so much variation among operators that results are misleading or inconclusive **(4)** (see 9.3 and 9.4). A ruggedness study conducted in a single laboratory is particularly useful for such investigations and should be conducted to prove a test method is ready for interlaboratory testing (see Guide E 1169 for details).

6.2 Only after a proposed test method has been tried, proved, and reduced to unequivocal written form should a determination of its precision and bias be attempted.

7. Planning the Collaborative Test

7.1 Based upon the task group's knowledge of a test method and having the unequivocal write-up, several factors must be considered in planning the collaborative test to properly assess the precision of the test method. The testing variables that must be considered in planning are discussed below. It is generally not acceptable to control significant sources of variability in the

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[5] *Annual Book of ASTM Standards*, Vol 14.02.

collaborative study which cannot be controlled in routine use of the test method, because this leads to false estimates of the test method precision and bias. In addition, the task group must determine within the resources available how to best estimate the bias of the test method.

7.2 *Testing Variables*:

7.2.1 It is desirable to develop a statement of precision of a test method that indicates the contribution to overall variation of selected causes such as laboratory, operator, sample matrix, analyte concentration, and other factors that may or have been shown to have strong effects on the results. Since any test method can be tried in only a limited number of applications, the standard deviation calculated from the results of a study can be only an estimate of the universe standard deviation. For this reason, the symbol s (sample standard deviation) is used herein. The precision estimates generated from the study data will usually be the overall standard deviation (s_T) and the pooled single-operator standard deviation (s_o) for each sample matrix and concentration studied.

7.2.2 Laboratories, operators, sample matrices, and analyte concentrations are the only sources of variability represented in the precision and bias statements resulting from the usual collaborative study. They may not represent the additional influence that can arise from differences in sample splitting, field preservation, transportation, etc., all of which may influence routine analytical results as shown in the general precision definitions in Terminology D 1129.

7.2.3 *Laboratories*—The final precision and bias statistics for each analyte, matrix, and concentration must be based on data from at least six laboratories that passed all of the outlier tests (see 10.3 and 10.4), that is, retained data. To be assured of meeting this requirement, it is recommended that usable data be obtained from a minimum of eight independent laboratories. To guarantee eight providing usable data, it will often be necessary to get ten or more laboratories to agree to participate, because some may not provide data and others may not provide usable data. Maximizing the number of participating laboratories is often the most important thing that can be done to guarantee a successful study.

7.2.4 Even if the single-operator standard deviation is the only statistic to be estimated in the study (see 1.3.2), there should be a minimum of eight operators providing usable data, so you are assured of data from six operators after all outlier removal.

7.2.5 *Sample Matrices*—The collaborative study shall be conducted with at least one representative sample matrix, which should be reproducible by subsequent user-laboratories so that they can compare their results with the results of the collaborative study.

7.2.5.1 Typically, a reagent water prepared according to Specification D 1193 or a synthetic medium, such as the substitute wastewater described in Specification D 5905 or the substitute ocean water described in Specification D 1141, is used as the reference matrix. Analytes may be supplied separately as concentrates for addition to this matrix by each laboratory or the reference matrix containing the analyte(s) may be supplied to each participant. Information on how the reference matrix was prepared in the study shall be clear in the precision and bias statement of the test method so users can reproduce it properly.

7.2.5.2 Additional collaborative testing should also be conducted using other matrices specified in the scope of the test method. Since these matrices must be the same for each study participant, they may have to be prepared (or obtained from a single source), preserved, and distributed to all laboratories. As with the reference matrix, analytes may be supplied in a separate spiking solution or already added to the matrix. A particularly attractive matrix might be a standard material available from an organization such as the National Institute of Standards and Technology (NIST). Use of uniform sample matrices is necessary in these studies since they enable a more certain comparison with the reference matrix than is possibly with matrices supplied separately by each participant.

(1) Use of matrices with naturally occurring, non-zero background levels of the analyte(s) being studied will result in precision and bias estimates that will be much more difficult to properly compare with estimates from the reference matrix.

(2) Any matrix spiking that may be necessary shall not significantly change the natural characteristics of the matrix.

(3) With the exception of the kind of limited study described in 1.3.2, the matrix-of-choice approach, in which each participant is expected to acquire their own sample of a designated type, should not be used. Such studies are basically incompatible with the statistical approaches employed in this practice; both the ranking test and the individual outlier test are incapable of distinguishing laboratory effects from matrix effects. In addition, the presence of variable background concentrations prevents the assignment of a proper mean concentration level to each precision estimate produced in the study.

7.2.5.3 The same study design should be used for all sample matrices. A separate precision and bias statement should be generated for each sample matrix with a brief description of the matrix tested.

7.2.5.4 When studies are available indicating the applicability of the test method for matrices untested in 7.2.5.1 and 7.2.5.2 and not meeting the other requirements of this practice, at the discretion of the task group responsible for the test method and the Results Advisor, and providing the data are analyzed in accordance with Section 10 of this practice, this supporting data may be included in a separate section of the precision and bias statement. A clear but brief description of the matrices shall be included and the study protocol employed. It is the intent of this practice that ultimately, data concerning the precision and bias of the test method in the full range of matrices covered in the scope and analyzed in accordance with this practice, will be made available to the users of the test method.

7.2.6 *Analyte Concentrations*—If pilot work has shown that precision is linear with increasing analyte concentrations, at least three Youden pairs **(5)**, that is, six concentrations, covering the range of the test method should be included for each matrix. If the pilot work suggests that precision is other than constant or linear, more concentration levels should be analyzed. The study concentrations should generally be rather uniformly distributed over the range of the test method.

7.2.6.1 Study samples with concentrations at or near the detection limit of a test method are likely to produce non-quantitative results from many of the participating laboratories if participants are permitted to use their detection limit to censor their results. Zeroes or less thans that result from this censoring process are non-quantitative results and cannot be included in the statistical analysis of study results specified later in this practice. Conducting the specified statistical analysis on whatever quantitative data are available under such circumstances can produce misleading precision and bias estimates. If it is considered necessary to include samples at or near the detection limit, such samples shall be in addition to the minimum required three Youden pairs at concentrations that can be readily measured by qualified laboratories. Data from analyses of the basic three or more Youden pairs that can be quantified can then be statistically analyzed as specified to produce a proper traditional precision and bias statement for the test method. Results from analyses of Youden pairs at or near the detection limit can be included in this traditional statistical analysis if it turns out that most laboratories report quantified results. Otherwise, results for low-level samples must be statistically analyzed using specialized procedures, for example, procedures similar to those under development in Subcommittee D19.02, which are beyond the scope of this practice.

7.2.7 Since the order of analyses should not be a source of systematic variability in the study, each participant should either be told to randomize the order of study sample analyses or be given a specific random order for their analyses.

7.2.7.1 Whenever the time of analyses has been shown to influence the analytical results, close control over the time of analyses will be essential.

7.2.8 If pilot work has shown that the sample container must be of a specific material prepared in a specific manner prior to use, the variation in containers obtained and prepared by the participants will be a random variable and should be treated as such in the planning of the study and in the statistical analysis of the data.

7.2.9 The manner of preservation or other treatment of the sample prior to typical use of the test method, if known to affect the precision or bias, or both, of results, shall be incorporated into the collaborative study design.

7.3 *Measurement of Precision:*

7.3.1 Every interlaboratory study done to provide precision and bias estimates for a D-19 test method must use a Youden-pair design rather than a replicate sample design. Justifiable exceptions to this requirement shall be approved through the process provided in 1.5. In a Youden-pair design, each participant receives (or prepares from a concentrate) a separate sample *for each analysis required in the study*. There are no replicate analyses; each participant analyzes each study sample once and only once, per analyte if appropriate. Among the set of samples each laboratory analyzes for a specific matrix, there are pairs of samples containing similar but usually different analyte concentrations that differ from each other by up to 20 %. As a matter of convenience to whomever is preparing the samples or spiking concentrates, up to half the Youden pairs may have the same concentration, that is, be blind duplicates, but the participants must have no basis for comparing their single test results from analyses of different study samples.

7.3.2 The only difference in treatment of data from a Youden-pair study is the calculation used to estimate the means and standard deviations; these calculations may be found in Youden and Steiner **(6)**. Once developed, these mean and standard deviation estimates are treated the same as statistics from a study with the usual replicate design. A detailed example with and without raw experimental data is given in Refs. **(7)** and **(8)**, respectively.

7.3.3 The value of the nonreplicate design is that the single-operator standard deviation estimates are free of any conscious or unconscious analyst bias. The procedures for calculating overall and single-operator standard deviations are given in 10.4 and 10.5 and illustrated in Appendix X3.

7.4 *Measurement of Bias:*

7.4.1 The concept of accuracy comprises both precision and bias (see Terminology D 1129 and Practice E 177). As discussed in Practice E 177, there is not a single form for statements of accuracy that can be universally recommended. Since the accuracy of a measurement process is affected by both random and systematic sources of error, measures of both kinds of error are needed. The standard deviation is a universal measure of random sources of error (or precision). Bias is a measure of the systematic errors of a test method.

7.4.2 A collaborative study evaluation of bias for a specific matrix produces a set of analyte/sample means. The difference between a true value (however defined) and the related mean is an estimate of the average systematic error, that is, bias of the test method.

7.4.3 There are three major approaches commonly used to test a measurement procedure: (*1*) measurement of known materials, (*2*) comparison with other measurement procedures, and (*3*) comparison with modifications of the procedure itself **(9)**. The third approach may involve the standard addition technique or the simultaneous analysis of several aliquots of different sizes (for example, 0.5, 1, 1.5, 2, 2.5 units). The task group will select the approach that best suits its needs within the resources available to it.

7.4.4 The most likely task group approach will be the use of known materials. Since reference standards are unlikely to be available, the task group will prepare its samples with added (therefore known to them) quantities of the constituent(s) being tested. The best available chemical and analytical techniques for preparing, stabilizing, if necessary, storing and shipping the prepared samples should be known within the task group and will not be addressed in this practice. However, if the sample preparation and handling techniques used for the study are different from those expected to be used for samples during routine application of the test method, those differences shall be pointed out in the precision and bias statement. Future users of the test method may decide that these differences had an effect on the precision or bias results, or both, from the study.

7.5 *Quality Control During the Study:*

7.5.1 The Quality Control section to appear in the test method must be drafted before the collaborative study design is finalized and the study design must assure that the collaborative study will produce any background data not otherwise available to properly complete the final Quality Control section. Each part of the draft Quality Control section must be used during the collaborative study unless insufficient background data exist to establish credible interim required performance criteria for that part.

7.5.2 All quality control data/information produced to meet the requirements of 7.5.1 shall be reported to the task group chair along with results from analyses on the study samples.

8. Collaborative Study Design Approval

8.1 After approval by the task group, the task group chair (or designee) will summarize the proposed design of the collaborative study. This summary will include: (*1*) the test method to be tested in ASTM format and as approved by the task group; (*2*) the analytes to be included in the study; (*3*) the number of samples in accordance with the paired-sample plan of 7.3.1; (*4*) the approach for determining the bias of the test method as exemplified in the collaborative study; (*5*) the range of concentration covered, and approximate concentration of material in each sample or set; (*6*) the approximate number of laboratories and analysts; (*7*) the matrices and QC samples being tested; (*8*) plans for developing study samples; and (*9*) a copy of the instruction and data reporting package to be given to each study participant. This summary should be presented to the Results Advisor in the form of a letter.

8.1.1 As an aid, the task group chairman may use, "Approval of Plans for Interlaboratory Testing," Form A, and in Appendix X1 (a completed example is shown in Fig. X1.1).

8.2 Upon review of the plan, the Results Advisor will advise the task group chairman whether the plan meets the requirements of this practice or what changes are necessary to meet the requirements of this practice.

8.3 Upon receipt of approval of the collaborative test plan by the Results Advisor, the task group chairman (or designee) will conduct the collaborative test.

9. Conducting the Collaborative Study

9.1 A single entity, acting for the task group, will prepare the samples for the collaborative study and ship them to the participants with instructions for the study, a copy of the exact test method (if not already supplied), and the participant reporting form (or reporting instructions).

9.1.1 The instructions for the collaborative study shall require sufficient preliminary work by potential collaborators to adequately familiarize them with the test method prior to study measurements. This is necessary to ensure that each collaborative study is made by a peer group and that a learning experience is not included in the statistics of the collaborative study. The task group may also develop procedures to qualify prospective collaborators, and this approach is strongly recommended.

9.1.2 Each laboratory should usually supply its own calibration materials, as independent calibration materials are a significant source of interlaboratory variability. However, if the cost of availability of calibration materials is judged to be a significant deterrent to participation or if currently available materials are inadequate and not considered typical for subsequent routine use of the test method, these materials may be distributed with the study samples. If calibration standards are provided, the Precision and Bias section of the test method should so note, including the concentrations and matrix of the standards and any specific instructions for their use.

9.1.3 As an aid, the task group chairman may use Form B, "Data Report from Individual Laboratories," as in Appendix X2 (a completed example is shown in Fig. X2.1).

9.2 The batch of samples containing a specific member of a Youden pair should be clearly marked with a common unique code, informative to the distributors but not informative to the study participants. Samples should be sized to supply more than the minimum amount necessary to participate in the study (with reasonable allowance for pipetting, rinsing, etc.) to allow for trial runs and analytical restarts that may be necessary. A separate set of samples shall be provided for each operator. Sample concentrations should not be easily surmised values (1, 5, etc.). The assignment of samples to the participating laboratories should be randomized within each concentration level. The above recommendations should help assure statistical independence of results.

9.3 A copy of the test method under investigation, the written instructions for carrying out his/her part of the program, and the necessary study samples should be supplied to each operator. No supplementary instructions or explanations such as by telephone or from a task group member within a cooperating laboratory should be supplied to one participant if not to all. Study materials should be distributed from one location, and the operator's reports should be returned to one location.

9.4 The written instructions should cover such items as: (*1*) directives for storing and subdividing the sample; (*2*) preparation of sample prior to using the test method; (*3*) order of analyses of samples (random order within each laboratory is often best); (*4*) details regarding the reporting of study results on the reporting form; and (*5*) the time limit for return of the reporting form.

9.4.1 Laboratories shall be required to report all figures obtained in making measurements, instead of rounding results before recording them. This may result in recording one or more significant figures beyond what may be usual in the Report section of the test method. A decision about rounding all data can be made by the task group when the final statistical analyses are performed.

9.4.2 The laboratories shall report results from analyses of study samples without background subtraction and shall also report background levels for every matrix that they use in the study. The task group will make any background corrections that may be necessary.

9.4.3 Zeros and negative numbers should be reported whenever they represent the actual test results produced. Test results should never be censored by a participant. The reporting of less than or greater than results negates the objectivity of subsequent statistical calculations and should be avoided. Never report zero in place of a less-than or other nonquantitative test result.

9.5 The task group chair (or designee) should monitor the collaborative study to assure that results are reported back within the agreed upon time limit and are free of obvious procedural, transcription, clerical, or calculation errors. Careful design of the reporting form (or reporting instructions) will facilitate this task.

10. Collaborative Study Data Analysis

10.1 For each matrix/analyte, the steps involved by the task group chair in the data analysis consist of: (*1*) tabulating the data; (*2*) eliminating any laboratories that did not follow significant study instructions, were not in control during the study, or were so consistently high or low that their results are unreasonable (see 10.3); (*3*) eliminating any individual outlier data points (10.4); (*4*) for each matrix and analyte concentration studied, calculating the overall and single-operator standard deviations and means from the retained data and calculating the bias from each mean spike recovery (must subtract the mean reported background value whenever necessary); (*5*) tabulating the statistics; (*6*) assembling information required for the research report; and, if desired, (*7*) summarizing these results in a graph or regression equation for the test method statement.

10.1.1 As an aid to following the steps, the task group chair may find it helpful to review the sample calculations of precision and bias given in Appendix X3.

10.2 *Tabulation of Data*—The data reported by the laboratories shall be made consistent in reporting units and, if possible, in the number of reported values per operator or laboratory **(10)**. Before beginning, remove any unusable data sets generated by laboratories that did not follow significant study instructions or used an unacceptable variation of the test method being studied. Unless each laboratory used its own matrix with a unique background concentration, all outlier testing and precision estimates are to be based on the concentration reported rather than on background-corrected results.

10.2.1 Sometimes looking at the histogram of a set of data will help one recognize or understand, or both, the cause of unusual data.

10.3 *Rejection of Outlier Laboratories*— If one or more laboratory's data for an analyte in a specific matrix are so consistently high or low that there must be a large systematic error specific to that laboratory, all the data from the laboratory for that analyte/matrix should be rejected. Identify outlier laboratories by applying the Youden laboratory ranking test **(11)** at the 5 % significance level.

10.3.1 For example, say *n* laboratories reported results for a specific matrix and analyte. Within the data set reported for each concentration, assign a rank score from 1 for the highest result to *n* for the lowest result.

10.3.1.1 For this test, all *n* rank scores for each concentration shall be assigned, even if one or more of the laboratories did not report a result for this particular concentration. The rank of any missing results should be the mean rank of the actual data reported by that laboratory for the other concentrations of the same analyte and matrix. Also, assign an appropriate rank to nonquantitative results.

10.3.1.2 Identical results would each be given the average of the ranks the group is entitled to receive.

10.3.2 For the matrix/analyte, total the rank scores for each laboratory over all of the *q* concentrations. If the total rank sum for any particular laboratory is designated as *R*, then if either:

$R <$ the lower value in Table 1, or

$R >$ the upper value in Table 1,

that laboratory is a candidate to be marked as an outlier and ignored in subsequent calculations with a 5 % risk of this judgement being incorrect.

10.3.2.1 If more than 20 % of the laboratories reporting usable data for the matrix/analyte are outlier candidates, order the candidate laboratories according to the difference between their total rank sum and the nearest critical value given above, and reject individual or tied groups of laboratories until rejection of the next laboratory would exceed the 20 % limit. If rejection of a group of laboratories with equal distances would cause the 20 % limit to be exceeded, randomly reject laboratories from the group until rejection of the next laboratory would exceed the 20 % limit. Data from laboratories ultimately marked as outliers should be ignored for subsequent calculations.

10.3.3 Repeat 10.3 for every matrix and analyte studied.

10.4 *Rejection of Unusable Data and Individual Outlier Results, and Calculation of Final Mean and Overall Standard Deviation Estimates*:

10.4.1 Reject nonquantitative responses since they are useless for subsequent calculations. These rejections do not count against the 10 % limit in 10.4.4 because such responses are unusable. It is the task group's responsibility to judge whether reported zeros are truly quantitative analytical results, and this should usually be done after consulting with each laboratory that reported a zero, whenever that is possible.

10.4.2 Let the remaining data reported for a specific matrix/analyte/concentration be designated x_i, $i = 1$ to n. Then calculate the mean ($\bar{x}$) and overall standard deviation (s_T) as follows:

$$\bar{x} = \frac{\left(\sum_{i=1}^{n} x_i\right)}{n} \qquad (1)$$

and

$$s_T = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}} \qquad (2)$$

10.4.3 Calculate the *T* value for the most extreme remaining value (x_e) as follows:

$$T = (x_e - \bar{x}) / s_T \qquad (3)$$

If the absolute value of *T* is greater than the critical value for *n* measurements from Table 2, x_e is considered an outlier value and ignored for subsequent calculations **(12,13,14)**.

10.4.4 If an outlier was just removed in 10.4.3, return to 10.4.2 unless the removal of one more individual outlier would exceed 10 % of the usable data originally reported for this matrix, analyte, and concentration. If 10.4.2 cannot be repeated for this matrix/analyte/concentration, proceed to the next step.

10.4.5 Return to 10.4.2 for the next matrix, analyte and concentration, until final retained data sets and the related mean and overall standard deviation estimates are available for every combination studied.

TABLE 1 Upper and Lower Limits of the Acceptable Ranges for Total Rank Sums (5 % Level of Significance)

NOTE 1—This table was prepared by James Longbottom, USEPA, NERL, Cincinnati, OH, and is an adaptation and extension of Youden's Table 7 **(3)**. According to Thompson and Willke **(15)**, lower values in this table = $g + n\ (0.05(g!)/2\ n)^{1/g} - (g + 1)/2$, and upper values = $ng - n\ (0.05(\ g!)/2n)^{1/g} + (g + 1)/2$, where n = the number of laboratories and g = the number of concentrations.

Number of Laboratories	Number of Concentrations									
	6		8		10		12		14	
	Lower	Upper	Lower	Upper	Lower	Upper	Lower	Upper	Lower	Upper
7	11	37	17	47	23	57	29	67	35	77
8	12	42	18.5	53.5	25	65	32	76	39	87
9	13	47	20	60	27.5	72.5	35	85	42.5	97.5
10	14	52	21.5	66.5	29.5	80.5	38	94	46	108
11	14.5	57.5	23	73	32	88	41	103	50	118
12	15.5	62.5	24.5	79.5	34	96	43.5	112.5	53.5	128.5
13	16.5	67.5	26	86	36.5	103.5	46.5	121.5	57	139
14	17.5	72.5	27.5	92.5	38.5	111.5	49.5	130.5	60.5	149.5
15	18	78	29	99	40.5	119.5	52.5	139.5	64	160
16	19	83	30.5	105.5	42.5	127.5	55	149	67.5	170.5
17	20	88	32	112	45	135	58	158	71.5	180.5
18	21	93.5	33.5	118.5	47	143	61	167	75	191
19	21.5	98.5	35	125	49	151	63.5	176.5	78.5	201.5
20	22.5	103.5	36.5	131.5	51	159	66.5	185.5	82	212
21	23	109	38	138	53.5	166.5	69	195	85	223
22	24	114	39	145	55.5	174.5	72	204	88.5	233.5
23	25	119	40.5	151.5	57.5	182.5	74.5	213.5	92	244
24	25.5	124.5	42	158	59.5	190.5	77.5	222.5	95.5	254.5
25	26.5	129.5	43.5	164.5	61.5	198.5	80	232	99	265
26	27	135	45	171	63.5	206.5	83	241	102.5	275.5
27	28	140	46	178	65.5	214.5	85.5	250.5	106	286
28	29	145	47.5	184.5	67.5	222.5	88	260	109.5	296.5
29	29.5	150.5	49	191	69.5	230.5	91	269	112.5	307.5
30	30.5	155.5	50.5	197.5	71.5	238.5	93.5	278.5	116	318
31	31	161	51.5	204.5	73.5	246.5	96.5	287.5	119.5	328.5
32	32	166	53	211	75.5	254.5	99	297	123	339
33	32.5	171.5	54.5	217.5	77.5	262.5	101.5	306.5	126	350
34	33.5	176.5	55.5	224.5	79.5	270.5	104.5	315.5	129.5	360.5
35	34	182	57	231	81.5	278.5	107	325	133	371
36	35	187	58.5	237.5	83.5	286.5	109.5	334.5	136	382
37	35.5	192.5	59.5	244.5	85.5	294.5	112.5	343.5	139.5	392.5
38	36.5	197.5	61	251	87.5	302.5	115	353	143	403
39	37	203	62.5	257.5	89.5	310.5	117.5	362.5	146	414
40	38	208	63.5	264.5	91.5	318.5	120	372	149.5	424.5
41	38.5	213.5	65	271	93.5	326.5	123	381	153	435
42	39	219	66	278	95.5	334.5	125.5	390.5	156	446
43	40	224	67.5	284.5	97	343	128	400	159.5	456.5
44	40.5	229.5	69	291	99	351	130.5	409.5	162.5	467.5
45	41.5	234.5	70	298	101	359	133	419	166	478
46	42	240	71.5	304.5	103	367	136	428	169.5	488.5
47	43	245	72.5	311.5	105	375	138.5	437.5	172.5	499.5
48	43.5	250.5	74	318	107	383	141	447	176	510
49	44	256	75.5	324.5	108.5	391.5	143.5	456.5	179	521
50	45	261	76.5	331.5	110.5	399.5	146	466	182.5	531.5

10.5 *Calculation of Single-Operator Standard Deviation Estimates*:

10.5.1 To complete the required statistical calculations, estimate the single-operator standard deviation (s_o) from the retained data pairs available for each Youden pair, analyte, and matrix in the study as follows:

$$s_O = \sqrt{\frac{\sum_{i=1}^{m} (D_i - \bar{D})^2}{2\,(m-1)}} \qquad (4)$$

where:

m = the number of retained pairs of results available for that Youden pair, analyte, and matrix,

D_i = the difference between the retained value from laboratory i for the Youden sample with the higher true value of the pair minus the retained value from laboratory i for the other sample of the pair, and

$\bar{D}$ = the mean of the m usable D_i values.

10.5.2 The calculation of s_o for a blind duplicate is the same

TABLE 2 Critical Values for *T* (Two-Sided Test at a 5 % Significance Level) When Standard Deviation is Calculated from the Same Samples (for Single-Value Outlier Testing) (see 10.4)[A]

Number of Useable Values, *n*	Critical Value for *T*
7	2.02
8	2.13
9	2.21
10	2.29
11	2.36
12	2.41
13	2.46
14	2.51
15	2.55
16	2.58
17	2.62
18	2.65
19	2.68
20	2.71
21	2.73
22	2.76
23	2.78
24	2.80
25	2.82
30	2.91
35	2.98
40	3.04
45	3.08
50	3.13
60	3.20
70	3.26
80	3.30
90	3.35
100	3.38

[A] Values of *T* for $n \leq 25$ are based on Grubbs **(12)**. For $n > 25$, the values of *T* are approximate. All values have been adjusted for division by $n - 1$ instead of *n* in calculating *s*. Tabulated values come from Practice E 178 and may also be found in Grubbs **(14)**, although the level of significance shown in Practice E 178 has been doubled because our use here is a two-sided test, rather than a one-sided test.

as for a Youden pair. One of the duplicate samples is arbitrarily selected as the higher sample for this calculation.

10.6 *Calculation of Bias:*

10.6.1 The calculation of the bias of a test method will logically follow the collaborative study design (7.4). The usual collaborative study technique will involve reporting the recovery of added (therefore known) amounts of the analytes being measured.

10.6.2 The calculation of bias for a specific matrix, analyte, and concentration is as follows:

$$Bias\ (\%) = 100(\bar{x} - b - c) / c \qquad (5)$$

where:

$\bar{x}$ = the mean of retained data for that matrix, analyte and concentration,

c = the true concentration added, and

b = the mean background concentration reported, if necessary.

10.6.3 Where other types of studies are used to develop a true concentration for use in estimation of the test method bias, special care shall be taken to assure that the other study provides a logical reference value. Consultation with the Results Advisor and other recognized experts may be appropriate in such cases.

11. Format of the Precision and Bias Statement Required in Each Test Method

11.1 For most test methods, a collaborative study will be conducted and the following requirements apply.

11.1.1 A brief note shall provide the reader of the test method with a complete understanding of the collaborative study conducted. At a minimum, this note shall include the number of laboratories that contributed data, the matrices studied, the version of Practice D 2777 followed in designing and analyzing the study data, and any other significant aspects of the study not presented elsewhere in the test method.

11.1.1.1 Regarding significant study aspects that *must* be described, if the analytical conditions used during the collaborative study were more restrictive than those allowed in the test method, it is particularly important that these restrictive conditions be fully described in the Precision and Bias statement of the test method. Results from the collaborative study may not apply to other analytical conditions allowed in the test method.

11.1.2 The following caution shall also be included, "Results of this collaborative study may not be typical of results for matrices other than those studied."

11.1.3 The study results shall always be available in the form of a table, which, for each matrix, analyte, and concentration studied, will usually include the true concentration (*c*) added to the matrix, and must include the number of values reported, the number of values retained (that is, left after outlier testing), and (from the retained data): (*1*) the mean response ($\bar{X}$), (*2*) bias as a percent of *c*, and (*3*) the overall standard deviation (s_T). For each matrix, analyte, and Youden pair of sample concentrations, the table shall include the number of retained data *pairs* and the single-operator standard deviation (s_o) estimated from these pairs of retained values. This table shall be included in the test method unless equivalent mathematical or graphical relationships of the mean (or bias), s_T and s_o, to concentration are provided instead. If a matrix had a naturally occurring, non-zero background level for this analyte, the mean background level reported by laboratories passing the outlier testing for the Youden pair with the lowest study concentration shall also be reported in this table, and the bias estimates shall be calculated from the recovery of the true spikes, that is, *x*—average background. This table shall always be included in the research report provided to the Results Advisor and filed at ASTM Headquarters. If the full table is not included in the test method, at least a listing of the true concentrations studied for each matrix and analyte, and the number of values retained for each, shall be included in the precision and bias statement.

11.1.4 Mathematical or graphical relationships developed from the study results shall represent the general way precision and bias vary with concentration. These relationships can be very helpful to a user of a test method who must estimate the precision and bias at a specific concentration within the range studied. Graphs that simply connect the estimates from the collaborative study (connect the dots) are not acceptable. Mathematical relationships shall be accompanied by some indication of the goodness of their fit to the study statistics, unless those statistics are given in the test method.

11.2 If there is some reason why a full collaborative study could not be done, the precision and bias statement shall present a complete justification with reference to 1.3, 1.4, or 1.5, whenever appropriate. If a special exemption was approved by Committee D-19 on the recommendation of the Results Advisor and the Technical Operations Section of the Executive Subcommittee of Committee D-19, the date of that exemption shall also be provided.

11.3 *Test Methods with Non-Numerical Reports*:

11.3.1 When a method specifies that a test result is a non-numerical report of success or failure based on criteria in the procedure, the statement on precision and bias should read as follows:

11.3.1.1 *Precision and Bias*—No statement is made about either the precision or the bias of Method D XXXX for measuring (insert here the name of property) since the result merely states whether there is conformance to the criteria for success specified in the procedure.

11.4 *Test Methods Specifying Other Procedures*:

11.4.1 When a method specifies that the procedures in another ASTM method are to be used, a statement such as the following should be used to assure the user that precision and bias statements apply.

11.4.1.1 *Precision and Bias*—The precision and bias of this test method of measuring (insert here the name of the property) are as specified in Method (insert here the designation of the other method).

12. Approval of Data Analysis and Statements

12.1 Approval of the precision and bias statement shall be obtained from the Results Advisor before the test method is submitted for committee ballot, providing him/her with a copy of:

12.1.1 All test data resulting from the collaborative test.

12.1.2 All statistical calculations.

12.1.3 A summary of the final statistical estimates in tabular form.

12.1.4 A copy of the final test method, including the precision and bias statement based on the study results.

12.1.5 A copy of every document given to the participants during the collaborative study.

12.1.6 A complete list of the laboratories (names, addresses, principal contact, etc.) that participated in the study. Do not identify the source of specific study data using anything other than randomly assigned laboratory numbers or codes. The relationship between these numbers/codes and the contributing laboratories must be held strictly confidential.

12.1.7 A description of how the study samples were prepared, etc.

12.1.8 Any background information that may have influenced the results and any other information required for the research report, along with a copy of correspondence documenting approval by the Results Advisor.

12.1.9 Once satisfied with this study file, the Results Advisor shall see that it is sent to ASTM for filing as the official research report.

12.2 *Experimental Data*—The precision and bias statement in the test method shall include a footnote indicating where the supporting data can be found. The footnote shall read as in the following example:

Supporting data for the precision and bias statements have been filed at ASTM Headquarters. Request RR:D_____.

13. Keywords

13.1 collaborative study; interlaboratory study; method bias; method precision; method recovery; round-robin study; statistical analysis; Youden study design

APPENDIXES

(Nonmandatory Information)

X1. APPROVAL OF STUDY DESIGN

X1.1 Using Test Method D 5790 also known as USEPA Method 524.2, as an example, Fig. X1.1 was sent by the Task Group Chair to the Results Advisor for his approval before preparation of the samples for the interlaboratory study actually began.

TO: D-19 Results Advisor

FROM: Robin Austermann 9/30/91
Task Group Chairman Date

The following details for a proposed collaborative study are respectfully submitted for your review and approval:

X.1.1 Test method title (inc. draft number and date): "Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry"; Draft 3, dated 7/18/91
Copy of test method in ASTM format and as approved by Task Group, see ATTACHMENT # 1

X.1.2 Analyte(s): 68 analytes, 3 surrogates (See Attachment #1)

X.1.3 Procedure for estimating bias: Spike recovery after background correction.

X.1.4 Number of Youden sample pairs 5 (Minimum of 3 req.)

X.1.5 Intended operating range of test method: 0.1 - 80

and approx. mean concentration of each sample pair in study: 0.2, 1, 5, 20, 75

Units (spelled out): micrograms / litre

X.1.6 Estimated number of laboratories 73 and analysts 73
(Should be ≥ 8 labs to guarantee 6 values after outlier testing.)

X.1.7 Matrices being tested (at least 1 reproducible matrix): Reagent Water, Drinking Water, Ground Water, Wastewater, TCLP Leachate Buffer

X.1.8 QC Samples being tested: Known QC spike with each matrix (8-10 samples). Also surrogate spike recoveries.

X.1.9 Plans for developing study samples: ATTACHMENT # 2

X.1.10 Participant's instruction package: ATTACHMENT # 3

X.1.11 Participant's data reporting form: ATTACHMENT # 4

Approved by ______________________ ____________
D-19 Results Advisor Date

FIG. X1.1 Approval of Study Design: Form A—Approval of Plans for Interlaboratory Testing

X2. REPORTING OF STUDY DATA

X2.1 An example of the data reporting forms that could have been submitted by each participating laboratory for each analyte is provided as Fig. X2.1.

X2.2 Each participant was also required to provide specific information defining their analytical system and the analytical conditions they used from among options allowed in the test method. On this questionnaire, they were also encouraged to provide any comments they considered appropriate.

Complete Title of Test Method, Draft Number, and Date: Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography, Draft 3, July 18, 1991.

Laboratory Code: 1

Analyte: Chlorobenzene

Reagent Water		Drinking Water		Wastewater		Ground Water		TCLP Buffer	
Sple No.	Result µg/L	Sple No.	Result µg/L	Sple No.	Result µg/L	Sple No.	Result µg/L	Sple No.	Result µg/L
QC1	9.06	QC2		QC3		QC4	9.98	QC5	
Bkg	nd	Bkg		Bkg		Bkg	nd	Bkg	
1	0.23	11		21		31	nd	41	
2	0.21	12		22		32	0.20	42	
3	1.24	13		23		33	1.14	43	
4	23.82	14		24		34	21.95	44	
5	1.08	15		25		35	0.97	45	
6	5.71	16		26		36	5.25	46	
7	19.21	17		27		37	18.04	47	
8	4.45	18		28		38	4.61	48	
9	82.99	19		29		39	77.89	49	
10	67.65	20		30		40	65.23	50	

FIG. X2.1 Reporting of Study Data: Sample of Form B—Data Report from Individual Laboratories

X3. SAMPLE CALCULATION OF PRECISION AND BIAS

X3.1 The following is a sample of the precision and bias calculations from the data reported in the Test Method D 5790 study for one analyte in one matrix. These procedures shall be followed for each analyte and matrix combination in the study.

X3.2 Example data are presented in Table X3.1, as suggested in 10.2. Note that values shown represent analytical results after correction for background concentration by the task group or its representative, the study coordinator.

X3.3 Test for lab-ranking outliers (see 10.3). Table X3.2 shows the results of the lab-ranking calculations on the data in

TABLE X3.1 ASTM Test Method D 5790: Reagent Water, 5 mL Purge—Raw Data for Chlorobenzene Analysis [A]

	Concentration in µg/L							
Laboratory or Analyst	Sample 5 [B] 0.88	Sample 3 1.10	Sample 8 4.41	Sample 6 5.29	Sample 7 17.64	Sample 4 22.05	Sample 10 61.73	Sample 9 74.96
1	1.08	1.24	4.45	5.71	19.21	23.82	67.65	82.99
6	2.35	0.96	4.53	5.24	17.14	21.43	64.30	70.40
8	1.30	1.30	4.90	6.80	21.70	25.60	61.40	85.40
15	1.20	1.40	3.90	4.80	15.70	18.70	54.10	66.10
21	2.20	0.93	4.90	4.00	16.90	18.10	53.80	81.80
25	1.21	1.10	4.50	5.37	17.90	22.22	62.10	75.10
26	1.20	1.20	4.40	4.90	16.70	21.50	62.40	71.80
27	1.10	1.00	4.30	5.80	22.10	26.60	75.00	89.10
31	0.80	0.00	5.30	5.50	19.10	24.03	74.80	88.90
38	1.30	1.70	4.70	6.60	23.50	24.10	74.40	89.50
47	1.10	1.20	4.10	5.30	17.90	22.40	77.90	63.50
49	1.00	1.30	4.90	5.40	12.80	18.70	26.10	37.60
52	1.20	1.10	4.80	5.60	19.80	23.50	69.80	83.10
54	0.55	0.79	3.33	3.65	14.31	17.86	50.41	60.89
56	1.00	1.30	4.70	5.80	19.30	24.10	66.50	82.90

[A] Values represent analytical results after correction for background concentration by the study coordinator.

[B] Change to match sample identification used during study.

TABLE X3.2 ASTM Test Method D 5790: Reagent Water, 5 mL Purge—Ranking Test for Chlorobenzene Analyses

Laboratory or Analyst	Sample 5 [A]	Sample 3	Sample 8	Sample 6	Sample 7	Sample 4	Sample 10	Sample 9	Rank Sum by Laboratory or Analyst
1	11	6	10	5	6	6	6	6	56
6	1	12	8	11	10	11	8	11	72
8	3.5	4	3	1	3	2	11	4	31.5
15	7	2	14	13	13	12.5	12	12	85.5
21	2	13	3	14	11	14	13	8	78
25	5	9.5	9	9	8.5	9	10	9	69
26	7	7.5	11	12	12	10	9	10	78.5
27	9.5	11	12	3.5	2	1	2	2	43
31	14	15	1	7	7	5	3	3	55
38	3.5	1	6.5	2	1	3.5	4	1	22.5 [B]
47	9.5	7.5	13	10	8.5	8	1	13	70.5
49	12.5	4	3	8	15	12.5	15	15	85
52	7	9.5	5	6	4	7	5	5	48.5
54	15	14	15	15	14	15	14	14	116 [C]
56	12.5	4	6.5	3.5	5	3.5	7	7	49

[A] Change to match sample identification used during study.

[B] This rank sum is below the lower limit given in Table 1; reject all data from this laboratory for this analyte.

[C] This rank sum is above the upper limit given in Table 1; reject all data from this laboratory for this analyte.

Table X3.1. Since 20 % of the 15 laboratories reporting usable data is exactly three, up to three laboratories can be removed with this test. Laboratory 38 fails for providing consistently high responses and Laboratory 54 fails for providing consistently low responses, relative to the other laboratories that reported.

X3.4 There are no less-than values to reject as unusable; however, the zero reported by Laboratory 31 for Sample 3 is not considered to be a legitimate quantitative response and is therefore rejected as unusable. Under normal study conditions, Laboratory 31 would be contacted to resolve questions regarding their zero response, but this was not possible for preparation of this example.

X3.5 Calculate the initial mean (*XBAR*) and standard deviation (s_T) of the remaining data for each concentration and calculate the initial single-outlier test values, *T* (see 10.4). Since at least one value, but not more than 10 % of the usable data, can be removed for each concentration, and 10 % of 13 is less than two, at most, one value can be removed using single-outlier testing, for each concentration. Only the *T* values for the most extreme values for Samples 10 and 9 exceed the 2.46 critical value for sets of 13 values, and so are removed as outliers. Table X3.3 gives the results of these calculations.

X3.6 Table X3.4 shows the data with all outliers indicated and Table X3.5 contains the final statistics.

X3.7 From the final statistics, the responsible task group chose to develop the following regressions to relate *XBAR*, s_T, and s_o to the true concentration (*C*) for *C* values between 0.88 and 75 micrograms per litre:

$$XBAR = 1.035\ (C) + 0.03,\ (R^2 = 1.00)$$
$$s_T = 0.119\ (C) + 0.01,\ (R^2 = 0.97)$$
$$s_o = 0.074\ (C) + 0.08,\ (R^2 = 0.75)$$

R^2 indicates the proportion of the total variability in the dependent variable which can be explained by the regression.

NOTE X3.1—This X3.7 step is optional and need not be followed by other task groups.

TABLE X3.3 ASTM Test Method D 5790: Reagent Water, 5 mL Purge—Single-Outlier Tests for Chlorobenzene Analyses

Sample Number	5	3	8	6	7	4	10	9
True concentration (*C*), µg/L	0.88	1.10	4.41	5.29	17.64	22.05	61.73	74.96
Number of retained values	13	12	13	13	13	13	13	13
Mean recovery (*XBAR*)	1.29	1.17	4.59	5.40	18.17	22.36	62.76	75.28
Overall standard deviation (s_T)	0.46	0.15	0.38	0.65	2.48	2.65	13.28	14.08
Most extreme value	2.35	0.93	5.30	4.00	12.80	18.10	26.10	37.60
Single-outlier test value (*T*)	2.30	1.60	1.87	2.15	2.17	1.61	2.76 [A]	2.68 [A]

[A] This *T* value exceeds the critical value of 2.46 in Table 2 for sets of 13 reported values.

TABLE X3.4 ASTM Test Method D 5790: Reagent Water, 5 mL Purge—Retained Data for Chlorobenzene Analyses

NOTE 1—Current significance levels:
1. Lab ranking data rejection tests, alpha = 0.05.
2. Individual outlier tests using Thompson(s) role, alpha = 0.05.

		Concentration in μg/L							
Laboratory or Analyst	Lab Rejected	Sample 5 0.88	Sample 3 1.10	Sample 8 4.41	Sample 6 5.29	Sample 7 17.64	Sample 4 22.05	Sample 10 61.73	Sample 9 74.96
1		1.08	1.24	4.45	5.71	19.21	23.82	67.65	82.99
6		2.35	0.96	4.53	5.24	17.14	21.43	64.30	70.40
8		1.30	1.30	4.90	6.80	21.70	25.60	61.40	85.40
15		1.20	1.40	3.90	4.80	15.70	18.70	54.10	66.10
21		2.20	0.93	4.90	4.00	16.90	18.10	53.80	81.80
25		1.21	1.10	4.50	5.37	17.90	22.22	62.10	75.10
26		1.20	1.20	4.40	4.90	16.70	21.50	62.40	71.80
27		1.10	1.00	4.30	5.80	22.10	26.60	75.00	89.10
31		0.80	0.00 [A]	5.30	5.50	19.10	24.03	74.80	88.90
38	[B]	1.30 [B]	1.70 [B]	4.70 [B]	6.60 [B]	23.50 [B]	24.10 [B]	74.40 [B]	89.50 [B]
47		1.10	1.20	4.10	5.30	17.90	22.40	77.90	63.50
49		1.00	1.30	4.90	5.40	12.80	18.70	26.10 [B]	37.60 [B]
52		1.20	1.10	4.80	5.60	19.80	23.50	69.80	83.10
54	[B]	0.55 [B]	0.79 [B]	3.33 [B]	3.65 [B]	14.31 [B]	17.86 [B]	50.41 [B]	60.89 [B]
56		1.00	1.30	4.70	5.80	19.30	24.10	66.50	82.90

[A] = Rejected as a nonquantitative response.
[B] = Rejected.

TABLE X3.5 ASTM Test Method D 5790: Reagent Water, 5 mL Purge—Final Statistical Summary for Chlorobenzene Analyses

Sample Number	5	3	8	6	7	4	10	9
Number of retained values	13	12	13	13	13	13	12	12
True concentration (C) μg/L	0.88	1.10	4.41	5.29	17.64	22.05	61.73	74.96
Mean recovery ($XBAR$)	1.29	1.17	4.59	5.40	18.17	22.36	65.81	78.42
Percent recovery	146.33	106.29	104.10	102.11	103.02	101.41	106.61	104.62
Overall standard deviation (s_T)	0.46	0.15	0.38	0.65	2.48	2.65	7.74	8.74
Overall relative standard deviation,%	35.50	12.91	8.24	11.99	13.64	11.85	11.77	11.15
Number of retained pairs	12		13		13		12	
Single standard deviation, (s_o)	0.40		0.48		0.80		7.31	
Analyst relative deviation,%	32.60		9.68		3.94		10.14	

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Designation: D 2879 – 97

An American National Standard

Standard Test Method for Vapor Pressure-Temperature Relationship and Initial Decomposition Temperature of Liquids by Isoteniscope[1]

This standard is issued under the fixed designation D 2879; 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 vapor pressure of pure liquids, the vapor pressure exerted by mixtures in a closed vessel at 40 ± 5 % ullage, and the initial thermal decomposition temperature of pure and mixed liquids. It is applicable to liquids that are compatible with borosilicate glass and that have a vapor pressure between 133 Pa (1.0 torr) and 101.3 kPa (760 torr) at the selected test temperatures. The test method is suitable for use over the range from ambient to 748 K. The temperature range may be extended to include temperatures below ambient provided a suitable constant-temperature bath for such temperatures is used.

NOTE 1—The isoteniscope is a constant-volume apparatus and results obtained with it on other than pure liquids differ from those obtained in a constant-pressure distillation.

1.2 Most petroleum products boil over a fairly wide temperature range, and this fact shall be recognized in discussion of their vapor pressures. Even an ideal mixture following Raoult's law will show a progressive decrease in vapor pressure as the lighter component is removed, and this is vastly accentuated in complex mixtures such as lubricating oils containing traces of dewaxing solvents, etc. Such a mixture may well exert a pressure in a closed vessel of as much as 100 times that calculated from its average composition, and it is the closed vessel which is simulated by the isoteniscope. For measurement of the apparent vapor pressure in open systems, Test Method D 2878, is recommended.

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

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 hazard statements, see Note 3, Note 4, and Note 5.

2. Referenced Documents

2.1 *ASTM Standards:*

D 2878 Test Method for Estimating Apparent Vapor Pressures and Molecular Weights of Lubricating Oils[2]

E 230 Temperature Electromotive Force (EMF) Tables for Standardized Thermocouples[3]

3. Terminology

3.1 *Definition of Term Specific to This Standard*

3.2 *ullage*—that percentage of a closed system which is filled with vapor.

3.2.1 *Discussion*—Specifically, on Fig. 1, that portion of the volume of the isoteniscope to the right of point *A* which is filled with vapor.

3.3 *Symbols:*

C = temperature, °C,
K = temperature, K,
p = pressure, Pa or torr,
t = time, s,
P_e = experimentally measured total system pressure,
P_a = partial pressure due to fixed gases dissolved in sample,
P_c = corrected vapor pressure, Pa or torr.

$$K = C + 273.15 \tag{1}$$

4. Summary of Test Method

4.1 Dissolved and entrained fixed gases are removed from the sample in the isoteniscope by heating a thin layer of a sample at reduced pressure, removing in this process the minimum amount of volatile constituents from the sample.

4.2 The vapor pressure of the sample at selected temperatures is determined by balancing the pressure due to the vapor of the sample against a known pressure of an inert gas. The manometer section of the isoteniscope is used to determine pressure equality.

4.3 The initial decomposition temperature is determined from a plot of the logarithm of the vapor pressure versus the reciprocal of absolute temperature. The initial decomposition temperature is taken as that temperature at which the plot first departs from linearity as a result of the decomposition of the sample. An optional method provides for the use of isothermal rates of pressure rise for this purpose (see Annex A1). These are measured at several temperatures and the logarithm of the

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[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 D02.11 on Engineering Sciences of High Performance Fluids and Solids.

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

[3] *Annual Book of ASTM Standards*, Vol 14.03.

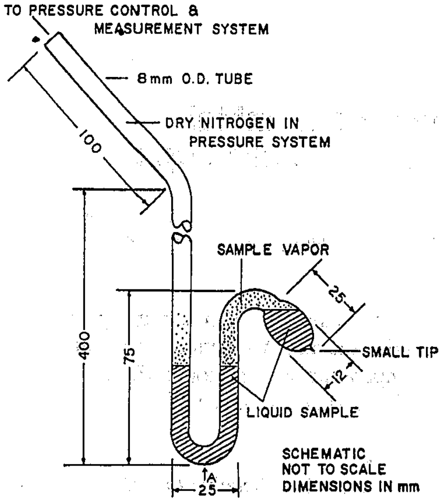


FIG. 1 Isoteniscope

rate of pressure rise is plotted versus the reciprocal of absolute temperature. The decomposition temperature of the sample is taken to be that temperature at which the rate of increase of pressure is sufficient to produce a rise of 185 Pa (0.0139 torr/s).

NOTE 2—Vapor pressures less than 133 Pa (1.0 torr), but greater than 13.3 Pa (0.1 torr) at a selected test temperature can be determined directly with reduced accuracy. In some cases the tendency of the sample to retain dissolved or occluded air may prevent direct determinations of vapor pressure in this range. In such cases, data points obtained at higher pressures can be extrapolated to yield approximate vapor pressures in this range.

5. Significance and Use

5.1 The vapor pressure of a substance as determined by isoteniscope reflects a property of the sample as received including most volatile components, but excluding dissolved fixed gases such as air. Vapor pressure, *per se*, is a thermodynamic property which is dependent only upon composition and temperature for stable systems. The isoteniscope method is designed to minimize composition changes which may occur during the course of measurement.

6. Apparatus

6.1 *Isoteniscope* (Fig. 1).

6.2 *Constant-Temperature Air Bath* (Fig. 2) for use over the temperature range from ambient to 748 K, controlled to ±2 K in the zone occupied by the isoteniscope beyond point "A" (Fig. 1).

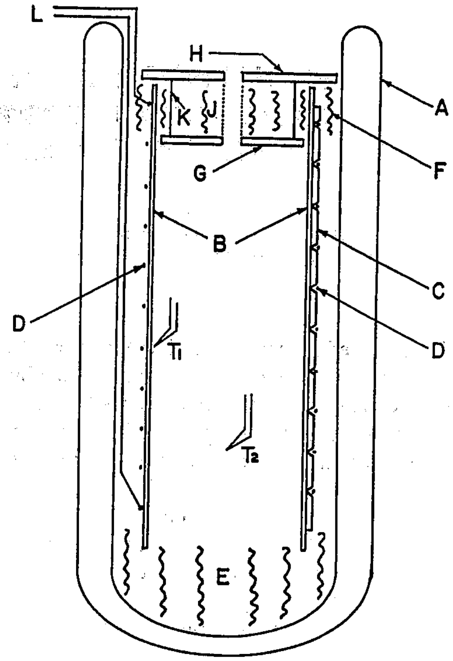
6.3 *Temperature Controller.*

6.4 *Vacuum and Gas Handling System* (Fig. 3).

6.5 *Mercury Manometer*, closed end, 0 to 101.3 kPa (0 to 760 torr) range.

NOTE 3—**Warning:** Poison. May be harmful or fatal if inhaled or swallowed. Vapor harmful; emits toxic fumes when heated. Vapor pressure at normal room temperature exceeds threshold limit value for occupational exposure. See A2.1.

6.6 *McLeod Vacuum Gage*, 0 to 2.00 kPa (0 to 15 torr), vertical primary standard type.



A	Dewar, strip silvered, 110 mm ID by 400 mm deep.
B	Borosilicate glass tube, 90 mm OD by 320 mm long.
C	Glass rod, ⅛-in. in diameter by 310 mm long. Three of these heater element holders are fused along their entire length to the outer surface of Tube B at 120-deg intervals. Slots cut into the fused glass rods on ⅜-in. centers serve as guides for the heating wire D.
D	Resistance wire, B. and S. No. 21 gage, spirally wrapped around Tube B and its attached guides.
E	Glass wool pad.
F	Glass wool pad for centering Tube B and sealing annular opening.
G	Lower plate of insulated isoteniscope holder. Transite disk ⅛ in. thick, loose fit in Tube B. With hole for isoteniscope.
H	Upper plate of insulated isoteniscope holder. Transite disk ⅛ in. thick, loose fit in Dewar A. With hole for isoteniscope.
J	Glass wool insulation between plates G and H.
K	Plate spacer rods.
L	Heater leads connected to power output of temperature controller.
T_1	Temperature-control thermocouple affixed to inside wall of Tube B.
T_2	Temperature-indicating thermocouple affixed to isoteniscope.

FIG. 2 Constant-Temperature Air Bath

6.7 *Mechanical Two-Stage Vacuum Pump.*

6.8 *Direct Temperature Readout*, either potentiometric or electronic.

6.9 *Thermocouple*, in accordance with American National Standard for Temperature Measurement Thermocouples (ANSI C96.1) from Tables E 230.

6.10 *Nitrogen*, pre-purified grade.

NOTE 4—**Warning:** Compressed gas under high pressure. Gas reduces oxygen available for breathing. See A2.2.

6.11 *Nitrogen Pressure Regulator*, single-stage, 0 to 345 kPa gage (0 to 50 psig).

6.12 *Alcohol Lamp.*

NOTE 5—**Warning:** Flammable. Denatured alcohol cannot be made nontoxic. See A2.3.

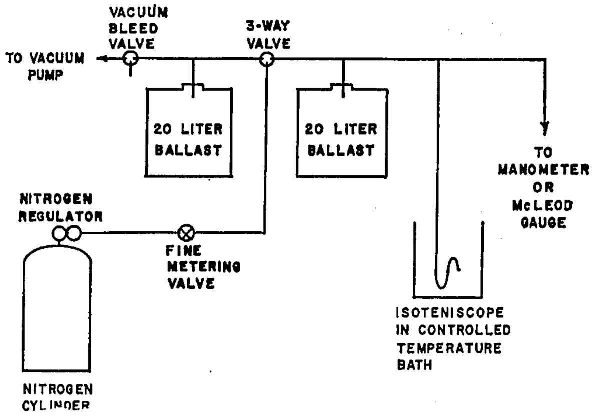


FIG. 3 Vacuum and Gas Handling System

7. Hazards

7.1 The procedure requires measuring pressures with devices containing mercury (**Warning**—See Note 3). Spillage of this material creates a safety hazard in the form of toxic vapor in the room. This can be prevented by use of catchment vessels under the devices. If these fail, and the ventilation of the room during occupancy is below 0.01 m^3 ($s \cdot m^2$), 2 $ft^3/min \cdot ft^2$), thorough cleaning of the floor followed by inspection with a mercury vapor-detecting device is recommended. The following procedures for floor cleaning have been found effective:

7.1.1 A 5 % aqueous solution of sodium polysulfide penetrates well into porous surfaces, but should not be used on polished metal objects.

7.1.2 Sweeping with flowers of sulfur, or agricultural colloidal sulfur, is effective on nonporous floors.

7.1.3 Sweeping with granular zinc, about 20 mesh (840 µm) that has been rinsed in 3 % hydrochloric acid, is effective in catching macro-drops.

7.2 The apparatus includes a vacuum system and a Dewar flask (constant temperature air bath) that is subjected to elevated temperatures. Suitable means should be employed to protect the operator from implosion of these systems. These means include wrapping of vacuum vessels, use of safety shield in front of Dewar flask, and use of safety glasses by the operator.

8. Procedure

8.1 Add to the isoteniscope a quantity of sample sufficient to fill the sample bulb and the short leg of the manometer section (**Warning**—See Note 6) to point *A* of Fig. 1. Attach the isoteniscope to the vacuum system as shown in Fig. 3, and evacuate both the system and the filled isoteniscope to a pressure of 13.3 Pa (0.1 torr) as measured on the McLeod gage. Break the vacuum with nitrogen (**Warning**—See Note 7). Repeat the evacuation and purge of the system twice to remove residual oxygen.

NOTE 6—**Warning:** Poison. Can be harmful or fatal if inhaled or swallowed. Vapor harmful; emits toxic fumes when heated. Vapor pressure at normal room temperature exceeds threshold limit value for occupational exposure. See A1.1.

NOTE 7—**Warning:** Compressed gas under high pressure. Gas reduces oxygen available for breathing. See A1.2.

8.2 Place the filled isoteniscope in a horizontal position so that the sample spreads out into a thin layer in the sample bulb and manometer section. Reduce the system pressure to 133 Pa (1 torr). Remove dissolved fixed gases by gently warming the sample with an alcohol (**Warning**—See Note 8) lamp until it just boils. Continue for 1 min.

NOTE 8—**Warning:** Flammable. Denatured alcohol cannot be made nontoxic. See A2.3.

NOTE 9—During the initial evacuation of the system, it may be necessary to cool volatile samples to prevent boiling or loss of volatiles.

NOTE 10—If the sample is a pure compound, complete removal of fixed gases may readily be accomplished by vigorous boiling at 13.3 Pa (0.1 torr). For samples that consist of mixtures of substances differing in vapor pressure, this procedure is likely to produce an error due to the loss of volatile components. Gentle boiling is to be preferred in such cases. The rate of boiling during degassing may be controlled by varying both the pressure at which the procedure is carried out and the amount of heating. In most cases, satisfactory degassing can be obtained at 133 Pa (1 torr). However, extremely viscous materials may require degassing at lower pressures. Samples of high volatility may have to be degassed at higher pressures. In the event that the vapor pressure data indicate that the degassing procedure has not completely removed all dissolved gases, it may be necessary to apply a correction to the data or to disregard data points that are so affected (see 8.7). The degassing procedure does not prevent the loss of volatile sample components completely. However, the described procedure minimizes such losses, so that for most purposes the degassed sample can be considered to be representative of the original sample less the fixed gases that have been removed.

8.3 After the sample has been degassed, close the vacuum line valve and turn the isoteniscope to return the sample to the bulb and short leg of the manometer so that both are entirely filled with the liquid. Create a vapor-filled, nitrogen-free space between the bulb and the manometer in the following manner: maintain the pressure in the isoteniscope at the same pressure used for degassing; heat the drawn-out tip of the sample bulb with a small flame until sample vapor is released from the sample; continue to heat the tip until the vapor expands sufficiently to displace part of the sample from the upper part of the bulb and manometer arm into the manometer section of the isoteniscope.

8.4 Place the filled isoteniscope in a vertical position in the constant-temperature bath. As the isoteniscope approaches temperature equilibrium in the bath, add nitrogen to the gas-sampling system until its pressure equals that of the sample. Periodically adjust the pressure of the nitrogen in the gas-handling system to equal that of the sample. When the isoteniscope reaches temperature equilibrium, make a final adjustment of the nitrogen pressure to equal the vapor pressure of the sample. Pressure balance in the system is indicated by the manometer section of the isoteniscope. When the liquid levels in the manometer arms are equal in height, balance is indicated. Read and record the nitrogen pressure in the system at the balance point. Use the McLeod gage to measure pressures below 2.00 kPa (15 torr) and the mercury manometer for pressures from 2.00 kPa (15 torr) to 101 kPa (760 torr).

8.4.1 It is extremely important that adjustments of the nitrogen pressure be made frequently and carefully. If the nitrogen pressure is momentarily too great, a bubble of nitrogen may pass through the manometer and mix with the sample vapor. If the nitrogen pressure is momentarily too low, a bubble of sample vapor may escape. If either action occurs, the test is terminated immediately and restarted from 8.3.

NOTE 11—Because the densities of most samples are very much less than that of mercury, small errors in the final adjustment of the levels of the liquid level in the manometer have a negligible effect on the measured values of vapor pressure above 133 Pa (1 torr).

8.5 Increase the temperature of the constant-temperature bath 25 K. As the temperature rises, maintain pressure balance in the system in the manner described in 7.4 . When temperature equilibrium is reached, make a final adjustment of pressure to establish balance. Read and record the system pressure. Repeat at intervals of 25 K until the system pressure exceeds 101 kPa (760 torr).

8.6 Plot the logarithm and the measured vapor pressure at each temperature versus the reciprocal of the absolute temperature, $(K)^{-1}$.

NOTE 12—Three or four-cycle semilog graph paper is useful for making this type of plot.

8.7 If the slope of the vapor pressure curve at its low-temperature end indicates that the sample contains fixed gases as a result of incomplete degassing, one of three procedures must be followed. (For examples, see Fig. 4 and Fig. 5.)

8.7.1 Repeat the determination of vapor pressure in the manner described in 8.1-8.7, but employ a more vigorous degassing procedure. This procedure is recommended for pure compounds and mixtures that do not have a vapor pressure greater than 133 Pa (1 torr) at 323 K.

NOTE 13—In general, vapor pressure determinations are made after both temperature equilibrium in the air bath and pressure equilibrium in the isoteniscope and measuring system are attained. However, when a sample begins to decompose, the observed vapor pressure of the sample usually increases even at constant temperature. In such cases, the measured pressure of the system is no longer a function only of the temperature and is not a vapor pressure in the usual sense of the term. It is sometimes useful to continue to take pressure readings even after a system has become unstable. In such cases, the pressure reading is taken after temperature equilibrium is reached in the air bath, regardless of whether a stable pressure balance can be maintained.

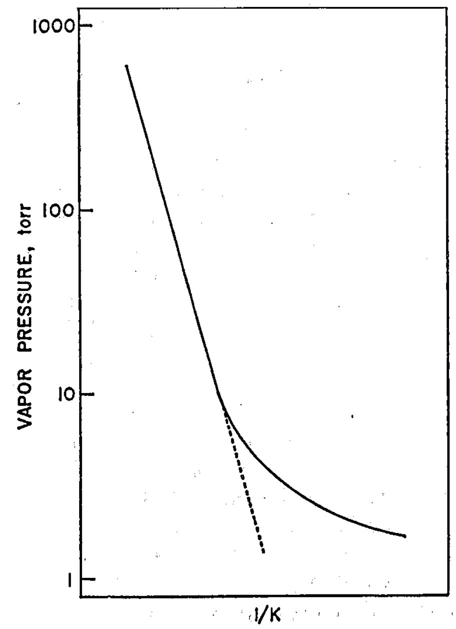


FIG. 4 Log P_e versus 1/K with Linear Region

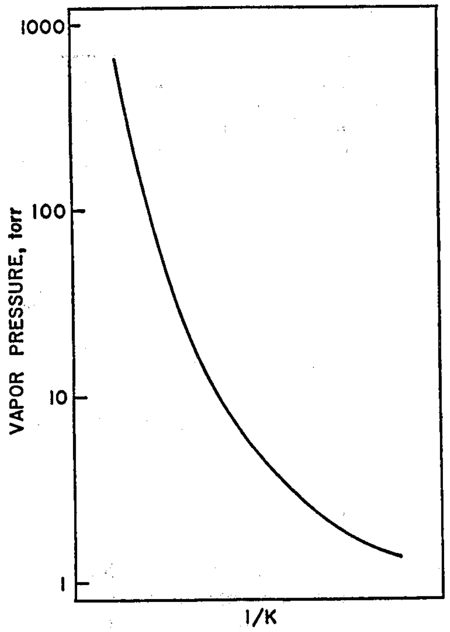


FIG. 5 Log P_e versus 1/K Without Linear Region

8.7.2 In many cases, despite the presence of fixed gases in the sample, the plot of the vapor pressure may be linear over a rather wide range of temperature (see Fig. 4). Extrapolate the linear section to lower temperatures to estimate the vapor pressure even though the presence of fixed gases prevents the direct determination. Extrapolation over more than one decade of pressure is not recommended.

8.7.3 If the lack of a suitable region of linearity prevents the use of the procedure described in 8.7.2 (see Fig. 5), the following arithmetic correction procedure is used: Assume that the pressure at the lowest temperature, K_1, at which measurements were made is predominantly due to fixed gases. Calculate the pressure that would be developed at constant volume if this volume of fixed gases were to be heated to the temperature, K_2, of the next data point.

$$P_{a2} = P_{a1} \times K_2/K_1 \tag{2}$$

Repeat this procedure for each data point. Calculate the corrected vapor pressure of the sample by subtracting each value of P_a from the corresponding P_e for each successive data point.

$$P_c = P_e - P_a \tag{3}$$

9. Calculation and Report

9.1 Plot the logarithms of the calculated values of the corrected vapor pressure versus the reciprocal of the absolute temperature in the manner described in 8.6.

9.2 From the plot of the logarithm of the corrected vapor pressure versus the reciprocal of the absolute temperature, read the smoothed values of the vapor pressure at the desired temperature intervals. Report these values as the vapor pressure of the sample at the indicated temperatures.

9.3 Use the plot of the logarithm of the corrected vapor pressure versus the reciprocal of absolute temperature to determine the initial decomposition temperature of the sample. The initial decomposition temperature is that temperature at which the vapor pressure plot first deviates from linearity. Report this value as the initial decomposition temperature of the sample.

NOTE 14—The initial deviation from linearity is usually due to an increase in rate of pressure rise. A decrease in rate of pressure rise may be observed if the sample undergoes reactions such as polymerization. The vapor-pressure curve above the initial decomposition temperature is not necessarily linear or even approximately linear. Do not confuse nonlinearity due to the presence of fixed gases (see 9.3) with that caused by the decomposition of the sample. Some samples do not decompose under the conditions of the test. In those instances the vapor-pressure curve is practically linear except for low-temperature deviations due to residual quantities of fixed gases.

10. Precision and Bias

10.1 Because of the complex nature of Test Method D 2879 for vapor pressure-temperature relationship and because of the expensive equipment involved, there is not a sufficient number of volunteers to permit a comprehensive laboratory program for determining the precision and bias. If the necessary volunteers can be obtained, a program will be undertaken at a later date.

11. Keywords

11.1 decomposition temperature; initial decomposition temperature; isoteniscope; liquids; vapor pressure

ANNEXES

(Mandatory Information)

A1. ALTERNATIVE METHOD FOR DETERMINATION OF DECOMPOSITION TEMPERATURE

A1.1 Scope

A1.1.1 This annex describes a procedure for the determination of the decomposition temperature of liquids whose vapor pressure can be measured in the apparatus described in the standard method.

A1.2 Summary of Test Method

A1.2.1 Dissolved and entrained gases are removed from the sample in the same manner described in the standard method. The isothermal rate of pressure change with respect to time is measured for several temperatures above the expected decomposition temperature of the sample. The logarithms of the rates of pressure rise are plotted against the reciprocals of the absolute temperatures at which the rates were measured. The decomposition temperature is defined as the temperature at which the rate of pressure increase of the sample is equivalent to a rise of 67 kPa (500 torr) in 10 h (1.85 Pa/s).

A1.3 Procedure

A1.3.1 Determine the vapor pressure and initial decomposition temperature of the sample in accordance with the procedures described in Sections 8 and 9 of the standard method of test.

A1.3.2 If the sample is found to have an initial decomposition temperature that falls within the range of pressures and temperatures covered by the data in A1.3.1, fill an isoteniscope with a fresh quantity of sample and remove the dissolved fixed gas from it in accordance with the procedures described in 8.2. Prepare the isoteniscope for test as described in 8.3. Place the filled isoteniscope in the constant-temperature bath maintained at a temperature at which a rate of pressure increase greater than 1.85 Pa/s (0.0139 torr/s) will be obtained. Maintain pressure balance in the system in the manner described in 8.4 until the isoteniscope and its contents reach temperature equilibrium. As soon as temperature equilibrium is attained, measure the system pressure at selected intervals of time until a constant rate is given by successive measurements.

A1.3.3 Repeat the determination of rate of pressure rise in accordance with A1.3.2 at temperature intervals of 10 to 15 K until a total of three or four determinations have been made.

A1.4 Calculation

A1.4.1 Plot the logarithm of the measured rates of pressure rise versus the reciprocal of the absolute temperature. Draw the best straight line through the data.

A1.4.2 Determine the temperature at which the rate of pressure rise is equal to 1.85 Pa/s (0.0139 torr/s). Report that temperature as the decomposition temperature of the sample.

A1.4.3 The interval between measurements is selected so that a minimum pressure change of approximately 2.66 kPa (20 torr) occurs during each interval.

A1.4.4 If the pressure in the sample chamber of the isoteniscope reaches 101 kPa (760 torr) as a result of the accumulation of decomposition products, the balancing gas pressure may be reduced slightly to allow some of these products to bubble through the manometer section of the isoteniscope. When the pressure has been reduced to a workable level, the system can be rebalanced and rate measurement resumed.

A2. PRECAUTIONARY STATEMENTS

A2.1 Mercury

Warning—Poison. Can be harmful or fatal if inhaled or swallowed. Vapor harmful; emits toxic fumes when heated. Vapor pressure at normal room temperature exceeds threshold limit value for occupational exposure.

Do not breathe vapor.

Keep container closed.

Use with adequate ventilation.

Do not take internally.

Cover exposed surfaces with water, if possible, to minimize evaporation.

Do not heat.

Keep recovered mercury in tightly sealed container prior to sale or purification.

Do not discard in sink or in rubbish.

A2.2 Nitrogen

Warning—Compressed gas under high pressure. Gas reduces oxygen available for breathing.

Keep cylinder valve closed when not in use.

Use with adequate ventilation.

Do not enter storage areas unless adequately ventilated.

Always use a pressure regulator. Release regulator tension before opening cylinder.

Do not transfer to cylinder other than one in which gas is received.

Do not mix gases in cylinders.

Never drop cylinder. Make sure cylinder is supported at all times.

Stand away from cylinder 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.

A2.3 Alcohol

Warning—Flammable. Denatured alcohol cannot be made nontoxic.

Keep away from heat, sparks, and open flame.

Keep container closed.

Use with adequate ventilation.

Avoid prolonged breathing of vapor or spray mist.

Avoid contact with eyes and skin.

Do not take internally.

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Document Name: ASTM D2986: Standard Method for Evaluation of Air, Assay Media by the Monodisperse DOP (Dioctyl Phthalate) Smoke Test

CFR Section(s): 40 CFR 86.1310-2007(b)(7)(i)(A)

Standards Body: American Society for Testing and Materials

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Designation: D 2986 – 95a (Reapproved 1999)

An American National Standard

Standard Practice for Evaluation of Air Assay Media by the Monodisperse DOP (Dioctyl Phthalate) Smoke Test[1]

This standard is issued under the fixed designation D 2986; 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 The dioctyl phthalate (DOP) smoke test is a highly sensitive and reliable technique for measuring the fine particle arresting efficiency of an air or gas cleaning system or device. It is especially useful for evaluating the efficiency of depth filters, membrane filters, and other particle-collecting devices used in air assay work.

1.2 The technique was developed by the U.S. Government during World War II.[2] Its validity for use in evaluation of air sampling media has been well demonstrated.[3]

1.3 Although a little latitude is permissible in the associated equipment and in the operation method, experience has shown the desirability of operating within established design parameters and recognized test procedures.[4]

1.4 This practice describes the present DOP test method, typical equipment, calibration procedures, and test particles. It is applicable for use with commercially available equipment.

1.5 *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 safety precaution, see 6.1.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres[5]

3. Terminology

3.1 *Definitions*—For other definitions of terms used in this practice, refer to Terminology D 1356.

3.2 Other terms are defined as follows:

3.3 *optical owl, n*—an optical instrument for visual estimation of the particle diameter of the monodisperse aerosol by the angular dependence of light scattering, in accordance with the Mie theory.

4. Summary of Practice

4.1 A monodispersed aerosol of 0.3-μm diameter is continuously generated by condensation of DOP vapor under controlled conditions. By selective value arrangement, a metered portion of this aerosol is drawn through a specimen mount containing the item under test. Flow rate through the specimen is adjustable and the corresponding flow resistance is noted as part of the test.

4.2 With aerosol generation stabilized (constant particle size and concentration), aerosol concentration is measured upstream and downstream of the specimen under test by use of a linear forward light-scattering photometer.

4.3 Results are expressed as percent of DOP penetration at the flow rate used.

5. Apparatus

5.1 Equipment for use with this technique consists of several interoperational parts. These are indicated in proper relative arrangement by the diagrammatic sketch, Fig. 1. In Fig. 1, the letter designations refer to the same parts as described in the immediately following subsections:

5.2 *Air Supply Source* (a)—This can be a blower as shown diagrammatically or a compressed air source with stepdown regulator. In any case, the air supply source must be clean, free of entrainment, and sufficient to provide full flow against the total resistance of aerosol generator and aerosol conductor lines to the excess aerosol exhaust point.

5.3 *DOP Aerosol Generator* (b)—The generator is designed to produce uniform size liquid droplet particles of 0.3-μm diameter at a concentration of about 100 ± 20 μg/L of air. Further description of the generator is given in 8.3.

5.4 *Aging Chamber* (c)—This is simply a large vessel (usually about 20 L in volume) wherein some dwell time is provided to permit stabilization of the aerosol.

5.5 *Sample Holder* (d)—Size and design of the sample holder can be accommodated to the item under test. However, for evaluation of filter media, a circular test area of 100 cm^2 ± 2 % is specified. Provision is made to measure flow resistance

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[1] This practice is under the jurisdiction of ASTM Committee D-22 on Sampling and Analysis of Atmospheresand is the direct responsibility of Subcommittee D22.01on Quality Control.

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[2] Knudson, H. W., and White, Locke, Ens. USNR, "Development of Smoke Penetration Meters," *Naval Research Laboratory Report No. P-2642*, P.B. No. 119781, September 1945.

[3] Smith, Walter, J., and Surprenant, N. F., "Properties of Various Filtering Media for Atmospheric Dust Sampling," *Proceedings*, ASTM, Vol 53, 1953, pp. 1122–1135.

[4] *Instruction Manual—Penetrometer,* Filter Testing, DOP, Q127 136-300-138B, Edgewood Arsenal, MD, July 1963.

[5] *Annual Book of ASTM Standards,* Vol 11.03.

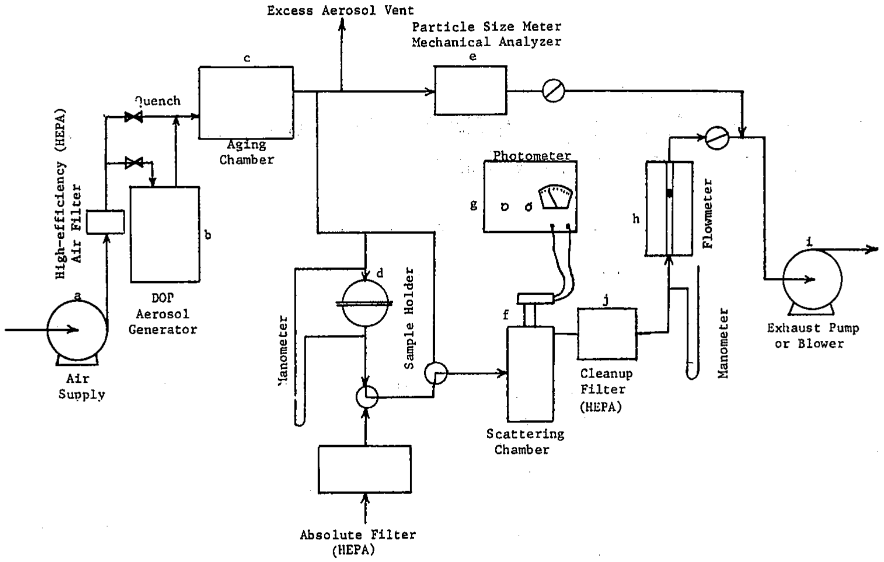


FIG. 1 Simplified Diagram Showing Relation of Principal Parts of DOP Aerosol Test Apparatus

across the test piece. A wire screen may be used to support the sample.

5.6 *Particle Size Analyzer* (e)—Particle size in the aerosol is indicated by the particle size analyzer. The visual owl may be used to verify the aerosol particle size. The electronic owl is an adaption designed to remove the human factor; it has proven to be highly successful. Both instruments operate by optical rotation of light scattered at a 90° angle. Paragraph 8.4 gives further detail for the optical owl.

5.7 *Scattering Chamber* (f)—The scattering chamber is used to determine concentration of aerosol either upstream or downstream of the item under test. Further detail for a typical chamber is given in 8.5.

5.8 *Photometer* (g)—This is a combination of sensitive multiplier phototube and meter. The multiplier phototube mounts on the scattering chamber and detects light forward scattered by any particles in the chamber. Further description of the photometer is given in 8.6.

5.9 *Flowmeter* (h)—A float-type flowmeter (rotameter) is used, capable of reading a flow rate well in excess of the maximum test rate to be used. A meter reading somewhat above 100 L/min is the common size. It must be protected against fouling by any DOP accumulation.

5.10 *Exhaust Pump or Blower* (i)—This can be either a positive displacement pump or blower or a multistage turbine-type blower. In any case, there must be more than sufficient capacity to draw air through the total resistance of test specimen, scattering chamber, flowmeter, and all of the related lines, valves, filters, etc., at the maximum test rate (usually 85 L/min).

5.11 *Cleanup Filter* (j)—This should be a filter of sufficiently high capacity and efficiency to remove smoke from the airstream before it passes through the flowmeter. Aerosol particles would ultimately affect the accuracy of the meter.

6. Reagents and Materials

6.1 *dioctyl phthalate, (DOP)*—Technical grade.

NOTE 1—DOP is under investigation as a possible carcinogen. Use only by trained personnel wearing appropriate safety equipment to avoid skin contact and inhalation.

7. Procedure

7.1 It is necessary to have the equipment prepared and calibrated in advance of any test work. Once prepared and in adjustment, the equipment can be turned on at any time and operated as long as desired with only occasional minor readjustment. Instruction for preparation and operation of each item of equipment is given below.

7.2 *Aerosol Generator*—Turn on the air supply and heating units of the DOP aerosol generator. Wait until the aerosol output has been stabilized; usually this will require ½ h or more from a cold start. Draw a portion of the aerosol through the particle size analyzer, verify the aerosol particle size, and adjust generator conditions until particle diameter is 0.30 µm (by adjustment of quench air temperature).

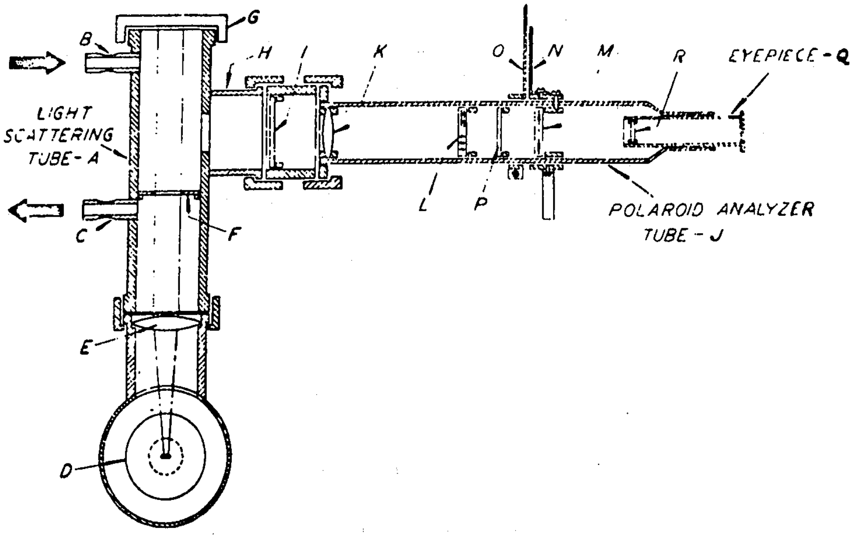
7.3 *Adjustment of Photometer*—Using the same flow rate that will be used for the test specimen (usually 32 L/min ± 2 % through 100 cm^2 of area ± 2 % when testing filter media), aerosol from the generator is passed directly through the scattering chamber. Adjust the *Gain* potentiometer of the galvanometer circuit in the photometer until the meter reads 100.0.

7.3.1 Draw clean filtered air through the scattering chamber. Adjust for stray light so that the photometer meter reads zero on the most sensitive scale.

7.4 *Penetration Measurement*—Mount the sample to be tested in the sample holder, making certain that all seals are tight. Draw aerosol through the test specimen. Adjust flow rate to the desired level, for example, 32 L/min. Starting with the least sensitive range, use progressively higher sensitivity until a reading can be obtained.

7.4.1 Read the photometer. Report the value as percent DOP penetration.

7.5 *Flow Resistance*—At the beginning of the penetration



A—Smoke chamber and light-scattering tube
B—Smoke inlet port
C—Smoke outlet port
D—Light source
E—Lens to form parallel beam of light through smoke chamber
F—Baffle to reduce stray light scattered from walls of chamber
G—Velvet-lined cap on chamber
H—Side arm to light scattering tube
I—Smoke-retaining window

J—Polaroid analyzer tube
K—Light collecting lens
L—Bipartite disc (split field polaroid)
M—Polaroid disc mounted in movable collar
N—Indicator on polaroid holder to show angle of displacement from verticle axis
O—Degree scale for indicator (N)
P—Green filter for obtaining monochromatic light
Q—Adjustable eyepiece
R—Lens in eyepiece

FIG. 2 "Owl" Particle Size Meter

test and after the desired flow rate has been established, the manometer is read, showing the resulting pressure drop across the test specimen. This may change after a short time due to accumulation of DOP in the test piece. Ordinarily, the reading is reported in millimetres of water pressure.

7.6 *Other Data*—Line temperature and manometer readings at the flowmeter should be noted along with the current barometer reading so that airflow rates may be reduced to standard conditions if this is required at some later time.

7.7 *Q Value*—When comparing the filter efficiency of various media, it is often useful to report filter performance in terms of the Q value. Calculate Q value as follows:

$$Q = [-100 \log (P/100)]/\Delta p \quad (1)$$

where:

P = DOP penetration, %, and

Δp = airflow resistance, mm of water.

8. Discussion of Equipment

8.1 *Availability*—Although equipment for the DOP test is commercially available, some care must be exercised in its procurement. While the test is well developed and very reliable, the equipment is complex. It must be within certain design parameters and must be carefully fabricated. Design details are available[4] but it is strongly recommended that purchase be made of equipment from a professional fabricator.[6]

8.2 *Air Supply*—Any reliable air source may be used that is capable of supplying 120 L/min. If taken from a compressed air system, a stepdown regulator should be used, followed by a control value, and a good commercial air-line filter ahead of the high-efficiency (HEPA) filter.

8.2.1 For a mobile unit or where a compressed air line is not available, a blower can be used. A multistage blower, turbine-type, is effective and will run continuously with very little maintenance. An absolute (HEPA) type filter is used customarily in the supply line to ensure that the air is entirely clean.

8.2.2 In any case, provision must be made to either cool or heat the air as conditions may require. Commercial heat exchange equipment is satisfactory.

8.3 *Aerosol Generator*—The aerosol generator consists of a pot containing about 500 mL of DOP at about 170°C. DOP vapor is carried from the container by a small heated airstream (about 215°C) and mixed with a larger stream of quench air (about 25°C) to form the aerosol particles. The airstream temperatures determine particle size and, once established must be precisely controlled. The aerosol is generated continuously; excess aerosol is disposed of away from the test area.

8.4 *Owl*—A typical "Owl" is shown in Fig. 2. A reading of 29 ± 1° corresponds to 0.3-µm diameter DOP particles.

8.5 *Light-Scattering Chamber*—The light-scattering chamber shown diagrammatically in Fig. 3 is an essential component of the photometer system. Any airborne particles entering the chamber are strongly illuminated and the forward-scattered light intensity is detected by a multiplier phototube (H).

8.5.1 Light from the lamp bulb filament (A) is focused at the

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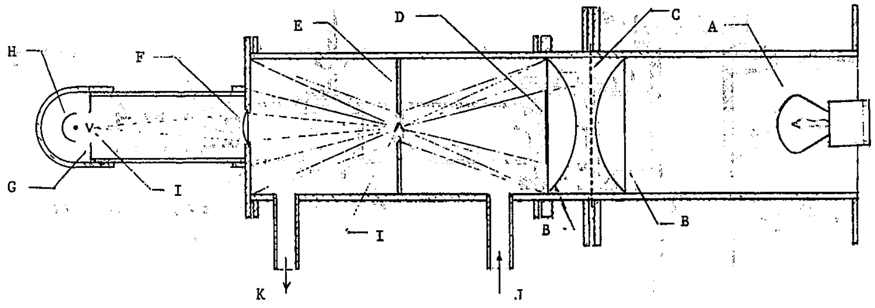
[6] Equipment suitable for the DOP test may be obtained from Air Technology, Inc., 1717 Whitehead Rd, Baltimore, MD 21207.



A—Light source
B—Front lenses
C—Optical filter or light screen
D—Opaque disk
E—Center light baffle
F—Back lens
G—Rear light baffle
H—Multiplier prototube
I—Filament image
J—Inlet port
K—Outlet port

FIG. 3 Light-Scattering Chamber—Schematic Section Showing Optical System

center of the light tube (E) by means of condensing lenses (B). An opaque patch (D) cemented to the inside facing of the condensing lens intercepts any direct light from the filament to the phototube.

8.5.2 The stop opening at (E) has a beveled edge, thus providing a knife edge periphery to the opening. This is important in keeping the amount of light scatter from this illuminated edge at a bare minimum.

8.5.3 Take every care to ensure that only light forward-scattered by the test aerosol is seen by the phototube. Following are points requiring special attention:

8.5.3.1 Optics must be accurately aligned with the optical axis. The light bulb filament image should be focused at the center of the light stop opening.

8.5.3.2 All lens surfaces must be perfectly clean; otherwise, light scatter will result.

8.5.3.3 All lens edges, especially if they are ground surfaces, should be painted with flat black.

8.5.3.4 No frosted or etched design or figure can be permitted on the light bulb envelop facing the condensing lenses.

8.5.3.5 The sharp edge of the light stop must be free of nicks, burrs, or even attached particles.

8.5.3.6 Light bulb current must be supplied from a voltage-stabilized circuit.

8.6 *Photometer*—Various types of photometers are in use. In most, a Type 931A multiplier phototube is operated at output currents below 30 µA to ensure stable operation. A scale switch permits the measurements down to 0.001 % or 0.0001 % penetration of DOP smoke.

9. Maintenance and Troubleshooting

9.1 When used routinely, the DOP test is reliable and seldom presents any serious problems. Experience will soon show the operator what steps must be followed to maintain fully satisfactory equipment performance. However, to assist the neophyte especially, the following basic suggestions are offered:

9.2 *Daily Care*:

9.2.1 Ascertain that the DOP liquid level or supply is adequate.

9.2.2 See that all temperatures are correct and that controls are functioning properly.

9.2.3 If supply air or quench air must be cooled, see that the cooling water is turned on.

9.2.4 Check aerosol particle size and make any adjustments needed to maintain 0.3-µm diameter.

9.3 *No Aerosol Generation*:

9.3.1 Make sure that air supply is working properly.

9.3.2 See that all heaters are on and working.

9.3.3 Check DOP level or supply.

9.3.4 See that both heated air and quench air are being supplied and at the proper rates.

9.4 *Particle Size Analyzer*:

9.4.1 See that the analyzer lamp is lighted.

9.4.2 Make sure that aerosol is flowing through the instrument (exhaust blower or pump turned on and the analyzer line valve open).

9.4.3 See that connection tubes to the analyzer are not pinched.

9.4.4 Adjust quench air temperature to attain correct particle size.

9.5 *Photometer Not Reading*:

9.5.1 See that the lamp is lighted in the scattering chamber.

9.5.2 See that the amplifier is plugged in and operating.

9.5.3 Make sure that aerosol is flowing through the scattering chamber (selector valve in *run* position and not *purge*).

9.5.4 See that multipler phototube is mounted on the scattering chamber and that lead wires are connected in the amplifier.

9.6 *Photometer Cannot be Adjusted for 100 % Reading*:

9.6.1 Make sure that aerosol generator is operating properly.

9.6.2 Make sure that multiplier phototube is properly adjusted.

9.7 *Photometer Cannot be Adjusted for Stray Light*:

9.7.1 The usual fault is excessive stray light in the scattering chamber. Adjust position of the light source (instrument manual) to attain minimum reading on clean air.

9.7.2 Ascertain that the amplifier is performing correctly.

9.7.3 Have the phototube and connecting leads checked.

9.7.4 Make sure there are no leaks into the filtered air supply line. Leaks will introduce particulate matter and cause a meter reading.

9.7.5 If the problem persists, the source of stray light sometimes can be detected by removing the multiplier phototube and looking into the scattering chamber. This approach should be taken only by someone thoroughly familiar with the equipment.

10. Quality Control

10.1 Following are steps that can be taken to help ensure a reliable bias and agreement between laboratories:

10.1.1 *Calibrated Orifice Plate*—Orifice plates are available with calibrations traceable to the National Institute of Standards and Technology (formerly NBS). The plate is inserted in the sample holder and used as a flowmeter against which the instrument flowmeter is compared. For information regarding calibrated plates, inquire of the manufacturer.[7]

10.1.2 *Leaks* in the system can be serious since they will impair the accuracy of flow rate readings. Every precaution must be taken to ensure tightness in lines, instrument filters, and fittings.

10.1.3 *Reference Filter Paper*—It is convenient to have on hand a supply of high-efficiency filter paper that has been pretested and preferably cross-checked by at least one other laboratory. An occasional test run on one of these filter samples will be reassuring and indicative that all is well. Results may be plotted on a control chart to demonstrate attainment of statistical control of the measurement process.[7]

11. Keywords

11.1 atmospheric analysis; air assay media; collection efficiency evaluation of filters; dioctyl phthalate, use for filter evaluation; high efficiency filters; membrane filters; particle collecting devices; smoke test for filter evaluation

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[7] Taylor, John K., "Quality Assurance of Chemical Measurements," Lewis Publishers, Inc., Chelsea, MI (1987).

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An American National Standard

Standard Test Method for
Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry[1]

This standard is issued under the fixed designation D 3120; 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 sulfur in the range from 3.0 to 100 ppm (µg/g) in light liquid hydrocarbons boiling in the range from 26 to 274°C (80 to 525°F).

1.2 This test method may be extended to liquid materials with higher sulfur concentrations by appropriate dilution.

1.3 The preferred units are micrograms per grams. Values stated in SI units are to be regarded as the standard. Values in inch-pound units are for information only.

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 hazard statements, see 6.3, 6.4, 6.8, and 6.10.

2. Summary of Test Method

2.1 A liquid sample is injected into a combustion tube maintained at about 800°C having a flowing stream of gas containing about 80 % oxygen and 20 % inert gas (for example, nitrogen, argon, etc.). Oxidative pyrolysis converts the sulfur to sulfur dioxide which then flows into a titration cell where it reacts with triiodide ion present in the electrolyte. The triiodide thus consumed, is coulometrically replaced and the total current required to replace it is a measure of the sulfur present in the sample injected.

2.2 The reaction occurring in the titration cell as sulfur dioxide enters is:

$$I_3^- + SO_2 + H_2O \rightarrow SO_3 + 3I^- + 2H^+$$

The triiodide ion consumed in the above reaction is generated coulometrically thus:

$$3I^- \rightarrow I_3^- + 2e^-$$

2.3 These microequivalents of triiodide (iodine) are equal to the number of microequivalents of titratable sample ion entering the titration cell.

3. Significance and Use

3.1 This test method is used to determine trace quantities of sulfur in reformer charge stocks and similar petroleum fractions where such trace concentrations of sulfur are deleterious to the performance and life of the catalyst used in the process. Higher concentrations of sulfur in products analyzed by this test method after appropriate dilution are often detrimental to the use of the product.

4. Interferences

4.1 This test method is applicable in the presence of total halide concentrations of up to 10 times the sulfur level and total nitrogen concentrations of up to 1000 times the sulfur level.

4.2 This test method is not applicable in the presence of total heavy metal concentrations (for example, Ni, V, Pb, etc.) in excess of 500 µg/g (ppm).

NOTE 1—To attain the quantitative detectability that the method is capable of, stringent techniques must be employed and all possible sources of sulfur contamination must be eliminated.

5. Apparatus[2]

5.1 *Pyrolysis Furnace*—The sample should be pyrolyzed in an electric furnace having at least two separate and independently controlled temperature zones, the first being an inlet section that can maintain a temperature sufficient to volatilize all the organic sample. The second zone shall be a pyrolysis section that can maintain a temperature sufficient to pyrolyze the organic matrix and oxidize all the organically bound sulfur. A third outlet temperature zone is optional.

5.1.1 Pyrolysis furnace temperature zones for light liquid petroleum hydrocarbons should be variable as follows:

Inlet zone	up to at least 700°C
Center pyrolysis zone	800 to 1000°C
Outlet zone (optional)	up to at least 800°C

5.2 *Pyrolysis Tube,* fabricated from quartz and constructed in such a way that a sample, which is vaporized completely in the inlet section, is swept into the pyrolysis zone by an inert gas where it mixes with oxygen and is burned. The inlet end of the tube shall hold a septum for syringe entry of the sample and side arms for the introduction of oxygen and inert gases. The center or pyrolysis section should be of sufficient volume to ensure complete pyrolysis of the sample.

5.3 *Titration Cell,* containing a sensor-reference pair of electrodes to detect changes in triiodide ion concentration and a generator anode-cathode pair of electrodes to maintain constant triiodide ion concentration and an inlet for a

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[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 D02.03 on Elemental Analysis.

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[2] The apparatus described in Sections 5.1 to 5.5 inclusive, is similar in specifications to equipment available from Dohrmann Div. of Rosemount, 3240 Scott Blvd., Santa Clara, CA 95050. For further detailed discussions, in equipment, see: Preprints—Division of Petroleum Chemistry, American Chemical Society, Vol 1, No. 3, Sept. 7–12, 1969, p. B232 "Determination of Sulfur, Nitrogen, and Chlorine in Petroleum by Microcoulometry," by Harry V. Drushel.

gaseous sample from the pyrolysis tube. The sensor electrode shall be platinum foil and reference electrode platinum wire in saturated triiodide half-cell. The generator anode and cathode half-cell shall also be platinum. The titration cell shall require mixing, which can be accomplished through the use of a magnetic stirring bar, stream of inert gas, or other suitable means.

NOTE 2: **Caution**—Excessive speed will decouple the stirring bar, causing it to rise in the cell and damage the electrodes. The creation of a slight vortex is adequate.

5.4 *Microcoulometer,* having variable attenuation, gain control, and capable of measuring the potential of the sensing-reference electrode pair, and comparing this potential with a bias potential, amplifying the potential difference, and applying the amplified difference to the working-auxiliary electrode pair so as to generate a titrant. Also the microcoulometer output voltage signal shall be proportional to the generating current.

5.5 *Recorder,* having a sensitivity of at least 0.1 mV/in. with chart speeds of ½ to 1 in./min. Use of a suitable electronic or mechanical integrator is recommended but optional.

5.6 *Sampling Syringe*—A microlitre syringe of 10-µL capacity capable of accurately delivering 1 to 10 µL of sample into the pyrolysis tube. 3-in. by 24-gage needles are recommended to reach the inlet zone of the pyrolysis furnace.

NOTE 3—Since care must be taken not to overload the pyrolyzing capacity of the tube by too fast a sample injection rate, means should be provided for controlling the sample addition rate (0.1 to 0.2 µL/s).

6. Reagents and Materials

6.1 *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.[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.

6.2 *Purity of Water*—The water used in preparing the cell electrolyte should be demineralized or distilled or both. Water of high purity is essential.

NOTE 4—Distilled water obtained from an all borosilicate glass still, fed from a demineralizer, has proven very satisfactory.

6.3 *Acetic Acid* (rel dens 1.05)—Glacial acetic acid (CH_3COOH).

NOTE 5: **Warning**—Poison. Corrosive. Combustible. May be fatal if swallowed. Causes severe burns. Harmful if inhaled.

6.4 *Argon, Helium, or Nitrogen,* high purity grade (HP),[4] used as carrier gas.

NOTE 6: **Warning**—Compressed gas under high pressure. Gas reduces oxygen available for breathing.

6.5 *Cell Electrolyte Solution*—Dissolve 0.5 g of potassium iodide (KI) and 0.6 g of sodium azide (NaN_3) in approximately 500 mL of high-purity water, add 5 mL of acetic acid (CH_3COOH) and dilute to 1000 mL.

NOTE 7—Bulk quantities of the electrolyte should be stored in a dark bottle or in a dark place and be prepared fresh at least every 3 months.

6.6 *Gas Regulators*—Two-stage gas regulators must be used on the reactant and carrier gas.

6.7 *Iodine* (I), 20 mesh or less, for saturated reference electrode.

6.8 ***Iso*****octane**[5] (2,2,4-trimethylpentane).

NOTE 8: **Warning**—Extremely flammable. Harmful if inhaled. Vapors may cause flash fire.

NOTE 9—The most reliable solvent is a sulfur-free form of the sample type to be analyzed. Alternatively, use a high-purity form of cyclohexane [boiling point 80°C (176°F)], *iso*octane (2,2,4-trimethyl pentane) [boiling point, 99.3°C (211°F)], or hexadecane [boiling point, 287.5°C (549.5°F)].

6.9 *n-Butyl Sulfide* ($(CH_3CH_2CH_2CH_2)_2S$).

6.10 Oxygen, high purity grade (HP),[4] used as the reactant gas.

NOTE 10: **Warning**—Oxygen vigorously accelerates combustion.

6.11 *Potassium Iodide* (KI), fine granular.

6.12 *Sodium Azide* (NaN_3), fine granular.

NOTE 11: **Warning**—Toxic, causes eye and skin irritation; explosive.

6.13 *Sulfur, Standard Solution* (*approximately 30 µg/g (ppm)*)—Pipet 10 mL of sulfur stock solution (reagent 6.14) into a 100-mL volumetric flask and dilute to volume with *iso*octane.

NOTE 12—The analyst may choose other sulfur compounds for standards appropriate to sample boiling range and sulfur type which cover the concentration range of sulfur expected.

6.14 *Sulfur, Standard Stock Solution* (*approximately 300 µg/g (ppm)*)—Weigh accurately 0.5000 g of *n*-butyl sulfide into a tared 500-mL volumetric flask. Dilute to the mark with *iso*octane and reweigh.

$$\text{S, ppm } (\mu g/g) = \frac{\text{g of } n\text{-butyl sulfide} \times 0.2187 \times 10^6}{\text{g of } (n\text{-butyl sulfide} + \text{solvent})}$$

7. Preparation of Apparatus

7.1 Carefully insert the quartz pyrolysis tube in the pyrolysis furnace and connect the reactant and carrier gas lines.

7.2 Add the electrolyte solution to the titration cell and flush several times. Maintain an electrolyte level of ⅛ to ¼ in. (3.2 to 6.4 mm) above the platinum electrodes.

7.3 Place the heating tape on the inlet of the titration cell.

7.4 Position the platinum foil electrodes (mounted on the moveable cell head) so that the gas inlet flow is parallel to the electrodes with the generator anode adjacent to the generator cathode. Assemble and connect the coulometer and recorder (integrator optional) as designed or in accordance with the manufacturer's instructions. Figure X1.2 illustrates the typ-

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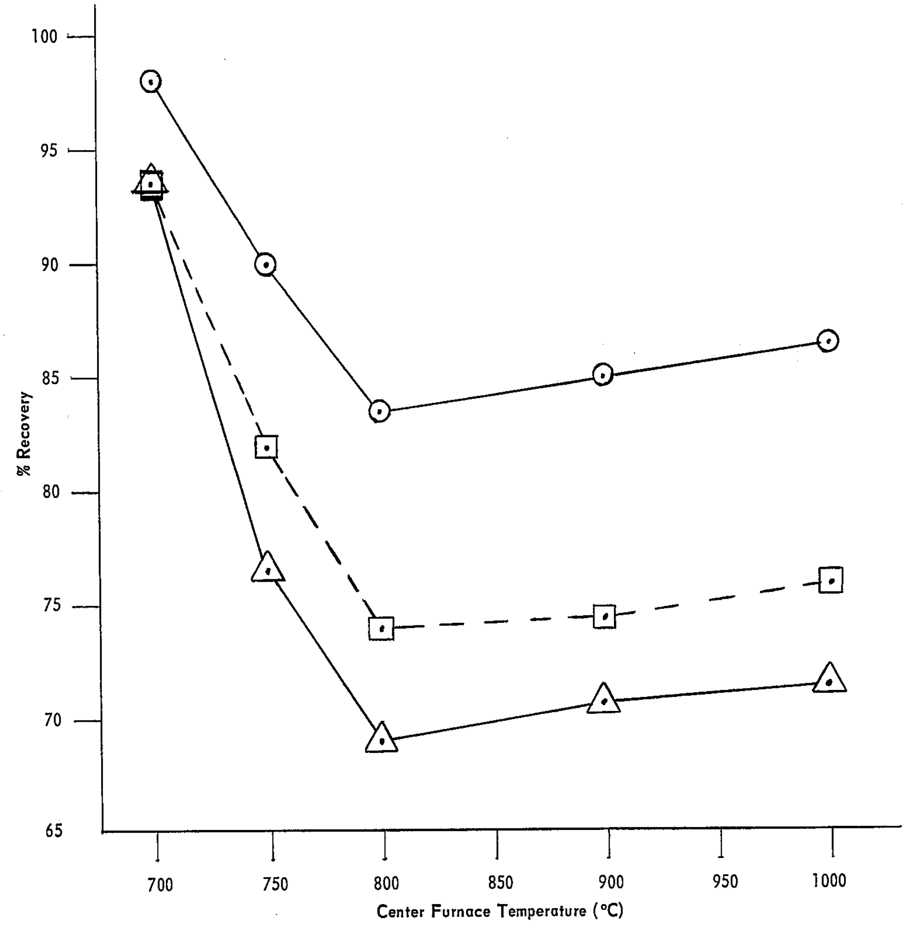
[3] *Reagent Chemicals, American Chemical Society Specifications,* American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States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

[4] High-purity grade gas has a minimum purity of 99.995 %.

[5] Pesticide test grade such as Mallinckrodt "Nano-grade" *iso*octane has been found satisfactory.



Oxidative sulfur system: Thiophene in cyclohexane (10 ppm S) using 0.06% azide electrolyte

Legend	Flow rate (cc/min) Oxygen	Argon	O_2/Ar ratio
⊙——⊙	40	160	1:4
▣---▣	100	100	1:1
△——△	160	40	4:1

FIG. 1 Percent Recovery versus Temperature (°C)

ical assembly and gas flow through a coulometric apparatus.

7.4.1 Turn the heating tape on.

7.5 Adjust the flow of the gases, the pyrolysis furnace temperature, titration cell, and the coulometer to the desired operating conditions. Typical operational conditions are given in Table 1.

8. Calibration and Standardization

8.1 Prepare a series of calibration standards covering the range of sulfur concentration expected. Follow instructions in 6.13, 6.14, or dilute to appropriate level with *iso*octane.

8.2 Adjust the operational parameters (7.5).

NOTE 13—See Fig. 1 for the variance of percent recoveries with gas ratios and temperature.

8.3 The sample size can be determined either volumetrically or by mass. The sample size should be 80 % or less of the syringe capacity.

8.3.1 Volumetric measurement can be obtained by filling the syringe with about 8 µL or less of sample, being careful to eliminate bubbles, retracting the plunger so that the lower liquid meniscus falls on the 1-µL mark, and recording the volume of liquid in the syringe. After the sample has been injected, again retract the plunger so that the lower liquid meniscus falls on the 1-µL mark, and record the volume of liquid in the syringe. The difference between the two volume

TABLE 1 Typical Operational Conditions

Reactant gas flow (oxygen), cm^3/min	160
Carrier gas flow (Ar, He, N) cm^3/min	40
Furnace temperature; °C:	
Inlet zone	700
Pyrolysis zone	800
Outlet zone	800
Titration cell	set to produce adequate mixing
Coulometer:	
Bias voltage, mV	160
Gain	low (approximately 200)

readings is the volume of sample injected.

8.3.2 Alternatively, the sample injection device may be weighed before and after the injection to determine the amount of sample injected. This technique provides greater precision than the volume delivery method, provided a balance with a precision of ±0.00001 g is used.

8.4 Insert the syringe needle through the inlet septum up to the syringe barrel and inject the sample or standard at an even rate not to exceed 0.1 to 0.2 µL/s. If a microlitre syringe is used with an automatic injection adapter, the injection rate (volume/pulse) should be calibrated to deliver 0.1 to 0.2 µL/s.

8.5 Repeat the measurement of each calibration standard at least three times.

NOTE 14—Not all of the sulfur in the sample comes through the furnace as titratable SO_2. In the strongly oxidative conditions of the pyrolysis tube some of the sulfur is also converted to SO_3 which does not react with the titrant. Accordingly, sulfur standards of *n*-butyl sulfide in *iso*octane or sulfur standards appropriate to sample boiling range and sulfur type and sulfur concentration should be prepared to guarantee adequate standardization. Recoveries less than 75 % are to be considered suspect. Low recoveries are an indication to the operator that he should check his parameters, his operating techniques, and his coulometric system. If the instrument is being operated properly, recoveries between 75 and 90 % are to be expected. Satisfactory standard materials[6] are given in Table 2.

8.6 If the fraction of sulfur converted to SO_2 drops below 75 % of the standard solutions, fresh standards should be prepared. If a low conversion factor persists, procedural details should be reviewed.

9. Procedure

9.1 Flush the 10-µL syringe several times with the unknown sample. Determine the sulfur concentration in accordance with 8.2 to 8.6.

9.2 Sulfur concentration may require adjustment of sensitivity settings or sample volume or both.

10. Calculation

10.1 Calculate the sulfur content of the sample in parts per million, ppm µg/g, by mass as follows:

$$\text{Sulfur, ppm } \mu g/g = (A \times 1.99)/(R \times M \times F) \qquad (1)$$

$$\text{Sulfur, ppm} = (A \times 1.99 \times 10^3)/(R \times V \times D \times F) \qquad (2)$$

where:

A = area under curve, in.^{2},

1.99 = derivation will be found in X1.3,

TABLE 2 Satisfactory Standard Materials

Sample Type	Boiling Point Range °C (°F)	Sulfur Compound
Naphthas	26 to 204 (80 to 400)	cyclohexane sulfide
Jet fuels and stove oil	177 to 274 (350 to 525)	benzyl-thiophene

R = coulometer range switch setting, Ω,

M = mass of sample, g (volume × density),

V = volume of sample, µL,

D = density of sample, g/mL, and

F = recovery factor, fraction of sulfur in standard that is titrated, ratio of ppm sulfur determined in standard divided by the known ppm sulfur in standard. $F = (A \times 1.99)/(R \times M \times C_{std})$

where:

C_{std} = concentration of standard, ppm.

10.2 Derivation of the calculation equation will be found in X1.3.

NOTE 15—The calculation equation is valid only when the chart speed is 0.5 in./min and a 1-mV (span) recorder with a sensitivity of 0.1 mV/in. is used.

NOTE 16—If a disk integrator is used, see X1.3 for calculations, derivations, and equations.

NOTE 17—A more general form of the equation in 10.1 which is not dependent on the use of a particular recorder scale nor a disk integrator is as follows:

$$\text{sulfur, ppm } (\mu g/g) = \frac{(A)\,(X)\,(0.166)}{(R)\,(Y)\,(M)\,(F)}$$

where:

A = area in appropriate units,

X = recorder sensitivity for full-scale response (mv),

$$0.166 = \frac{(16 \text{ gS/eq})\,(10^{-3} \text{ V/mV})\,(10^6\ \mu g/g)}{(96\ 500 \text{ coulombs/eq})},$$

R = resistance, Ω,

Y = area equivalence for a full-scale response on the recorder per second . . . area units per second,

M = mass of sample, g, and

F = recovery factor.

11. Precision and Bias

11.1 The precision of this test method as obtained by statistical examination of interlaboratory test results is as follows:

11.1.1 *Repeatability*—The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method exceed 28 % of the average value only in one case in twenty.

11.1.2 *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, in the normal and correct operation of the test method exceed 38 % of the average only in one case in twenty.

11.2 *Bias*—Since there is no accepted reference material suitable for determining the bias for the procedure in this test

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[6] Wallace, L. D., "Comparison of Oxidative and Reductive Methods for the Microcoulometric Determinations of Sulfur in Hydrocarbons," *Analytical Chemistry*, Vol 42, March 1970, p. 393.

method, no statement on bias is made.[7]

12. Keywords

12.1 light hydrocarbons; microcoulometry; sulfur

APPENDIX

(Nonmandatory Information)

X1. DERIVATION OF COULOMETRIC CALCULATIONS USED IN SECTION 10.1

X1.1 The configuration of the pyrolysis tube and furnace may be constructed as is desirable as long as the operating parameters are met. Figure X1.1 is typical of apparatus currently in use.

X1.2 A typical assembly and oxidative gas flow through a coulometric apparatus for the determination of trace sulfur is shown in Fig. X1.2.

X1.3 *Derivation of Equations:*

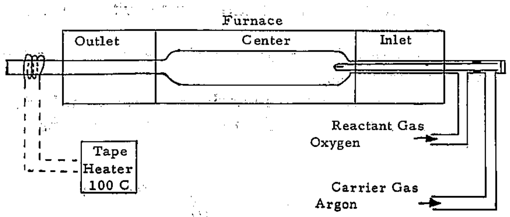

FIG. X1.1 Pyrolipis Tube

X1.3.1 The derivation of the equations used in the calculation section is based on the coulometric replacement of the triiodide (iodine) ions consumed in the microcoulometric titration cell reaction ($I_3^- + 2e^- \rightarrow 3I^-$). The quantity of the reactant formed (triiodide ions) between the beginning and the interruption of current at the end of the titration is directly proportional to the net charge transferred, Q.

X1.3.2 In most applications a constant current is used so that the product of current, i, in amperes (coulombs per second), multiplied by the time, T (seconds), required to reach the end point provides a measure of the charge, Q (coulombs), necessary to generate the iodine equivalent to the reactant; that is, $Q = it$. Therefore, the number of equivalents of reactant is equal to Q/F, where F is the Faraday constant, 96 500 C per equivalent.

X1.3.3 Therefore, the expression to be solved to find the mass of reactant is:

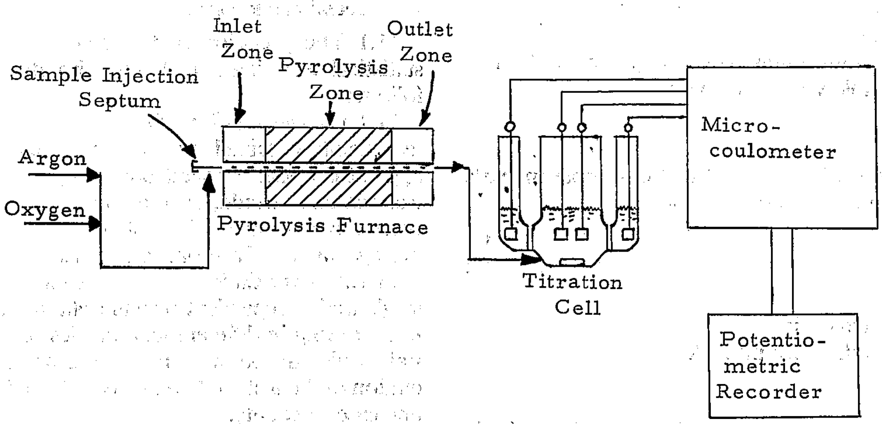

FIG. X1.2 Flow Diagram for Coulometric Apparatus for Trace Sulfur Determination

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[7] Supporting data are available from ASTM. Request RR: D02-1036.

$$\text{Concentration of sulfur} = \frac{\text{mass of sulfur, g}}{\text{mass of sample, g}} = \frac{\dfrac{Q(\mathrm{C})}{\dfrac{F\mathrm{C}}{\mathrm{eq}}} \times \dfrac{16\ \mathrm{g}}{\mathrm{eq}}}{\text{mass of sample, g}} \tag{X1.1}$$

$$\mu\mathrm{g\ S} = A\ \mathrm{in.}^2 \times \frac{\dfrac{0.1\ \mathrm{mV}}{\mathrm{in.}} \times \dfrac{2\ \mathrm{min}}{\mathrm{in.}} \times \dfrac{60\ \mathrm{s}}{\mathrm{min}} \times \dfrac{10^{-3}\ \mathrm{V}}{\mathrm{mV}} \times \dfrac{16\ \mathrm{g}}{\mathrm{eq}} \times \dfrac{10^6\ \mu\mathrm{g}}{\mathrm{g}}}{R(\Omega) \times \dfrac{96\,500\ \mathrm{C}}{\mathrm{eq}} \times \dfrac{\mathrm{A\,.\,s}}{\mathrm{C}} \times f)} \tag{X1.2}$$

where:

A in.^{2} = peak area measured in square inches,

0.1 mV/in. = millivolt span of upscale deflection for the recorder,

2 min/in. = chart speed in minutes per inch,

60 s/min = conversion of time in minutes to seconds,

10^{-3} V/mV = conversion of volts to millivolts,

16 g/eq = gram-equivalent of sulfur,

10^6 μg/g = micrograms per gram conversion factor,

R(Ω) = microcoulometer range switch setting in ohms,

substituting $V/R = 1$ (amps)

$$\mathrm{Q(A\cdot s)} = \frac{A\ \mathrm{in.}^2 \times \dfrac{0.1\ \mathrm{mV}}{\mathrm{in.}} \times \dfrac{2\ \mathrm{min}}{\mathrm{in.}} \times \dfrac{60\ \mathrm{s}}{\mathrm{min}} \times \dfrac{10^{-3}\ \mathrm{V}}{\mathrm{mV}}}{R(\Omega)} \tag{X1.3}$$

F = 96 500 C/eq = Faraday's constant[8] (electrical equivalence of one gram-equivalent mass of any substance)

A·s/C = conversion of coulombs to ampere-seconds, and

f = recovery factor (ratio of ppm S determined in standard versus known ppm S in standard)

Therefore,

$$\mu\mathrm{g\ S} = \frac{A \times 12 \times 10^{-3}\ \mathrm{A\cdot s} \times \dfrac{16\ \mathrm{g}}{\mathrm{eq}} \times \dfrac{10^6\ \mu\mathrm{g}}{\mathrm{g}}}{R \times \dfrac{96\ 500\ \mathrm{C}}{\mathrm{eq}} \times \dfrac{\mathrm{A\cdot s}}{\mathrm{C}} \times f} \tag{X1.4}$$

Therefore,

$$\mu\mathrm{g\ S} = \frac{A \times 12 \times 10^{-3} \times 16 \times 10^6\ \mu\mathrm{g}}{R \times 96\ 500 \times f} \tag{X1.5}$$

Therefore,

$$\mu\mathrm{g\ S} = (A \times 1.99)/(R \times f) \tag{X1.6}$$

Since ppm = μg/g:

$$\mathrm{ppm\ S} = \frac{A \times 1.99}{R \times f \times \text{volume, } \mu\mathrm{L} \times 10^{-3}\ \dfrac{\mathrm{mL}}{\mu\mathrm{L}} \times \text{density, } \dfrac{\mathrm{g}}{\mathrm{mL}}} \tag{X1.7}$$

$$\mathrm{ppm\ S} = \frac{A \times 1.99 \times 10^3}{R \times f \times \text{volume} \times \text{density}} \tag{X1.8}$$

Since mass = volume × density

$$\mathrm{ppm\ S} = (A \times 1.99)/(R \times f \times \text{mass, g}) \tag{X1.9}$$

X1.3.4 *Derivation with Disk Integrator*—A in Eq X1.6 is expressed as in.^{2} However, it may also be expressed as counts. Therefore, A in.^{2} = counts × 10^{-3} since 1 in.^{2} = 1000 counts. Therefore, substituting counts × 10^{-3} for A in Eq X1.6 gives

$$\mu\mathrm{g\ S} = (\text{counts} \times 1.99 \times 10^{-3})/(R \times f)$$

Then:

$$\mathrm{ppm\ S} = \frac{\text{counts} \times 1.99}{R \times \text{volume, } \mu\mathrm{L} \times \text{density, } \dfrac{\mathrm{g}}{\mathrm{mL}} \times f} \tag{X1.10}$$

$$\mathrm{ppm\ S} = (\text{counts} \times 1.99 \times 10^{-3})/(R \times \text{mass, g} \times f)$$

NOTE X1.1—Counts = 100 × number of integrator per full-scale excursions.

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[8] The value of the Faraday has been redetermined in 1960 by the National Bureau of Standards: the new value is 96 489 ± 2 coulombs (chemical scale).

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Designation: D 3173 – 87 (Reapproved 1996)

Standard Test Method for Moisture in the Analysis Sample of Coal and Coke[1]

This standard is issued under the fixed designation D 3173; 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 moisture in the analysis sample of coal or coke. It is used for calculating other analytical results to a dry basis. When used in conjunction with the air drying loss as determined in accordance with Method D 2013 or Practice D 346, each analytical result can be calculated to an as-received basis:

1.2 *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 346 Practice for Collection and Preparation of Coke Samples for Laboratory Analysis[2]

D 2013 Method of Preparing Coal Samples for Analysis[2]

D 3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases[2]

D 3302 Test Method for Total Moisture in Coal[2]

3. Summary of Test Method

3.1 Moisture is determined by establishing the loss in weight of the sample when heated under rigidly controlled conditions of temperature, time and atmosphere, sample weight, and equipment specifications.

4. Significance and Use

4.1 Moisture as determined by this test method is used for calculating other analytical results to a moisture free basis using procedures in Practice D 3180. Moisture percent determined by this test method may be used in conjunction with the air-dry moisture loss determined in Method D 2013 and Test Method D 3302 to determine total moisture in coal. Total moisture is used for calculating other analytical results to "as received" basis using Practice D 3180. Moisture, ash, volatile matter, and fixed carbon percents constitute the proximate analysis of coal and coke.

5. Analysis Sample

5.1 The analysis sample is that sample which has been pulverized to pass 250-µm (No. 60) sieve as prepared in accordance with Practice D 346 or Method D 2013.

6. Apparatus

6.1 *Drying Oven,* for coal samples:

6.1.1 For determining the moisture of coal, the oven shall be so constructed as to have a uniform temperature in all parts, have a minimum of air space, and be capable of temperature regulation between the limits of 104 and 110°C. It may be of the form shown in Fig. 1. Provision shall be made for renewing the preheated air in the oven at the rate of two to four times a minute, with the air dried as defined in 7.1.

6.1.2 In the oven shown in Fig. 1, the door should contain a hole of approximately ⅛ in. (3.2 mm) in diameter near the bottom to permit a free flow of air through the oven space.

6.2 *Drying Oven,* for coke samples. For determining the moisture of coke, an ordinary drying oven with openings for natural air circulation and capable of temperature regulation between limits of 104 and 110°C may be used.

6.3 *Capsules,* with covers. A convenient form, which allows the ash determination to be made on the same sample, is a porcelain capsule, ⅞ in. (22 mm) in depth and 1¾ in. (44 mm) in diameter, or a fused silica capsule of similar shape. These capsules shall be used with a well-fitting flat aluminum cover, illustrated in Fig. 2. Platinum crucibles or glass capsules with ground-glass caps may also be used. They should be as shallow as possible, consistent with convenient handling.

7. Reagents

7.1 *Dry Air*—Air used to purge the drying oven should be dried to a moisture content of 1.9 mg/L or less. (Dew point −10°C or less.) Any desiccant or drying method capable of achieving this degree of dryness is suitable.

7.2 *Desiccants*—Materials suitable for use in the desiccator may be chosen from the following:

7.2.1 *Anhydrous Calcium Sulfate* (0.004 mg/L).

7.2.2 *Silica Gel.*

7.2.3 *Magnesium Perchlorate* (0.0005 mg/L).

7.2.4 *Sulfuric Acid, Concentrated* (0.003 mg/L).

7.2.5 The desiccant must be kept fresh enough to assure that the air in the desiccator is dry as defined in 7.1. Values in parentheses ( ) are literature values for the residual amount of moisture in air at equilibrium with these desiccants.

NOTE—**Warning:** Sulfuric acid is corrosive and can cause severe damage to eyes, skin, and clothing. Magnesium perchlorate is a strong oxidant and can react violently with organic materials.

8. Procedure for Sample Passing a 250-µm (No. 60) Sieve

8.1 Heat the empty capsules under the conditions at which the sample is to be dried, place the stopper or cover on the capsule, cool over a desiccant for 15 to 30 min, and

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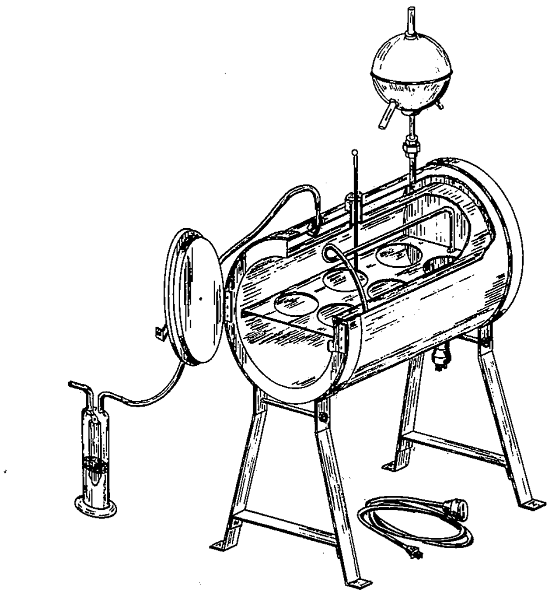
[1] This test method is under the jurisdiction of ASTM Committee D-5 on Coal and Coke and is the direct responsibility of Subcommittee D05.21 on Methods of Analysis.

Current edition approved June 8, 1987. Published August 1987. Originally published as D 3173 – 73. Last previous edition D 3173 – 85.

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



NOTE—Details in U.S. Bureau of Mines Bulletin No. 492, 1951, p 6

FIG. 1 Moisture Oven

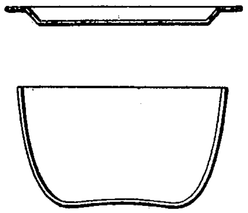


FIG. 2 Capsule for Use in Determining Moisture

weigh. Dip out with a spoon or spatula from the sample bottle approximately 1 g of the sample. Put this quickly into the capsule, close, and weigh at once to the nearest ± 0.1 mg.

8.2 An alternative procedure for weighing the sample (more subject to error) is as follows: After transferring an amount of the sample slightly in excess of 1 g, bring to exactly 1 g in weight (±0.5 mg) by quickly removing the excess weight of the sample with a spatula. The utmost dispatch must be used in order to minimize the exposure of the sample until the weight is determined.

8.3 After removing the covers, quickly place the capsules in a preheated oven (at 104 to 110°C) through which passes a current of dry air. (The current of dry air is not necessary for coke.) Close the oven at once and heat for 1 h. Open the oven, cover the capsules quickly, cool in a desiccator over desiccant, and weigh as soon as the capsules have reached room temperature.

8.4 Use the percentage of moisture in the sample passing a 250-µm (No. 60) sieve to calculate the results of the other analyses to a dry basis.

9. Calculations

9.1 Calculate the percent moisture in the analysis sample as follows:

$$\text{Moisture in analysis sample, \%} = [(A - B)/A] \times 100$$

where:

A = grams of sample used, and
B = grams of sample after heating.

10. Precision and Bias

10.1 The following criteria should be used for judging the acceptability of results:

10.1.1 *Repeatability*—Duplicate results by the same laboratory should not be considered suspect unless they differ by more than 0.2 % for coals having less than 5 % moisture and 0.3 % for coals having more than 5 % moisture.

10.1.2 *Reproducibility*—The results submitted by two or more laboratories should not be considered suspect unless they differ by more than 0.3 % for coals having less than 5 % moisture and 0.5 % for coals having more than 5 % moisture.

10.1.3 *Bias*—Certified standards are not available for the determination of bias by this test method.

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Standard Test Methods for Carbon and Hydrogen in the Analysis Sample of Coal and Coke[1]

This standard is issued under the fixed designation D 3178; 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 cover the determination of total carbon and hydrogen in samples of coal or coke. Both the carbon and hydrogen are determined in one operation. These test methods yield the total percentages of carbon and hydrogen in the coal as analyzed and the results include not only the carbon and hydrogen in the organic matter, but also the carbon present in mineral carbonates and the hydrogen present in the free moisture accompanying the sample as well as hydrogen present as water of hydration of silicates.

NOTE 1—It is recognized that certain technical applications of the data derived from this test procedure may justify additional corrections. These corrections could involve compensation for the carbon present as carbonates, the hydrogen of free moisture accompanying the sample, and the calculated hydrogen present as water of hydration of silicates.

1.2 When data are converted and reported on the "dry" basis, the hydrogen value is corrected for the hydrogen present in the free moisture accompanying the sample.

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.*

1.4 The values stated in SI units are to be regarded as the standard.

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 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]

TOTAL CARBON AND TOTAL HYDROGEN

3. Summary of Test Methods

3.1 The determination of carbon and hydrogen is made by burning a weighed quantity of sample in a closed system and fixing the products of combustion in an absorption train after complete oxidation and purification from interfering substances. These test methods give the total percentages of carbon and hydrogen in the coal as analyzed, and include the carbon in carbonates and the hydrogen in the moisture and in the water of hydration of silicates.

4. Significance and Use

4.1 Carbon and hydrogen values are used to calculate the amount of oxygen (air) required in combustion processes, and in the calculations of efficiency of combustion processes.

4.2 Carbon and hydrogen determinations are used in material balances on coal conversion processes; also one or the other is frequently used in correlations of chemical and physical properties, such as yields of products in liquefaction, reactivity in gasification, and the density and porosity of coal.

5. Sample

5.1 The sample shall be the material pulverized to pass No. 60 (250-µm) sieve and well mixed according to Method D 346 or Method D 2013. It may be beneficial to grind the ash, pit ash, calcined coke and high mineral content materials to pass a No. 100 (150-µm) sieve.

5.2 The test sample shall be weighed just prior to commencing the analysis to minimize chance for moisture change. A change in moisture content would introduce error in the hydrogen analysis. In order to provide the data necessary to correct for the hydrogen present in the moisture and ensuing final calculations of both the hydrogen and carbon, a separate sample shall be weighed out at the same time for a moisture analysis, and analyzed in accordance with Test Method D 3173.

6. Apparatus

6.1 *Oxygen Purifying Train*, consisting of the following units arranged as listed in the order of passage of oxygen:

6.1.1 *First Water Absorber*—A container for the solid dehydrating reagent. It shall be so constructed that the oxygen must pass through a column of reagent adequate to secure water equilibrium equal to that secured in the prescribed absorption train. A container of large volume and long path of oxygen travel through the reagent will be found to be advantageous where many carbon and hydrogen determinations are made.

6.1.2 *Carbon Dioxide Absorber*—A container for solid carbon dioxide absorbing agent. It shall be constructed as described in 6.1.1 and shall provide for a column of reagent adequate to remove carbon dioxide completely.

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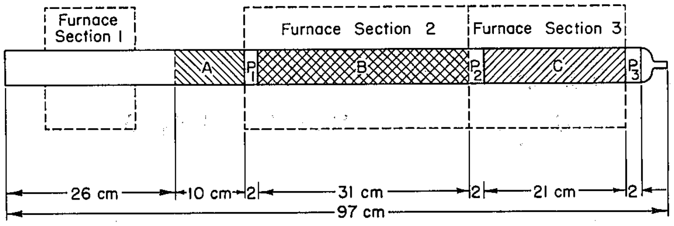
[1] These test methods are under the jurisdiction of ASTM Committee D-5 on Coal and Coke and are the direct responsibility of Subcommittee D05.21 on Methods of Analysis.

Current edition approved Sept. 29, 1989. Published February 1990. Originally published as D 3178 – 73. Last previous edition D 3178 – 84.

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

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



A—Clear fused quartz section (optional) when a translucent quartz tube is used.
B—Cupric oxide filling.
C—Lead chromate or silver filling.
P_1, P_2, or P_3—oxidized copper gauze plugs.

NOTE—All dimensions are given in centimetres. When furnace sections longer than those specified in 6.3 are to be used, changes in the above dimensions shall be in accordance with the provisions of Note 5.

FIG. 1 Arrangement of Tube Fillings for Combustion Tube

6.1.3 *Second Water Absorber*, same as specified in 6.1.1

6.2 *Flowmeter*, used to permit volumetric measurement of the rate of flow of oxygen during the determination. It shall be suitable for measuring flow rates within the range from 50 to 100 mL/min (standard temperature and pressure). The use of a double-stage pressure-reducing regulator with gage and needle valve preceding the first water absorber is recommended to permit easy and accurate adjustment of the rate of flow.

6.3 *Combustion Unit*—The combustion unit shall consist of three electrically heated furnace sections, individually controlled, which may be mounted on rails for easy movement; the upper part of each furnace may be hinged so that it can be opened for inspection of the combustion tube. The three furnace sections shall be as follows:

6.3.1 *Furnace Section 1*, nearest the oxygen inlet end of the combustion tube, approximately 130-mm long and used to heat the inlet end of the combustion tube and the sample. It shall be capable of rapidly attaining an operating temperature of 850 to 900°C. Combustion tube temperature shall be measured by means of a thermocouple placed immediately adjacent to the tube near the center of the tube section.

6.3.2 *Furnace Section 2*, approximately 330 mm in length and used to heat that portion of the tube filled with cupric oxide. The operating temperature shall be 850 ± 20°C. Combustion tube temperature shall be measured by means of a thermocouple placed immediately adjacent to the tube near the center of the tube section.

6.3.3 *Furnace Section 3*, approximately 230 mm-long, and used to heat that portion of the tube filled with lead chromate or silver. The operating temperature shall be 500 ± 50°C. Combustion tube temperature shall be measured by means of a thermocouple placed immediately adjacent to the tube near the center of the tube section.

6.3.4 *Combustion Tube*—The combustion tube shall be made of fused quartz or high-silica glass[4] and shall have a nominal inside diameter which may vary within the limits of 19 to 22 mm and a minimum total length of 970 mm. The exit end shall be tapered down to provide a tubulated section for connection to the absorption train. The tubulated section shall have a length of 20 to 25 mm, an internal diameter of not less than 3 mm, and an external diameter of approximately 7 mm. The total length of the reduced end shall not exceed 60 mm. If a translucent fused quartz tube is used, a transparent section 190-mm long, located 250 mm from the oxygen inlet end of the tube, will be found convenient (see Fig. 1).

6.3.5 *Combustion Boat*—This shall be either glazed porcelain, fused silica, or platinum. Boats with internal dimensions of approximately 70 by 8 by 8 mm have been found convenient.

6.4 *Absorption Train*—The absorption train shall consist of the following units arranged as listed in the order of passage of oxygen:

6.4.1 *Water Absorber*, having a capacity for 45 cm^3 of solid reagent and a minimum length of gas travel through the reagent of 80 mm.[5]

6.4.2 *Carbon Dioxide Absorber*—If solid reagents are used for carbon dioxide absorption the container shall be as described in 6.4.1. If a solution is used, the container shall be a Vanier bulb.

6.4.3 *Guard Tube*—A container as described in 6.4.1.

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 Analytical 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 Type IV reagent water, conforming to Specification D 1193.

7.3 *Oxygen*, 99.5 % purity or better (Note 5).

7.4 *Combustion Tube Reagents:*

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[4] Vycor has been found satisfactory for this purpose.

[5] Glass-stoppered containers such as the Nesbitt, Schwartz U-tube and the Stetser-Norton bulbs have been found satisfactory.

[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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

7.4.1 *Cupric Oxide* (*CuO*), wire form, dust-free.

7.4.2 *Fused Lead Chromate*, ($PbCrO_4$) approximately 2.38 to 0.84 mm size.

7.4.3 *Silver Gauze*, 99.9 % silver minimum purity, 0.84 mm, made from approximately No. 27 B&S gage wire.

7.4.4 *Copper Gauze*, 99.0 % copper minimum purity, 0.84 mm made from approximately No. 26 B&S gage wire.

7.5 *Purification and Absorption Train Reagents*:

7.5.1 *Water Absorbent*—Anhydrous magnesium perchlorate ($Mg(ClO_4)_2$) of approximately 2.38 to 0.35 mm size.

NOTE 2—Trade names of the reagents are Anhydrone and Dehydrite.

7.5.2 *Carbon Dioxide Absorbent*—If a solid reagent is used, it shall be sodium or potassium hydroxide (NaOH or KOH) impregnated in an inert carrier of approximately 2.38 to 0.84 mm size. Use of soda lime in place of the above or in admixture with them is permissible (Note 3). If a solution is used, it shall be 30 weight % potassium hydroxide (KOH).

NOTE 3—Trade names of the sodium and potassium hydroxide permissible solid carbon dioxide absorbing reagents are: Ascarite II, Caroxite, and Mikohbite. If soda lime is used in admixture with any of the foregoing, it should not exceed 30 weight % of the total reagent. In using Ascarite it may be necessary to add a few drops of water to this reagent to assure complete absorption of carbon dioxide.

8. Preparation of Apparatus

8.1 *Combustion Tube Packing*—To ensure complete oxidation of combustion products and complete removal of interfering substances such as oxides of sulfur, the combustion tube shall be packed with cupric oxide and lead chromate or silver. The arrangement and lengths of the tube fillings and separating plugs shall be as shown in Fig. 1. It is recommended that the tube be placed in a vertical position (constricted end downward) for packing. When filling the tube with lead chromate, any residual reagent adhering to the walls of the empty portion of the tube must be removed. When silver is used as a tube filling, the required length of filling may be prepared conveniently from three or four strips of silver gauze 150 to 200-mm long, by rolling each strip into a cylindrical plug and inserting the strips end-to-end in the tube.

NOTE 4—Longer furnaces with appropriate lengths of tube packing will be satisfactory.

8.2 *Absorption Train:*

8.2.1 *Water Absorber*—A container that is filled with a permissible solid desiccant by adding the required amount in small portions and settling each portion by gentle tapping between additions. Place a glass wool plug between the reagent and the absorber outlet to prevent loss of reagent dust.

8.2.2 *Carbon Dioxide Absorber*—If a solid reagent is used for the retention of carbon dioxide, fill the absorber as described in 8.2.1. Place in the outlet section of the container a layer or cap of desiccant that is the same as that used in the water absorber. This layer shall have a bulk volume not less than one fourth nor more than one third of the combined volume of both reagents. If a liquid absorbent is used, fill the inner tube of the Vanier bulb with the same desiccant used in the water absorber. Place a glass wool plug in the outlet section of the container to prevent loss of reagent dust.

8.2.3 *Guard Tube*, packed with equal volumes of the water absorbent and a solid carbon dioxide absorbent.

8.2.4 *Connections*—To ensure a closed system from the supply tank of oxygen to the guard tube at the end of the absorption train, it is recommended that all connections by glass-to-glass or glass-to-quartz butt joints be sealed with short lengths of flexible tubing. The connection between the purification train and the combustion tube may be made by means of a rubber stopper or other suitable device. All connections shall be gas tight. No lubricant shall be used for making tubing connections in the absorption train.

8.3 *Conditioning of Apparatus:*

8.3.1 *Newly Packed Combustion Tube*—Burn a sample of coal or coke as described in 9.4 except that the products of combustion need not be fixed in a weighed absorption train.

8.3.2 *Used Combustion Tube*—After any extended shut down, one day or more, test the combustion train under procedure conditions, but without burning a sample, for 40 min with weighed absorption bulbs connected. A variation of not more than 0.5 mg of either bulb shall be considered satisfactory.

NOTE 5—If the blank tests for flow indicate interfering impurities in the oxygen supply by consistent weight-gain in the absorption bulbs, eliminate these impurities by using a preheater furnace and tube, filled with cupric oxide. Operate this preheater furnace at 850 ± 20°C and insert in series between the supply tank of oxygen and the purification train.

8.3.3 *Absorption Train*—Condition freshly packed absorber and guard tubes by burning a sample of coal or coke as described in 9.4 except that tube weights need not be determined.

8.3.4 *Standard Checks* shall be made frequently, particularly when intermittent use of the combustion train is common or when any changes have been made in the system. A standard substance of certified analysis, such as benzoic acid or sucrose as furnished by the National Bureau of Standards shall be burned as described in Section 9. A variation from the theoretical of not more than 0.07 % for hydrogen nor more than 0.30 % for carbon shall be considered satisfactory.

9. Procedure

9.1 After the combustion tube and absorbers have been conditioned as prescribed in Section 8, conduct the test as follows:

9.2 *Absorption Train*—Bring the absorption tubes to room temperature near the balance for 15 to 20 min, vent momentarily to the atmosphere, wipe with a chamois or lint-free cloth in the areas where handled, and weigh to the nearest 0.1 mg.

9.3 *Sample*—Weigh approximately 0.2 g (weighed to the nearest 0.1 mg) of air-dry sample ground to pass a No. 60 (250-µm) sieve into a combustion boat.

9.4 *Sample Analysis*—With furnace (6.3.2 and 6.3.3) at specified temperatures and positioned as shown in Fig. 1, perform the following operations in rapid succession in the order listed:

9.4.1 If a conventional type of sample heating furnace is used for heating (6.3.1), place it so that its left-hand edge is about 100 mm from the oxygen inlet end of the combustion tube.

9.4.2 Attach the weighed absorption train to the tube:

9.4.3 Push the sample boat into the tube to a point within approximately 20 mm from plug P_1;

9.4.4 Close the tube and adjust the oxygen flow to a rate of 50 to 100 mL/min (standard temperature and pressure) being the same as used in blanking (see 8.3.2).

9.4.5 Apply full heat to heating section No. 1 to bring it to an operating temperature of 850 to 900°C as rapidly as possible. Move the heater slowly toward the boat so that it completely covers the boat and is brought into contact with heating (6.3.2) in a period of 10 to 20 min (Note 6). Allow it to remain in this position for an additional 5 to 10 min and then shut off the heat and return the sample heater to its original position. Continue to the flow of oxygen through the tube for 10 min (Note 7), close the absorbers under a positive pressure of oxygen, and detach them from the train. Remove the absorbers to the vicinity of the balance, allow them to cool to room temperature for 15 to 20 min, vent momentarily to atmosphere, wipe them with a chamois or lint-free cloth in the areas handled, and finally weigh them to the nearest 0.1 mg. While the absorbers are cooling, it is recommended that the ash remaining in the combustion boat be examined for traces of unburned carbon which, if present, will nullify the determination.

NOTE 6—Some variation in operating technique and heater manipulation may be permitted here at the discretion of the analyst, provided that it is conducive to a gradual and controlled release of volatile matter. Conditions that lead to visible burning (flame combustion) of the sample shall be avoided.

NOTE 7—Since water may condense in the cooler outlet end of the combustion tube or in the inlet arm of the water absorber, the use of an external or internal heat conducting device (a metal heat bridge) is recommended to prevent such condensation or promote reevaporation during this flushing period.

10. Calculation

10.1 Calculate the percentage of carbon (Note 8) in the analysis sample as follows:

$$\text{Carbon, \%} = (A \times 27.289)/B \qquad (1)$$

where:

A = increase in weight of CO_2 absorption bulb, g, and
B = grams of sample used.

NOTE 8—It is recognized that formation of oxides of nitrogen during the combustion procedure may lead to slightly high results for carbon. However, extensive study of this effect by five laboratories led to the conclusion that error so incurred would not be significant in commercial application. In certain research applications, where accuracy of a higher order is required, means of removing oxides of nitrogen prior to water and carbon dioxide absorption should be included.

10.2 *Hydrogen*—Calculate the percentage of hydrogen in the analysis sample (Note 9) as follows:

$$\text{Hydrogen, \%} = (C \times 11.19)/B \qquad (2)$$

where:

B = grams of sample used, and
C = increase of weight of water absorption bulb, g.

NOTE 9—The water absorbed in the water absorption tube includes not only water formed as a product of combustion, but also free water (moisture) in the sample and water of hydration of any clay minerals present.

11. Report

11.1 The results of the carbon and hydrogen analysis may be reported on any of a number of bases, differing from each other in the manner by which moisture is treated.

11.2 A separate portion of the analysis sample shall be analyzed for moisture content in accordance with Test Method D 3173, in order to allow calculation of the as-analyzed data to other bases.

11.3 Procedures for converting the values obtained on the analysis sample to other bases are described in Methods D 3176 and D 3180.

12. Precision and Bias

12.1 The permissible differences between two or more determinations shall not exceed the following values:

	Repeatability, %	Reproducibility, %
Carbon	0.3	. . .
Hydrogen	0.07	

12.2 The bias of this test method cannot be determined at this time.

CERTIFICATE

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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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Designation: D 3236 – 88 (Reapproved 1999)

An American National Standard

Standard Test Method for Apparent Viscosity of Hot Melt Adhesives and Coating Materials[1]

This standard is issued under the fixed designation D 3236; 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 apparent viscosity of hot melt adhesives and coating materials compounded with additives and having apparent viscosities up to 200 000 millipascal second (mPa·s) (Note 3) at temperatures up to 175°C (347°F).

Note 1—Although precision has not been studied, this procedure may be adaptable to viscosities higher than the present 200 000-mPa·s limit and temperatures above 175°C (347°F). Equipment described in this procedure permits testing of materials having viscosities as high as 16×10^6 mPa·s and provides temperatures up to 260°C (500°F).

Note 2—For petroleum waxes and their blends having apparent viscosities below 15 mPa·s, Test Method D 445 is especially applicable.

Note 3—One pascal second (Pa·s) = 1000 centipoise (CP); one millipascal second (mPa·s) = one centipoise.

1.2 The values stated in acceptable metric units are to be regarded as the standard. The values 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 445 Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (the Calculation of Dynamic Viscosity)[2]

3. Terminology

3.1 *Definitions:*

3.1.1 *viscosity*—the ratio of shear stress to shear rate. The viscosity of a liquid is a measure of the internal friction of the liquid in motion. The unit of dynamic viscosity is the pascal second. For a Newtonian liquid, the viscosity is constant at all shear rates. For a non-Newtonian liquid, viscosity will vary depending on shear rate.

3.1.2 *apparent viscosity*—the viscosity determined by this test method and expressed in millipascal seconds. Its value may vary with the spindle and rotational speed selected because many hot melts are non-Newtonian.

4. Summary of Test Method

4.1 A representative sample of the molten material to be tested is maintained in a thermally controlled sample chamber. Apparent viscosity is determined under temperature equilibrium conditions using a precision rotating spindle type viscometer. Data obtained at several temperatures can be plotted on appropriate semi-logarithmic graph paper and apparent viscosity at intermediate temperatures can be estimated.

5. Significance and Use

5.1 This test method distinguishes between hot melts having different apparent viscosities. It is believed that apparent viscosity determined by this procedure is related to flow performance in application machinery operating under conditions of low shear rate. Apparent viscosity as determined by this test method may not correlate well with end use applications where high shear rates are encountered.

5.2 Materials of the type described in this procedure may be quite non-Newtonian and as such the apparent viscosity will be a function of shear rate under the conditions of test. Although the viscometer described in this test method generally operates under conditions of relatively low shear rate, differences in shear effect can exist depending upon the spindle and rotational speed conditions selected for the test program. Maximum correlation between laboratories, therefore, depends upon testing under conditions of equivalent shear.

5.3 Approximate shear rates using various spindles are shown in Table A1.1 in the Annex to this procedure.

6. Apparatus

6.1 *Viscometer*, rotating spindle type with leveling stand.[3]

6.2 *Viscometer Spindles*, stainless steel.[3]

6.3 *Sample Chamber*, with precision proportional temperature controller[3],[4] that provides control accuracy of ±1.0°C

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[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 D02.10.0A on Physical and Chemical Properties.

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

[3] Suitable viscometers and accessories can be obtained from Brookfield Engineering Laboratories, Inc., Stoughton, MA 02072.

[4] A suitable temperature controller can be obtained from Athena Controls, Inc., 2 Union Road, West Conshohocken, PA 19428.

(1.8°F) or better through the range from 100 to 200°C (212 to 392°F).

6.4 *Graph Paper*, semi-logarithmic.

7. Calibration

7.1 The viscometer is precalibrated using Newtonian fluids by the manufacturer. No zero adjustment is provided since experience has shown that the zero point will not vary due to changes in the spring. The viscometer and spindles are precision equipment and should be kept from undue shock and mishandling. Physical damage to the instrument will often reveal itself as erratic or no oscillation of the pointer when the instrument, with or without the spindle in place, is operated in air. When operating normally, the pointer will be stable and have free oscillation about the zero point in air.

7.2 The instrument may be further calibrated using standard reference fluids. Suitable fluids are available in nominal viscosities up to 15 000 mPa·s at 149°C (300°F).[5] The procedure for instrument calibration using standard reference fluids is that encompassed by this test method. Results obtained using standard reference fluids should not deviate from the nominal viscosity by more than 2 %.

7.3 The temperature controller of the type recommended for this procedure is factory calibrated and has control capability of ±0.5 % of the control point (±1.0°C at 175°C). To further check the controller and further establish controller settings, use the following procedure: Place a sufficient quantity of low viscosity (500 mPa·s or less) hot melt in the sample container to permit immersion of the appropriate ASTM thermometer to the proper depth. Do not permit the thermometer bulb to rest on the bottom of the sample container. Suitable thermometers are shown in Table 1.

TABLE 1 Suitable ASTM Thermometers

Temperature Range	Immersion, mm	Scale Error, max	ASTM Thermometer Number
90°C to 170°C	51	0.2°C	35C-62
194°F to 338°F	51	0.5°F	35F-62
145°C to 205°C	76	0.4°C	100C-68

NOTE 4—Particular care must be taken not to overflow the sample chamber when using the 100°C, 76-mm immersion thermometer.

7.3.1 Insert the thermometer through the insulating cover of the sample container and hold it in place at the point required for proper immersion depth. Adjust the thermal controller to provide the desired test temperature. Rotate the thermometer during temperature reading to minimize the effect of thermal gradients in the sample. Continue temperature readings and controller adjustment until minimum deviation from test temperature is obtained. Minimum deviation may vary between laboratories, depending upon the controller, but should in no case exceed ±0.5°C (0.9°F). Repeat this procedure for any test temperature desired within the scope of this procedure.

8. Procedure

8.1 *Selection of Spindle*—From the estimated viscosity of the sample and Table A1.1 in the Annex, select a viscometer and spindle combination that will produce readings in the desired range.

NOTE 5—Use only the spindle shown to be appropriate for the viscometer to be used.

8.1.1 Where more than one spindle is available for the range selected, choose the spindle that produces results nearest the midpoint of the measurable viscosity range. Viscometer scale readings must be within the 10 to 95 range.

NOTE 6—Care must be taken in the storage and handling of spindles and assemblies. Protect them from dust, corrosive deposits, and mechanical abuse. Avoid touching the calibrated section of the spindle with the hands. Clean the spindle and sample chamber thoroughly after each use. A recommended cleaning procedure is included in Annex A2.

8.2 *Preparation of Sample*—Place the required amount of representative sample (see Table 2) measured to the nearest 0.005 g (or 0.05 mL if handled in the molten state) in the sample chamber. Melt the sample in an oven set at the desired test temperature or in the thermo-container preheated to the desired test temperature. Avoid excessive or prolonged heating of the sample to minimize thermal and oxidative effects. Use a fresh sample for each temperature for which a determination is to be made.

8.3 *System Alignment and Spindle Insertion*—After the sample is completely melted, lower the properly aligned and leveled viscometer until the tips of the alignment bracket just touch the top of the thermo-container, making contact directly behind the locating ring. Raise the viscometer, positioning the tips of the alignment bracket 2 mm (1⁄16 in.) above the top of the thermo-container. Using both hands, gently slide the thermo-container base until the tips of the alignment bracket *just touch* the locating ring. *Do not* forcibly displace the alignment bracket (see Fig. 1). Screw the link coupling nut onto the viscometer coupling nut (note left-hand thread). Connect the coupling link to the spindle (and the coupling nut). Lower the spindle into the sample chamber and connect the link coupling nut to the viscometer coupling nut, noting the left-hand thread. Pick up the insulating cap and place it over the sample chamber (see Fig. 1).

8.4 *Viscosity Determination*—Ensure that the material in the sample chamber is completely molten and that temperature controller settings are proper. Turn on the viscometer and allow the spindle to rotate at the lowest spindle speed available to

TABLE 2 Sample Size Requirement

Spindle	Approximate Volume, mL	Approximate Sample Weight, g[A]
SC 4-18	8.00	6.40
SC 4-21	8.00	6.40
SC 4-27	10.50	8.40
SC 4-28	11.50	9.20
SC 4-29	13.00	10.40
SC 4-31	10.00	8.00
SC 4-34	9.50	7.60

[A] Based on typical molten specific gravity of 0.800. If the specific gravity of the material to be tested varies greatly from this value, sample size must be adjusted to ensure proper liquid level on the spindle shaft.

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[5] Suitable calibration fluids may be obtained from Brookfield Engineering Laboratories, Inc., Stoughton, MA 02072 or Cannon Instrument Co., P. O. Box 16, State College, PA 16801.

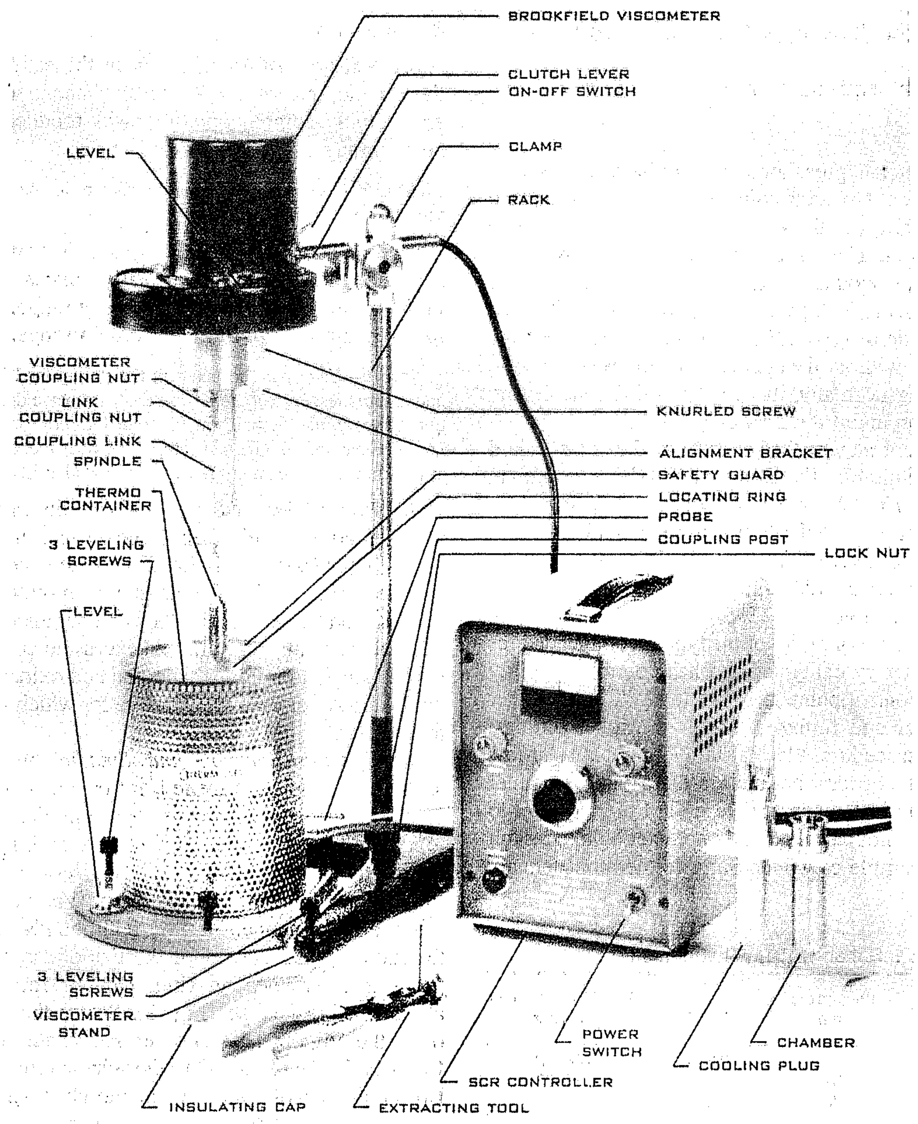

FIG. 1 Apparatus for Viscosity Determination

minimize temperature gradients in the sample as well as possible shear effects. When temperature equilibrium is indicated, turn off the viscometer, remove the insulating cap, raise the viscometer and spindle, and inspect the liquid level on the spindle shaft. It should extend about 3 mm (⅛ in.) up the spindle shaft beyond the upper, tapered portion of the spindle. If the liquid level varies significantly from this, add or remove sample to provide this level. Replace the insulating cap, and allow the unit to reestablish temperature equilibrium with the spindle rotating at the lowest available speed. Continue spindle rotation for 15 min after apparent equilibrium. Increase the spindle speed to that required to produce a scale reading nearest the midpoint of the scale, but in no case outside the 10 to 95 unit range. Engage the pointer clutch and stop the viscometer motor when the pointer is in view. Record the scale reading. Restart the viscometer motor, and allow at least five additional revolutions of the spindle. Engage the pointer clutch and stop the viscometer motor with the pointer in view. Record the second dial reading. Repeat the above operation until three consecutive scale readings are obtained which differ by no more than 0.5 unit.

9. Calculation

9.1 Determine the average of the three consecutive scale readings which differ by no more than 0.5 scale unit. To convert to millipascal seconds, multiply this value by the appropriate factor taken from either the instrument instruction manual or Table A1.2 in the Annex. Repeat this for each temperature.

NOTE 7—If it is necessary to interpolate for viscosity values at intermediate temperatures, plot a series of observed apparent viscosity values on the logarithmic scale and the corresponding test temperatures on the linear scale of appropriate semi-logarithmic paper, using a series of at least three different temperatures. From the plot, determine the apparent

TABLE 3 Summary of Precision Estimates, Total Round-Robin Data

Sample No.	Average Viscosity, mPa·s	Sa	deg freedom	Sa + b	deg freedom	Sa %	Sa + b %
MI69-28							
100°C	65.2	2.02	11	3.64	10	3.10	5.58
125°C	38.7	1.07	10	2.39	9	2.76	6.18
150°C	25.2	0.27	10	2.20	9	1.07	8.73
MI69-29							
100°C	170.2	4.39	10	19.7	9	2.58	11.58
125°C	93.4	2.54	9	9.10	8	2.72	9.74
150°C	55.8	1.00	9	4.23	8	1.79	7.59
MI69-30							
125°C	232,100	8540	6	9040	5	3.68	3.88
150°C	128,167	4280	6	7380	5	3.34	5.76
175°C	74,021	1840	7	5310	6	2.49	7.17
MI69-31							
125°C	3416	117	11	207	10	3.43	6.06
150°C	1456	43.2	11	70.0	10	2.96	4.81
175°C	756	16.7	11	46.2	10	2.21	6.11
MI69-32							
125°C	66,560	2850	9	7410	8	4.28	11.13
150°C	26,800	1130	9	2750	8	4.22	10.26
175°C	11,850	449	9	1030	8	3.79	8.69
MI69-33							
125°C	165,300	3730	7	7320	6	2.26	4.43
150°C	74,590	1880	8	2650	7	2.52	3.78
175°C	35,840	1820	9	2420	8	5.07	6.75

Pooled Data:

Sa (overall) = 3.14 % at 162 deg freedom	Sa + b (overall) = 7.60 % at 7 deg freedom
3.14 × 2.80 = 8.8 % relative	7.60× 3.34 = 25.4 % relative

TABLE 4 Summary of Precision Estimates, Selected Shear Equalized Data

Sample No.	Average Viscosity, mPa·s	Sa	deg freedom	Sa + b	deg freedom	Sa %	Sa + b %
MI69-28							
100°C	64.4	1.33	7	2.15	6	2.07	3.34
125°C	38.0	0.56	5	0.75	4	1.47	1.97
150°C	24.1	0.51	6	0.47	5	2.12	1.95
MI69-29							
100°C	163.2	0.63	6	4.09	5	0.38	2.51
125°C	90.3	0.75	5	1.90	4	0.90	2.11
150°C	53.7	0.83	5	1.30	4	1.55	2.42
MI69-30							
125°C	229,900	10,240	4	15,700	3	4.59	7.04
150°C	130,900	5200	5	5200	4	3.97	3.97
175°C	74,640	830	5	4750	4	1.11	6.36
MI69-31							
125°C	3429	40	6	77.6	5	1.17	2.26
150°C	1474	12.3	6	28.3	5	0.83	1.92
175°C	770	15.6	5	21.0	4	2.03	2.73
MI69-32							
125°C	68,680	1450	5	3440	4	2.11	5.00
150°C	28,000	255	6	1670	5	0.91	5.96
175°C	12,350	361	6	911	5	2.92	7.38
MI69-33							
125°C	167,700	1730	5	5000	4	1.03	2.98
150°C	75,700	756	7	1645	6	1.00	2.17
175°C	37,350	685	5	1070	4	1.83	2.86

Pooled Data:

Sa (overall) = 1.83 % at 99 deg freedom	Sa + b (overall) = 3.81 % at 4 deg freedom
1.83 × 2.82 = 5.16 % relative	3.81 × 3.92 = 14.93 % relative

viscosity at any temperature requested, within the range of test temperatures.

10. Report

10.1 Report the apparent viscosity at a given temperature along with the particulars of the instrument model, the spindle number and rotational speed. *Example:* Apparent viscosity at 125°C (RVT, SC 4-28, 20 rpm)—20 000 mPa·s.

NOTE 8—If it is desired to report the shear rate corresponding to the instrument/spindle/speed combination, refer to Table A1.1 for the appropriate calculation.

11. Precision and Bias

11.1 The precision of this test method as determined by statistical examination of interlaboratory results is as follows:

11.1.1 *Repeatability*— The difference between two test results, obtained by the same operator with the same apparataus under constant operating conditions on identical test material would, in the normal and correct operation of the test method, exceed the following values in one case in twenty:

8.8 % of the mean of the two results. (1)

11.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories in identical test material would, in the long run, exceed the following value only in one case in twenty:

25.4 % of the mean of the two results. (2)

NOTE 9—The precision of this test method is based on a round-robin conducted using six wax-based hot melt materials that are believed to be representative of the class. Tests were conducted at three temperatures by seven to eleven laboratories using the Brookfield viscometer model and spindle combination available to that laboratory. This encompassed a total of four viscometer models (Models LVF, LVT, RVT, and HBT) and seven different spindles, each appropriately tailored to the viscometer used. The effect of shear rate was disregarded.

11.1.3 A review of that portion of the data which can be considered comparable at equal shear rates indicates that those laboratories capable of comparing data at equal shear rates can expect improvement in reproducibility. It is estimated that under conditions of equal shear rate reproducibility the values would in the long run, exceed the following in one case in twenty:

15 % of the mean of the two results. (3)

11.1.4 A summary of data generated in this round-robin program is shown in Table 3 and Table 4.

11.2 *Bias*—The procedure in this test has no bias because the value of apparent viscosity can be defined only in terms of a test method.

12. Keywords

12.1 adhesives; apparent viscosity; coating materials; hot melt adhesives; viscosity

ANNEXES

(Mandatory Information)

A1. APPARATUS AND EQUIPMENT SET-UP

A1.1 *Viscometer and Stand*—Set up the viscometer stand on a firm, level surface convenient to a 15-A, 115-V, 60-Hz a-c electrical service and a cooling water supply and drain. Connect the coupling post to the rack, and screw both posts into the V-shaped base, leaving the lock nut loose. Place the three leveling screws in position in the base. Attach the viscometer to the stand, inserting it into the clamp on the rack. The viscometer must be leveled and centered on the viscometer base. Lock the posts tightly to the stand with the lock nut on the coupling post. Raise the viscometer to the highest position on the stand. Making certain that the power switch is off, plug in the viscometer power cord.

A1.2 *Alignment Bracket*—With the viscometer raised to the highest position on the stand and the dial directly in front, attach the alignment bracket to the back of the viscometer pivot cup, securing it tightly with the knurled screw.

A1.3 *Thermo-container, Sample Chamber, and Safety Guard* —Level the red thermo-container base using the three leveling screws in the base. Slide the perforated safety guard over the top of the thermo-container, sliding it past the power cord flush against the red base. Using the extracting tool, insert the sample chamber into the thermo-container. Rotate the sample chamber until it drops and locks in place preventing further rotation.

A1.4 *Controller and Probe*—Place the controller on the level surface adjacent to the thermo-container. Insert the three-pronged male plug from the thermo-container braided cord into the socket on the controller. **Caution:** This plug must be connected to the controller only. Insert the 4-in. stainless steel probe into the hole in the thermo-container located directly above the braided cord. Plug the other end of the probe into the connector on the controller. Making certain that the controller power switch is in the OFF position, plug the controller power cord "into" a 115-V, 60-Hz, grounded a-c power source.

TABLE A1.1 Viscometer-Spindle Data

LV Series Viscometers

Spindle	Viscosity Range, mPa·s			Shear Rate, s^{-1}	Sample Volume, mL	Approximate Sample Weight, g
	LVT	LVF	5 x LVT			
SC 4-18	5–10 000	5–500	25–50 000	1.32 (N)[A]	8.0	6.4
SC 4-31	50–100 000	50–5 000	250–500 000	0.34 (N)	10.0	8.0
SC 4-34	100–200 000	100–10 000	500–1 000 000	0.28 (N)	9.5	7.6

RV Series Viscometers

Spindle	Viscosity Range, mPa·s			Shear Rate, s^{-1}	Sample Volume, mL	Approximate Sample Weight, g
	RVT	RVF	RVF–100			
SC 4-21	50–100 000	250–25 000	50–5 000	0.93 (N)	8.0	6.4
SC 4-27	250–500 000	1 250–125 000	250–25 000	0.34 (N)	10.5	8.4
SC 4-28	5001 000 000	2 500–250 000	500–50 000	0.28 (N)	11.5	9.2
SC 4-29	1 000–2 000 000	5 000–500 000	1 000–100 000	0.25 (N)	13.0	10.4

HA Series Viscometers

Spindle	Viscosity Range, mPa·s		Shear Rate, s^{-1}	Sample Volume, mL	Approximate Sample Weight, g
	HAT	HAF			
SC 4-21	100–200 000	1 000–100 000	0.93 (N)	8.0	6.4
SC 4-27	500–1 000 000	5 000–500 000	0.34 (N)	10.5	8.4
SC 4-28	1 000–2 000 000	10 000–1 000 000	0.28 (N)	11.5	9.2
SC 4-29	2 000–4 000 000	20 000–2 000 000	0.25 (N)	13.0	10.4

HB Series Viscometers

Spindle	Viscosity Range, mPa·s		Shear Rate, s^{-1}	Sample Volume, mL	Approximate Sample Weight, g
	HBT	HBF			
SC 4-21	400–800 000	4 000–400 000	0.93 (N)	8.0	6.4
SC 4-27	2 000–4 000 000	20 000–2 000 000	0.34 (N)	10.5	8.4
SC 4-28	4 000–8 000 000	40 000–4 000 000	0.28 (N)	11.5	9.2
SC 4-29	8 000–16 000 000	80 000–8 000 000	0.25 (N)	13.0	10.4

[A] *N* = rpm at which dial readings are taken

Example: Model RVT Viscometer/SC 4-28 spindle at 20 rpm

$$\text{Shear Rate Factor} \times \text{Spindle Speed in rpm} = \text{Shear Rate in } s^{-1}$$

$$0.28 \times 20 = 5.6\ s^{-1}$$

A1.5 *System Alignment and Spindle Insertion*—Level the viscometer stand base and the thermo-container and base. Lower the viscometer until the tips of the alignment bracket *just touch* the top of the thermo-container, making contact directly behind the locating ring. Raise the viscometer, positioning the tips of the alignment bracket about 2 mm (1⁄16 in.) above the top of the thermo-container. Using both hands, gently slide the thermo-container base until the tips of the alignment bracket *just touch* the locating ring. *Do not* forcibly displace the alignment bracket. Screw the link coupling nut onto the viscometer coupling nut, noting the left-hand thread. Connect the coupling link to the spindle. Lower the spindle into the sample chamber and connect the spindle and link to the link coupling nut on the viscometer. Place the insulating cap over the sample chamber inlet, thus capping the system.

TABLE A1.2 Viscometer-Spindle Factor Data

NOTE 1—To calculate viscosity in millipascal seconds (mPa·s) multiply the dial reading by the factor, corresponding to the viscometer, spindle, and speed combination utilized.

LV Series Viscometer Spindle Factors

Speed, rpm	LVT			LVF			5 × LVT		
	SC4-18	SC4-31	SC4-34	SC4-18	SC4-31	SC4-34	SC4-18	SC4-31	SC4-34
60	0.5	5	10	0.5	5	10	2.5	25	50
30	1.0	10	20	1.0	10	20	5	50	100
12	2.5	25	50	2.5	25	50	12.5	125	250
6	5	50	100	5	50	100	25	250	500
3	10	100	200				50	500	1M
1.5	20	200	400				100	1M	2M
0.6	50	500	1M				250	2.5M	5M
0.3	100	1M	2M				500	5M	10M

RV Series Viscometer Spindle Factors

Speed, rpm	RVT				RVF				RVF-100			
	SC4-21	SC4-27	SC4-28	SC4-29	SC4-21	SC4-27	SC4-28	SC4-29	SC4-21	SC4-27	SC4-28	SC4-29
00	5	25	50	100	...	...	...	...	5	25	50	100
50	10	50	100	200	...	...	...	...	10	50	100	200
20	25	125	250	500	25	125	250	500	25	125	250	500
10	50	250	500	1M	50	250	500	1M	50	250	500	1M
5	100	500	1M	2M	...	...	...	...				
4	...	...	...	...	125	625	1.25M	2.5M				
2.5	200	1M	2M	4M	...	...	...	...				
2	...	...	...	...	250	1.25M	2.5M	5M				
1	500	2.5M	5M	10M	...	...	...	...				
0.5	1M	5M	10M	20M	...	...	...	...				

HA Series Viscometer Spindle Factors

Speed, rpm	HAT				HAF			
	SC4-21	SC4-27	SC4-28	SC4-29	SC4-21	SC4-27	SC4-28	SC4-29
100	10	50	100	200	...	...	...	...
50	20	100	200	400	...	...	...	...
20	50	250	500	1M	...	...	...	...
10	100	500	1M	2M	100	500	1M	2M
5	200	1M	2M	4M	200	1M	2M	4M
2.5	400	2M	4M	8M	...	...	...	...
2	...	...	...	...	500	2.5M	5M	10M
1	1M	5M	10M	20M	1M	5M	10M	20M
0.5	2M	10M	20M	40M	...	...	...	...

HB Series Viscometer Spindle Factors

Speed, rpm	HBT				HBF			
	SC4-21	SC4-27	SC4-28	SC4-29	SC4-21	SC4-27	SC4-28	SC4-29
100	40	200	400	800	...	...	...	...
50	80	400	800	1.6M	...	...	...	...
20	200	1M	2M	4M	...	...	...	...
10	400	2M	4M	8M	400	2M	4M	8M
5	800	4M	8M	16M	800	4M	8M	16M
2.5	1.6M	8M	16M	32M	...	...	...	...
2	...	...	...	...	2M	10M	20M	40M
1	4M	20M	40M	80M	4M	20M	40M	80M
0.5	8M	40M	80M	160M	...	...	...	...

A2. CLEANING OF EQUIPMENT

A2.1 The spindle and sample chambers are made from stainless steel and may be cleaned with most commercial chlorinated or hydrocarbon solvents. If the solvents are heated, adequate precautions must be taken to avoid toxicity, flammability, or explosive hazards. Spindles and cham-bers must not come in contact with sulfuric acid, hydrofluoric acid, hydrochloric acid, and ferric chloride. Care must also be exercised to avoid scratching or deforming the spindles.

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An American National Standard

Standard Test Method for Sulfur in Petroleum Gas by Oxidative Microcoulometry[1]

This standard is issued under the fixed designation D 3246; 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 determination of sulfur in the range from 1.5 to 100 mg/kg (ppm by mass) by weight in hydrocarbon products that are gaseous at normal room temperature and pressure.

NOTE 1—The test method has been tested cooperatively only on high-purity ethylene gas. Precision data have not been developed for other products.

1.2 The values stated in SI units are to be regarded as the standard.

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 1265 Practice for Sampling Liquified Petroleum (LP) Gases—Manual Method[2]

D 1193 Specification for Reagent Water[3]

D 3120 Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry[4]

F 307 Practice for Sampling Pressurized Gas for Gas Analysis[5]

2.2 *Other Standards:*

Compressed Gas Association Booklets G-4 and G-4-1 on the Use of Oxygen.[6]

3. Summary of Test Method

3.1 A sample is injected into a combustion tube maintained at about 800°C having a flowing stream of gas containing about 80 % oxygen and 20 % inert gas (for example, nitrogen, argon, etc.). Oxidative pyrolysis converts the sulfur to sulfur dioxide which then flows into a titration cell where it reacts with triiodide ion present in the electrolyte. The triiodide thus consumed, is coulometrically replaced and the total current required to replace it is a measure of the sulfur present in the sample injected.

3.2 The reaction occurring in the titration cell as sulfur dioxide enters is:

$$I_3^- + SO_2 + H_2O \rightarrow SO_3 + 3I^- + 2H^+ \qquad (1)$$

The triiodide ion consumed in the above reaction is generated coulometrically thus:

$$3I^- \rightarrow I_3^- + 2e^- \qquad (2)$$

3.3 These microequivalents of triiodide (iodine) are equal to the number of microequivalents of titratable sample ion entering the titration cell.

3.4 A liquid blend containing a known amount of sulfur is used for calibration.

4. Significance and Use

4.1 Trace quantities of sulfur compounds in hydrocarbon products can be harmful to many catalytic chemical processes in which these products are used. Maximum permissible levels of total sulfur are normally included in specifications for such hydrocarbons. It is recommended that this test method be used to provide a basis for agreement between two laboratories when the determination of sulfur in hydrocarbon gases is important.

4.2 On liquefied petroleum gas, total volatile sulfur is measured on an injected gas sample. For such material a liquid sample must be used to measure total sulfur.

5. Interferences

5.1 This test method is applicable in the presence of total halide concentrations of up to 10 times the sulfur level and total nitrogen content of up to 1.0 %. Free nitrogen does not interfere.

5.2 This test method is not applicable in the presence of total heavy metal concentrations (for example, Ni, V, Pb, etc.) in excess of 500 mg/kg.

NOTE 2—To attain the quantitative detectability that the method is capable of, stringent techniques should be employed and all possible sources of sulfur contamination must be eliminated.

6. Apparatus[7,8]

6.1 *Pyrolysis Furnace*—The sample should be pyrolyzed

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[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.D 0.02 on C3 Test Methods.

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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 15.03.

[6] Available from Compressed Gas Association, 1235 Jefferson Davis Hwy., Arlington, VA 22202.

[7] The apparatus described in 6.1 to 6.5 inclusive, is similar in specifications to equipment available from Tekmar-Dohrmann, 7143 E. Kemper Rd., Cincinnati, OH 524549. For further detailed discussions, in equipment, see: Preprints—Division of Petroleum Chemistry, American Chemical Society, Vol 1, No. 3, Sept. 7-12, 1969, p. B232 "Determination of Sulfur, Nitrogen, and Chlorine in Petroleum by Microcoulometry," by Harry V. Drushel.

[8] Tekmar-Dohrmann is the sole source of supply of the apparatus known to the committee at this time. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

in an electric furnace having at least two separate and independently controlled temperature zones, the first being an inlet section that can maintain a temperature sufficient to volatilize all the organic sample. The second zone shall be a pyrolysis section that can maintain a temperature sufficient to pyrolyze the organic matrix and oxidize all the organically bound sulfur. A third outlet temperature zone is optional.

6.1.1 Pyrolysis furnace temperature zones for light liquid petroleum hydrocarbons should be variable as follows:

Inlet zone	up to at least 700°C
Center pyrolysis zone	up to at least 1000°C
Outlet zone (optional)	up to at least 800°C

6.2 *Pyrolysis Tube*, fabricated from quartz and constructed in such a way that a sample, which is vaporized completely in the inlet section, is swept into the pyrolysis zone by an inert gas where it mixes with oxygen and is burned. The inlet end of the tube shall hold a septum for syringe entry of the sample and side arms for the introduction of oxygen and inert gases. The center or pyrolysis section should be of sufficient volume to assure complete pyrolysis of the sample.

6.3 *Titration Cell*, containing a sensor-reference pair of electrodes to detect changes in triiodide ion concentration and a generator anode-cathode pair of electrodes to maintain constant triiodide ion concentration and an inlet for a gaseous sample from the pyrolysis tube. The sensor electrode shall be platinum foil and the reference electrode platinum wire in saturated triiodide half-cell. The generator anode and cathode half-cell shall also be platinum. The titration cell shall require mixing, which can be accomplished through the use of a magnetic stirring bar, stream of inert gas, or other suitable means.

NOTE 3: **Caution**—Excessive speed will decouple the stirring bar, causing it to rise in the cell and damage the electrodes. The creation of a slight vortex is adequate.

6.4 *Microcoulometer*, having variable attenuation gain control, and capable of measuring the potential of the sensing-reference electrode pair, and comparing this potential with a bias potential, amplifying the potential difference, and applying the amplified difference to the working-auxiliary electrode pair so as to generate a titrant. Also the microcoulometer output voltage signal shall be proportional to the generating current.

6.5 *Recorder*, having a sensitivity of at least 0.1 mV/25 mm with chart speeds of 12 to 25 mm/min. Use of a suitable electronic or mechanical integrator is recommended but optional.

6.6 *Sampling Syringe for Liquid*—A microlitre syringe of 10-µL capacity capable of accurately delivering 1 to 10 µL of liquid blend into the pyrolysis tube 75 mm by 24-gage needles are recommended to reach the inlet zone of the pyrolysis furnace.

NOTE 4—Since care should be taken not to overload the pyrolyzing capacity of the tube by too fast a sample injection rate, means should be provided for controlling the sample addition rate (0.1 to 0.2 µL/s).

6.7 *Sampling Syringe for Gas*—A gas syringe capable of delivering up to 5 cm^3 of gas sample into the pyrolysis furnace. A 25 mm by 28-gage needle should be attached to the syringe.

6.8 *Exit Tube Insert*, with quartz wool.

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.[9] 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*—The water used in preparing the cell electrolyte should be demineralized or distilled or both. Water of high purity is essential. See Specification D 1193 for reagent water.

NOTE 5—Distilled water obtained from an all borosilicate glass still, fed from a demineralizer, has proven very satisfactory.

7.3 *Acetic Acid* (rel dens 1.05)—Concentrated acetic acid (CH_3COOH).

NOTE 6: **Warning**—May cause burns. See Annex A1.1.

7.4 *Argon, Helium, or Nitrogen*, high-purity grade (HP),[10] used as the carrier gas.

NOTE 7: **Warning**—Hazardous pressure. See Annex A1.2.

7.5 *Cell Electrolyte Solution*—Dissolve 0.5 g of potassium iodide (KI) and 0.6 g of sodium azide (NaN_3) in approximately 500 mL of high-purity water, add 5 mL of acetic acid (CH_3COOH) and dilute to 1000 mL.

NOTE 8—Bulk quantities of the electrolyte should be stored in a dark bottle or in a dark place and be prepared fresh at least every 3 months.

7.6 *Gas Regulators*—Two-stage gas regulators must be used on the reactant and carrier gas.

7.7 *Iodine* (I_2), 20 mesh or less, for saturated reference electrode.

NOTE 9: **Warning**—Toxic fumes. See A1.3.

7.8 *Isooctane*[11] *(2,2,4-trimethyl pentane).*

NOTE 10 **Warning**—Combustible, very harmful. See Annex A1.4.

NOTE 11—The most reliable solvent is a sulfur-free form of the sample type to be analyzed. Alternatively, use a high-purity form of cyclohexane [boiling point 80°C (176°F)], *iso*octane (2,2,4-trimethyl pentane) [boiling point, 99.3°C (211°F)], or hexadecane [boiling point, 287.5°C (549.5°F)].

7.9 *n-Butyl Sulfide* ($(CH_3CH_2CH_2CH_2)_2S$).

7.10 *Oxygen*, high-purity grade (HP),[9] used as the reactant gas.

NOTE 12: **Warning**—Oxygen accelerates combustion. See Annex A1.5.

7.11 *Potassium Iodide* (KI), fine granular.

7.12 *Sodium Azide* (NaN_3), fine granular.

NOTE 13: **Warning**—Highly toxic. Can react violently with shock, friction or heat.

7.13 *Sulfur, Standard Solution (approximately 30*

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[9] *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.

[10] High-purity grade gas has a minimum purity of 99.995 %.

[11] A high purity isooctane of pesticide quality has been found satisfactory.

mg/kg)—Pipet 10 mL of sulfur stock solution (reagent 7.14) into a 100-mL volumetric flask and dilute to volume with *iso*octane.

NOTE 14—The analyst may choose other sulfur compounds for standards appropriate to sample boiling range and sulfur type which cover the concentration range of sulfur expected.

7.14 *Sulfur, Standard Stock Solution* (*approximately 300 ppm* (µ*g/g*))—Weigh accurately 0.5000 g of *n*-butyl sulfide into a tared 500-mL volumetric flask. Dilute to the mark with *iso*octane and reweigh.

$$\text{S, mg/kg} = \frac{\text{g of } n\text{-butyl sulfide} \times 0.2187 \times 10^6}{\text{g of } (n\text{-butyl sulfide} + \text{solvent})} \quad (3)$$

8. Sampling

8.1 Supply samples to the laboratory in high-pressure sample cylinders, obtained using the procedures described in Practice D 1265 and Practice F 307.

8.2 Because of the reactivity of most sulfur compounds, it has been found desirable to use TFE-fluorocarbon-coated cylinders or other specially treated sample containers. Test samples as soon as possible after receipt.

9. Preparation of Apparatus

9.1 Carefully insert the quartz pyrolysis tube in the pyrolysis furnace and connect the reactant and carrier gas lines.

9.2 Add the electrolyte solution to the titration cell and flush several times. Maintain an electrolyte level of ⅛ to ¼ in. (3.2 to 6.4 mm) above the platinum electrodes.

9.3 Place the heating tape on the inlet of the titration cell.

9.4 Place an exit tube insert packed loosely with about 1 in. (25 mm) of quartz wool into the exit end of the pyrolysis tube. The quartz wool end of the exit tube should be in the hot zone of the pyrolysis tube.

9.5 Depending upon the instrumentation used, set up the titration cell to allow for adequate mixing of its contents and connect the cell inlet to the outlet end of the pyrolysis tube. Position the platinum foil electrodes (mounted on the movable cell head) so that the gas inlet flow is parallel to the electrodes with the generator anode adjacent to the generator cathode. Assemble and connect the coulometer and recorder (integrator optional) as designed or in accordance with the manufacturer's instructions. Figure X1.2 illustrates the typical assembly and gas flow through a coulometric apparatus.

9.5.1 Turn the heating tape on.

9.6 Adjust the flow of the gases, the pyrolysis furnace temperature, titration cell, and the coulometer to the desired operating conditions. Typical operational conditions are given in Table 1.

10. Calibration and Standardization

10.1 Prepare a series of calibration standards covering the range of sulfur concentration expected. Follow instructions in 7.13, 7.14, or dilute to appropriate level with *iso*octane.

10.2 Adjust the operational parameters (9.5).

NOTE 15—A ratio of 80 % oxygen to 20 % inert gas gives an acceptable recovery, and permits the use of a larger sample and a more rapid-charging rate.

10.3 The sample size can be determined either volumetrically or by mass. The sample size should be 80 % or less of the syringe capacity.

TABLE 1 Typical Operational Conditions

Reactant gas flow (oxygen), cm^3/min	160
Carrier gas flow (Ar, He, N), cm^3/min	40
Furnace temperature; °C:	
Inlet zone	700
Pyrolysis zone	800
Outlet zone	800
Titration cell	set to produce adequate mixing
Coulometer:	
Bias voltage, mV	160
Gain	low (approximately 200)

10.3.1 Volumetric measurement can be obtained by filling the syringe with about 8 µL or less of sample, being careful to eliminate bubbles, retracting the plunger so that the lower liquid meniscus falls on the 1-µL mark, and recording the volume of liquid in the syringe. After the sample has been injected, again retract the plunger so that the lower liquid meniscus falls on the 1-µL mark, and record the volume of liquid in the syringe. The difference between the two volume readings is the volume of sample injected.

10.3.2 Alternatively, the sample injection device can be weighed before and after the injection to determine the amount of sample injected. This test method provides greater precision than the volume delivery method, provided a balance with a precision of ±0.01 g is used.

10.4 Insert the syringe needle through the inlet septum up to the syringe barrel and inject the sample or standard at an even rate not to exceed 0.1 to 0.2 µL/s. When a microlitre syringe is used with an automatic injection adapter, the injection rate (volume/pulse) should be calibrated to deliver 0.1 to 0.2 µL/s.

10.5 Repeat the measurement of each calibration standard at least three times.

NOTE 16—Not all of the sulfur in the sample comes through the furnace as titratable SO_2. In the strongly oxidative conditions of the pyrolysis tube some of the sulfur is also converted to SO_3 which does not react with the titrant. Accordingly, sulfur standards of *n*-butyl sulfide in *iso*octane or sulfur standards appropriate to sample boiling range and sulfur type and sulfur concentration should be prepared to guarantee adequate standardization. Recoveries less than 75 % are to be considered suspect. Low recoveries are an indication to the operator that he should check his parameters, his operating techniques, and his coulometric system. If the instrument is being operated properly, recoveries between 75 and 90 % are to be expected.

10.6 Calculate the percent sulfur found by the coulometer. For a 1-mV (span) recorder with a sensitivity of 0.1 mV/in. and a speed of 0.5 in./min:

$$\text{Sulfur recovered, \%} = [(A \times 1.99)/(R \times S_o \times V_L/1000)] \times 100 \quad (4)$$

where:

A = area, cm^2,
R = coulometer range setting, Ω,
S_o = known concentration of sulfur in the standard blend, µg/mL, and
V_L = volume standard blend charged, µL.

10.6.1 *For a disk integrator:*

$$\text{Sulfur recovered, \%} = [(C \times 1.99 \times 10^{-3})/(R \times S_o \times V_L/1000)] \times 100 \quad (5)$$

where:

C = 100 × number of integrator pen full scale excursions.

Derivation of equations is given in Appendix X1.

10.6.2 *For an electronic integrator:*

$$\text{Sulfur Recovered, \%} = \frac{A}{B} \times 100 \quad \text{(using consistent sample sizes)} \tag{6}$$

where:

A = integrator result, mg/kg, and

B = known concentration of sulfur in standard blend, mg/kg.

NOTE 17—For further explanation of the derivation of the calculation, see Test Method D 3120.

10.7 If the fraction of sulfur converted to SO_2 drops below 75 % of the standard solutions, fresh standards should be prepared. If a low conversion factor persists, procedural details should be reviewed.

10.8 Calculate the average calibration factor, F, µg S/cm^2, as follows:

$$F = (S_o \times V_L/1000)/A \tag{7}$$

11. Procedure

11.1 Place a silicone rubber septum in a bushing and connect to the valve on the sample cylinder containing the gaseous sample (for liquefied gas samples, see Note 5). Crack the cylinder valve so as to flush the air from all connections and then turn the bushing down to hold slight back pressure on the septum. Close the cylinder valve until the gas syringe is ready for filling.

NOTE 18: **Warning**—Samples are extremely flammable. See Annex A1.7.

11.2 Crack the valve on the sample cylinder until slight flow of gas is detected around the septum. Insert the gas syringe in the septum carefully.

NOTE 19: **Warning**—High pressure. See Annex A1.8.

11.3 Withdraw the plunger and allow the gas to flow through the syringe. After sufficient time to flush the syringe with sample, withdraw the plunger so as to contain no less than 5 cm^3 of gas.

11.4 Insert the tip of the needle barely through the septum. Inject 5.0 cm^3 of gas into the instrument at a constant rate so that 15 s is required for the injection. Determine the sulfur concentration by the procedure described in 10.2 to 10.7.

11.5 Sulfur concentration can require adjustment of sample volume.

11.6 Report a needle blank with test results.

12. Calculation

12.1 Calculate the sulfur content of the sample in parts per million (ppm) by weight as follows:

$$\text{Sulfur, mg/kg} = (A \times F)/W \tag{8}$$

where:

A = area under curve, taking into account the area of the needle blank, in square centimetres using same range (Ω) as calibration,

W = weight of sample, g, and

F = calibration factor, µg S/cm^2

For gases:

$$W = \frac{V_g \times 273 \times P \times M}{(273 + C) \times 760 \times 22410} \tag{9}$$

where:

V_g = gas, cm^3

P = barometric pressure, mm Hg

M = molecular weight of gas, g/mol, and

C = temperature, gas, °C.

For ethylene at 23°C and 760 mm Hg:

$$W = V_g \times 0.001154 \tag{10}$$

For liquid:

$$W = V_L/1000 \times d \tag{11}$$

where:

V_L = volume, µL, and

d = density, g/mL.

13. Precision and Bias

13.1 The following criteria should be used for judging the acceptability of results:

13.1.1 *Repeatability*—The difference between successive test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, and in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

Range or Sample Type	Repeatability
0 to 10 mg/kg	0.4 mg/kg

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, and in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

Range or Sample Type	Reproducibility
0 to 10 mg/kg	5 mg/kg

13.2 *Bias*—The bias of the procedure of this test method cannot be determined since an appropriate standard reference material containing trace sulfur level in ethylene is not available.

14. Keywords

14.1 microcoulometer; oxidate microcoulometry; petroleum gas; pyrolysis furnace; sulfur; sulfur dioxide

ANNEX

(Mandatory Information)

A1. PRECAUTIONARY STATEMENTS

A1.1 Acetic Acid

Warning—May produce severe burns to skin and eyes.
Prolonged breathing of concentrated vapor may be harmful.
Avoid contact with skin, eyes, and clothing.
Use with adequate ventilation.

A1.2 Compressed Gases Argon, Helium, Nitrogen

Warning—Compressed gas under high pressure.
Gas reduces oxygen available for breathing.
Keep container closed.
Use with adequate ventilation.
Do not enter storage areas unless adequately ventilated.
Always use a pressure regulator.
Release regulator tension before opening cylinder.
Do not transfer to cylinder other than one in which gas is received.
Do not mix gases in cylinders.
Do not drop cylinder.
Make sure cylinder is supported at all times.
Stand away from cylinder outlet when opening cylinder valve.
Keep cylinder out of sun and away from heat.
Keep cylinders 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.

A1.3 Iodine

Warning—Fumes highly toxic.
Can cause irritation and burning of eyes, nose, and throat.
Avoid heating and prolonged breathing of vapors.
Avoid contact with skin.

A1.4 Isooctane

Warning—Extremely flammable.
Harmful if inhaled.
Vapors may cause flash fire.
Keep away from heat, sparks, and open flame.
Keep container closed.
Use with adequate ventilation.
Avoid build-up 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.

A1.5 Oxygen

Warning—Oxygen vigorously accelerates combustion.
Keep oil and grease away.
Do not use oil or grease on regulators, gauges, or control equipment.
Use only with equipment conditioned for oxygen service by careful 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.
For technical use only.
Do not use for inhalation purposes.
Keep cylinder out of sun and away from heat.
Keep cylinders from corrosive environment.
Do not use cylinder without label.
Do not use dented or damaged cylinders.
See Compressed Gas Association booklets G-4 and G-4.1 for details of safe practice in the use of oxygen.

A1.6 Sodium Azide

Warning—Highly toxic.
Inhalation may cause nausea, shortness of breath, dizziness, and headaches.
Contact with dust may cause eye irritation.
Avoid breathing dust or vapors from acidified solutions.
Avoid contact with skin, eyes, and clothing.
Wash thoroughly after handling.

A1.7 Flammable Gas

Warning—Extremely flammable (liquified) gas under pressure.
Keep away from heat, sparks, and open flame.
Use with adequate ventilation.
Never drop cylinder.
Make sure cylinder is supported at all times.
Keep cylinder out of sun and away from heat.
Always use a pressure regulator.
Release regulator tension before opening cylinder.
Do not transfer cylinder contents to another cylinder.
Do not mix gases in cylinder.

A1.8 Flammable Gas

Warning—Keep cylinder valve closed when not in use.
Do not inhale.
Do not enter storage areas unless adequately ventilated.
Stand away from cylinder outlet when opening cylinder valve.
Keep cylinder from corrosive environment.
Do not use cylinder without label.
Do not use dented or damaged cylinders.
For technical use only.
Do not inhale.

APPENDIX

(Nonmandatory Information)

X1. DERIVATION OF COULOMETRIC CALCULATIONS USED IN PARAGRAPH 12.1

X1.1 The configuration of the pyrolysis tube and furnace may be constructed as is desirable as long as the operating parameters are met. Figure X1.1 is typical of apparatus currently in use.

X1.2 A typical assembly and oxidative gas flow through a coulometric apparatus for the determination of trace sulfur is shown in Fig. X1.2.

X1.3 *Derivation of Equations:*

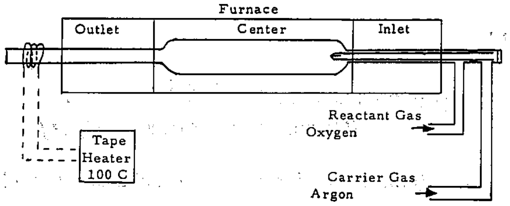

FIG. X1.1 Pyrolysis Tube

X1.3.1 The derivation of the equations used in the calculation section is based on the coulometric replacement of the triiodide (iodine) ions consumed in the microcoulometric titration cell reaction ($I_3^- \rightarrow 3I^- + H^+$). The quantity of the reactant formed (triiodide ions) between the beginning and the interruption of current at the end of the titration is directly proportional to the net charge transferred, *Q*.

X1.3.2 In most applications a constant current is used so that the product of current, *i*, in amperes (coulombs per second), multiplied by the time, *T* (seconds), required to reach the end point provides a measure of the charge, *Q* (coulombs), necessary to generate the iodine equivalent to the reactant; that is, $Q = it$. Therefore, the number of equivalents of reactant is equal to Q/F, where *F* is the Faraday constant, 95 500°C per equivalent.

X1.3.3 Therefore, the expression to be solved to find the mass of reactant is:

$$\text{Concentration of sulfur} = \frac{\text{mass of sulfur, g}}{\text{mass of sample, g}} = \frac{\dfrac{\dfrac{Q(C)}{FC}}{\text{eq}} \times \dfrac{16\text{ g}}{\text{eq}}}{\text{mass of sample, g}} \qquad \text{(X1.1)}$$

$$\mu\text{g S} = A\text{ cm}^2 \times \frac{\dfrac{0.1\text{ mV}}{\text{cm}} \times \dfrac{2\text{ min}}{\text{cm}} \times \dfrac{60\text{ s}}{\text{min}} \times \dfrac{10^{-3}\text{ V}}{\text{mV}} \times \dfrac{16\text{ g}}{\text{eq}} \times \dfrac{10^6\ \mu\text{g}}{\text{g}}}{R\ (\Omega) \times \dfrac{96\ 500°\text{C}}{\text{eq}} \times \dfrac{\text{A}\cdot\text{s}}{\text{C}} \times f)} \qquad \text{(X1.2)}$$

where:

A cm^2 = peak area measured in square inches,
0.1 mV/cm = millivolt span of upscale deflection for the recorder,
2 min/cm = chart speed in minutes per inch,
60 s/min = conversion of time in minutes to seconds,
10^{-3} V/mV = conversion of volts to millivolts,
16 g/eq = gram-equivalent of sulfur,
10^6 µg/g = micrograms per gram conversion factor,
R (Ω) = microcoulometer range switch setting in ohms,

substituting $V/R = I$(amps)

$$Q(A\cdot s) = \frac{A\text{ cm}^2 \times \dfrac{0.1\text{ mV}}{\text{cm}} \times \dfrac{2\text{ min}}{\text{cm}} \times \dfrac{60s}{min} \times \dfrac{10^{-3}\ V}{mV}}{R(\Omega)}$$

F = 96 500°C/eq
= Faraday's constant[8] (electrical equivalence of one gram-equivalent mass of any substance)
A·s/°C = conversion of coulombs to ampere-seconds, and
f = recovery factor (ratio of ppm S determined in standard versus known ppm S in standard).

Therefore,

$$\mu\text{g S} = \frac{A \times 12 \times 10^{-3}\text{ A}\cdot\text{s} \times \dfrac{16\text{g}}{\text{eq}} \times \dfrac{10^6\ \mu\text{g}}{\text{g}}}{R \times \dfrac{96\ 500°\text{C}}{\text{eq}} \times \dfrac{\text{A}\cdot\text{s}}{\text{C}} \times f} \qquad \text{(X1.3)}$$

Therefore,

$$\mu\text{g S} = \frac{A \times 12 \times 10^{-3} \times 16 \times 10^6\ \mu\text{g}}{R \times 96\ 500 \times f} \qquad \text{(X1.4)}$$

Therefore,

$$\mu\text{g S} = (A \times 1.99)/(R \times f) \qquad \text{(X1.5)}$$

Since ppm = µg/g:

$$\text{ppm S} = \frac{A \times 1.99}{R \times f \times \text{volume, }\mu\text{L} \times 10^{-3}\ \dfrac{\text{mL}}{\mu\text{L}} \times \text{density, } \dfrac{\text{g}}{\text{mL}}} \qquad \text{(X1.6)}$$

$$\text{ppm S} = \frac{A \times 1.99 \times 10^3}{R \times f \times \text{volume} \times \text{density}} \qquad \text{(X1.7)}$$

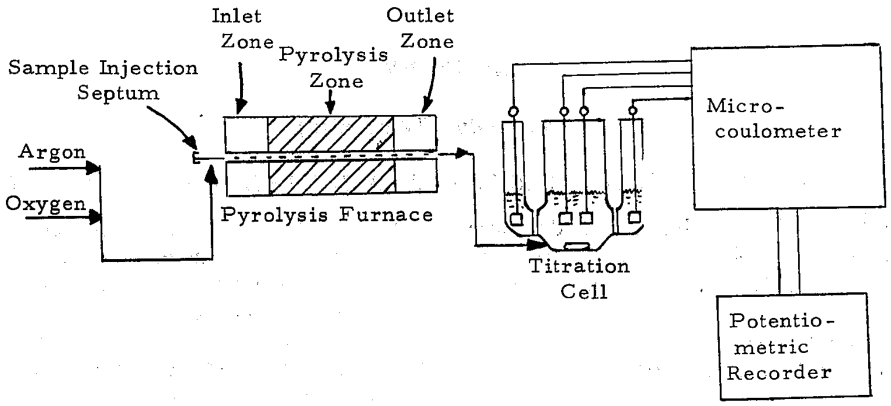

FIG. X1.2 Flow Diagram for Coulometric Apparatus for Trace Sulfur Determination

Since mass = volume × density

$$\text{ppm S} = (A \times 1.99)/(R \times F \times \text{mass, g}) \qquad \text{(X1.8)}$$

X1.3.4 *Derivation with Disk Integrator*—A in Eq X1.5 is expressed as in.^{2} However, it may also be expressed as counts. Therefore, A in.^{2} = counts × 10^{-3} since 1 in.^{2} = 1000 counts. Therefore, substituting counts × 10^{-3} for A in Eq 5 gives

$$\mu\text{g S} = (\text{counts} \times 1.99 \times 10^{-3})/(R \times f) \qquad \text{(X1.9)}$$

Then:

$$\text{ppm S} = \frac{\text{counts} \times 1.99}{R \times \text{volume, } \mu\text{L} \times \text{density, } \frac{\text{g}}{\text{mL}} \times f} \qquad \text{(X1.10)}$$

$$\text{ppm S} = (\text{counts} \times 1.99 \times 10^{-3})/(R \times \text{mass, } g \times f)$$

NOTE X1.1—Counts = 100 × number of integrator per full-scale excursions.

CERTIFICATE

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Standard Test Method for
Gross Calorific Value of Coal and Coke by the Isoperibol Bomb Calorimeter[1]

This standard is issued under the fixed designation D 3286; 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 gross calorific value of coal and coke by the isoperibol bomb calorimeter.

1.2 The values stated in SI units are to be regarded as the standard unless otherwise designated. 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.* For specific hazard statements, see Section 8.

2. Referenced Documents

2.1 *ASTM Standards:*

D 121 Terminology of Coal and Coke[2]
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 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke[2]
D 3177 Test Methods for Total Sulfur in the Analysis Sample of Coal and Coke[2]
D 3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases[2]
D 4239 Test Method for Sulfur in the Analysis Sample of Coal and Coke Using High Temperature Tube Furnace Combustion Methods[2]
E 1 Specification for ASTM Thermometers[4]
E 144 Practice for Safe Use of Oxygen Combustion Bombs[5]

3. Terminology

3.1 *Definitions:*

3.1.1 *calorific value, n*—the heat produced by combustion of a unit quantity of a test specimen under specific conditions.

3.1.1.1 *Discussion*—It is expressed in this test method in calories per gram (cal/g) and can also be expressed in British thermal units per pound (Btu/lb) or in the International System of Units (SI), in joules per gram (J/g), when required. The unit equivalents are given in Table 1.

3.1.2 *gross calorific value (gross heat of combustion at constant volume), Q_v (gross), n*—see Terminology D 121.

3.1.3 *net calorific value (net heat of combustion at constant pressure), Q_p (net), n*—see Terminology D 121.

3.1.4 *calorimeter, n—as used in this test method,* consists of the bomb and its contents, the calorimeter vessel (bucket) with stirrer, the water in which the bomb is immersed, and the portions of the thermometer and the ignition leads within the calorimeter vessel.

3.2 *Descriptions of Terms Specific to this Standard:*

3.2.1 *corrected temperature rise, n*—the temperature change of the calorimeter caused by the process that occurs inside the bomb; that is, the observed temperature change corrected for various effects as noted in 10.4.1.

3.2.1.1 *Discussion*—Temperature is measured in degrees Celsius. Thermometer corrections shall be applied. Temperatures may be recorded in ohms or other arbitrary units as the equivalent of degrees. Consistent units shall be used in standardization and the actual calorific value determination. If arbitrary units other than degrees Celsius are used, the temperature interval over which all tests are made shall not vary so much that an error greater than 0.001°C would result.

3.2.2 *energy equivalent, heat capacity, or water equivalent, n*—the energy required to raise the temperature of the calorimeter an arbitrary unit. This is the number that, when multiplied by the corrected temperature rise, then adjusted for extraneous heat effects, and divided by the weight of the sample, equates the gross calorific value.

NOTE 1—Conversion to other units is discussed in Appendix X2. Time is expressed in minutes. Mass is expressed grams.

4. Summary of Test Method

4.1 Calorific value is determined in this test method by burning a weighed sample, in oxygen, in a calibrated isoperibol bomb calorimeter under controlled conditions. The calorimeter is standardized by burning benzoic acid. The calorific value of the sample is computed from temperature observations made before, during, and after combustion, and making proper allowances for heat contributed by other processes, and for thermometer and thermochemical corrections.

4.2 Oxidation after sampling of susceptible low-rank coal or lignite may result in a reduction of calorific value.

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[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 July 10, 1996. Published September 1996. Originally published as D 3286 – 73. Last previous edition D 3286 – 91a.

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

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

[4] *Annual Book of ASTM Standards*, Vol 14.03.

[5] *Annual Book of ASTM Standards*, Vol 14.02.

TABLE 1 Calorific Value

1 Btu = 1055.06 J	1 Btu/lb = 2.326 J/g
1 Calorie[A] = 4.1868 J	1.8 Btu/lb = 1.0 cal/g

[A] International tables calorie.

Unnecessary exposure of the sample to air from the time of sampling or delay in analysis shall be avoided.

5. Significance and Use

5.1 When mutually agreed upon between the buyer and the seller, the gross calorific value may be used to compute the total calorific content of the quantity of coal represented by the sample for payment purposes.

5.2 The gross calorific value can be used to determine if the coal meets the regulatory requirement for industrial fuels.

5.3 The gross calorific value can be used for evaluating the effectiveness of benefaction process, or for research purposes.

6. Apparatus and Facilities

6.1 *Test Space*—A room or area free from drafts that can be kept at a reasonably uniform temperature for the time required for the determination. The apparatus shall be shielded from direct sunlight and radiation from other heat sources. Thermostatic control of room temperature and controlled relative humidity are desirable.

6.2 *Combustion Bomb,* shall be constructed of materials that are not affected by the combustion process or products sufficiently to introduce measurable heat input or alteration of end products. The bomb shall be designed so that all liquid combustion products can be completely recovered by washing the inner surfaces. There shall be no gas leakage during a test. The bomb shall be capable of withstanding a hydrostatic pressure test of 20 MPa (3000 psig) at room temperature without stressing any part beyond its elastic limit.

6.3 *Balance*—A laboratory balance having the capability to weigh the sample to the nearest 0.0001 g. The balance should be checked periodically to determine its accuracy.

6.4 *Calorimeter Vessel,* made of metal 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 calorimeter 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 low-heat conductivity.

6.5 *Jacket,* a double-walled, air, or water-filled jacket. The calorimeter shall be insulated from the jacket by an air space. The sides, top, and bottom of the calorimeter vessel shall be approximately 10 mm from the inner wall of the jacket to minimize convection currents. Mechanical supports for the calorimeter vessel shall provide as little thermal conduction as possible. The jacket shall be capable of maintaining the temperature constant to within ±0.1°C of room temperature at a calorimeter temperature 2°C below, and 2°C or more above room temperature throughout the determination. If a water-filled jacket is used, it shall have a device for stirring the water at a uniform rate with minimum heat input.

6.6 *Thermometers,* used to measure temperatures in the calorimeter and jacket shall be of any of the following types or combination thereof:

6.6.1 *Liquid-in-Glass Thermometers,* conforming to the requirements for ASTM Thermometers 56C, 116C, or 117C, as prescribed in Specification E 1. The thermometers shall be tested for accuracy against a known standard (preferably by the National Institute of Standards and Technology (NIST)). For thermometers 56C, the calibration should be at intervals no larger than 2.0°C over the entire graduated scale. The maximum difference in correction between any two test points shall be no more than 0.02°C. For thermometers 116C and 117C, the calibration should be at intervals no larger than 0.5°C over the entire calibrated range. The maximum difference in correction between any two test points shall not be more than 0.02°C.

6.6.2 *Beckmann Differential Thermometers,* (glass-enclosed scale, adjustable) having a range of approximately 6°C in 0.01°C subdivisions reading upward and conforming to the requirements for Thermometer 115C, as prescribed in Specification E 1, may be used. Each of these thermometers shall be tested for accuracy against a known standard (preferably by the NIST) at intervals no larger than 1°C over the entire graduated scale. The maximum difference in the correction between any two test points shall not be more than 0.02°C.

6.6.3 *Other Thermometers,* of precision equal to or better than 0.001°C, such as platinum resistance or linear thermistor thermometers are satisfactory and may be used if properly calibrated. A Wheatstone bridge and galvanometer capable of measuring resistance to 0.0001 Ω are necessary for use with 25 Ω platinum resistance thermometers.

6.7 *Thermometer Accessories*—A magnifier is required for reading liquid-in-glass thermometers to one tenth of the smallest scale division. This shall have a lens and holder designed so as to introduce no significant errors due to parallax.

6.8 *Sample Holder*—An open crucible of platinum, quartz, or acceptable base-metal alloy. Base-metal alloy crucibles are acceptable if, after a few preliminary firings, the weight does not change significantly between tests.

6.9 *Ignition Wire*—The ignition wire shall be 100 mm of 0.16-mm diameter (No. 34 B & S gage) nickel-chromium alloy, Chromel C alloy, or iron wire. Platinum wire or palladium, 0.10-mm diameter (No. 38 B & S gage) may be used, provided constant ignition energy is supplied. The length or mass of ignition wire shall remain constant for all calibrations and calorific value determinations.

6.10 *Ignition Circuit,* for ignition purposes shall provide a 6 to 16 V alternating or direct current to the ignition wire. An ammeter or pilot light is required in the circuit to indicate when current is flowing. A step-down transformer, connected to an alternating current lighting circuit, or batteries, may be used.

6.11 *Buret,* used for the acid titration, shall have 0.1-mL divisions.

6.12 *Automated Controller and Temperature Measuring Accessories,* may be used for measuring temperatures before, during, and after combustion of the sample; ignition of the sample; and calculation of results provided that they meet the minimal functional specifications in Sections 6 and 10.

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 specification of the Committee on Analytical 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 *Reagent Water,* conforming to Type II of Specification D 1193, shall be used for preparation of reagents and washing of the bomb interior.

7.3 *Benzoic Acid* (C_6H_5COOH), shall be NIST certified benzoic acid. The crystals shall be pelletized before use. Commercially prepared pellets may be used provided they are made from NIST certified benzoic acid or made from benzoic acid that has been calibrated against NIST certified benzoic acid. The value of heat of combustion of the benzoic acid for use in the calibration calculations shall be in accordance with the value listed in the NIST certificate issued with the standard.

7.4 *Methyl Orange, Methyl Red, or Methyl Purple Indicator,* may be used to titrate the acid formed during combustion. The indicator used shall be the same for both calibration and calorific value determinations.

7.5 *Oxygen,* shall be free of combustible matter. Only oxygen manufactured from liquid air, guaranteed to be greater than 99.5 % pure, should be used. Oxygen made by the electrolytic process may contain a small amount of hydrogen rendering it unfit without purification.

7.6 *Sodium Carbonate Standard Solution,* sodium carbonate (Na_2CO_3) should be dried for 24 h at 105°C. Dissolve 3.76 g in water and dilute to 1 L. One millilitre of this solution is equivalent to 1.0 cal in the nitric acid (HNO_3) titration.

8. Hazards

8.1 The following precautions are recommended for safe calorimeter operation. Additional precautions are given in Practice E 144. Also consult the calorimeter equipment manufacturer's installation and operating instructions before using the calorimeter.

8.2 The mass of coal or coke sample and the pressure of the oxygen admitted to the bomb shall not exceed the bomb manufacturer's recommendations.

8.3 Inspect the bomb parts carefully after each use and, after 3000 firings, check the bomb for thread wear on any closures. If an inspection reveals any wear, return the parts to the factory for further testing or replacement of the defective parts. It is good practice to return the bomb to the manufacturer for inspection at yearly intervals.

8.4 The oxygen supply cylinder shall be equipped with an approved type of safety device, such as a reducing valve, in addition to the needle valve and pressure gage used in regulating the oxygen feed to the bomb. Valves, gages, and gaskets must meet industry safety code. Suitable reducing valves and adaptors for 3 to 4-MPa (300 to 500-psi) discharge pressure are obtainable from commercial sources of compressed gas equipment. The pressure gage shall be checked periodically for accuracy.

8.5 During ignition of a sample, the operator shall not permit any portion of her or his body to extend over the calorimeter.

8.6 When combustion aids are employed, extreme caution shall be exercised not to exceed the bomb manufacturer's recommendations and to avoid damage to the bomb. Do not fire loose fluffy material, such as unpelleted benzoic acid, unless thoroughly mixed with the coal sample.

8.7 Do not fire the bomb if the bomb has been dropped or turned over after loading, or there is evidence of gas leakage when the bomb is submerged in the calorimeter water.

8.8 For manually operated calorimeters, the ignition circuit switch shall be of the momentary double-contact type, normally open, except when held closed by the operator. The switch should be depressed only long enough to fire the charge.

9. Sample

9.1 The sample shall be the material pulverized to pass a 250-µm (No. 60) sieve, prepared in accordance with either Practice D 346 for coke, or Method D 2013 for coal.

9.2 A separate portion of the sample should be analyzed simultaneously for moisture content in accordance with Method D 2013 and Test Method D 3173, so that calculations to other bases can be made.

9.3 Sulfur analysis shall be made in accordance with Test Methods D 3177 or D 4239.

10. Standardization

10.1 The calorimeter shall be standardized by combustion of benzoic acid.

10.2 Determine the energy equivalent as the average of a series of ten individual test runs. To be acceptable the relative standard deviation of the series shall be 0.15 % or less of the average energy equivalent (see Table 2). For this purpose, any individual test may be discarded if there is evidence of incomplete combustion. If, after considering the possibility of outliers utilizing criterion established in ASTM E 178, this limit is not met, one should review operation of the calorimeter for any assignable cause which should be corrected before repeating the series.

10.3 *Procedure:*

10.3.1 Regulate the weights of the pellets of benzoic acid in each series to yield approximately the same temperature rise as that obtained with the coals tested in the same laboratory. The usual range of masses is from 0.9 to 1.3 g. Weigh the pellet to the nearest 0.1 mg in the sample holder in which it is to be burned, and record the weight as the mass.

10.3.2 Rinse the bomb, invert to drain, and leave undried. Add 1.0 mL of water to the bomb prior to assembly for a determination.

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[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.

TABLE 2 Standard Deviations for Calorimeter Standardization[A]

Standardization Number	Column A	Column B	Column C
	Energy Equivalent (cal/°C)	Code to 2449 (Column A-2449)	(Column B)^2
1	2450	1	1
2	2448	−1	1
3	2453	4	16
4	2449	0	0
5	2447	−2	4
6	2448	−1	1
7	2446	−3	9
8	2452	3	9
9	2450	1	1
10	2447	−2	4
SUM	241 490	0	46

Average = $\bar{X}$ = 2449·24 490/10

$$\text{Variance} = s^2 = \frac{\Sigma\ \text{Column C} - [(\Sigma\text{Column B})^2/n]}{n-1} = 5.11$$

$$\text{Standard deviation} = s = \sqrt{\text{variance}} = \sqrt{5.11} = 2.26$$

[A] In this example the values of energy equivalent are typical for a calorimeter calibrated so that, if the energy equivalent is multiplied by the temperature rise in degrees Celsius per gram of sample, the calorific value of the sample will be obtained in British Thermal units per pound.

10.3.3 Connect a measured length of ignition wire to the ignition terminals, with enough slack to allow the ignition wire to maintain contact with the sample.

10.3.4 Assemble the bomb and charge it with oxygen to a consistent pressure between 2.5 to 3 MPa (25 to 30 atm). This pressure must remain the same for each calibration and each calorific-value determination. Admit the oxygen slowly into the bomb so as not to blow powdered material from the sample holder. If the pressure exceeds the specified pressure, do not proceed with the combustion. Instead, detach the filling connection and exhaust the bomb in the usual manner, and discard the sample.

10.3.5 Fill the calorimeter vessel (bucket) with the measured (or weighed) quantity of water adjusted from 1.0 to 5.0°C below the jacket temperature, but not lower than 20°C. Use the same mass of water in each test weighed to ±0.5 g. For 2000-mL calorimeters, the proper quantity can be obtained by use of a volumetric flask calibrated to deliver 1980 to 2020 mL with ±0.5 mL repeatability. As the density of water varies with temperature, make suitable corrections if the water temperature varies from the temperature at which the flask was calibrated. Place the assembled bomb in the calorimeter vessel. Check that no oxygen bubbles are leaking from the bomb. Place the calorimeter vessel in the jacket; connect the electrodes; place the stirrers, thermometers, and cover in position. Start the stirrer(s) and continue to operate it (them) throughout the determination. Examine the thermometers for liquid separation and correct any separation before proceeding. The starting temperature shall be within ±0.5°C of that used in the analysis of coal or coke samples.

10.3.5.1 The initial temperature adjustment will ensure a final temperature slightly above that of the jacket for 2000-mL calorimeters. Some operators prefer a lower initial temperature so that the final temperature is slightly below that of the jacket. This procedure is also satisfactory. Whichever procedure is used, the same procedure shall be used in all tests, including standardization. A small heater may be built into the calorimeter so that the desired starting temperature can be easily attained.

NOTE 2—Check all liquid-in-glass thermometers at least daily for any defects, for example, cracked glass, etc.

10.3.6 Allow 5 min for attainment of equilibrium; then record the calorimeter temperature at 1-min intervals for 5 min or until the rate of change has been nearly constant for 5 min. Use a magnifier when using ASTM Bomb Calorimeter Thermometers 56C, and estimate all of the readings (except those during the rapid-rise period) to the nearest 0.002°C. Estimate ASTM Thermometers 115C, 116C, or 117C readings to 0.001°C, and 25 Ω resistance thermometer readings to the nearest 0.0001 Ω. Tap mercury thermometers (for instance with a pencil) just before reading to avoid errors caused by mercury sticking to the walls of the capillary. Ignite the charge at the start of the sixth minute and record the time, *i*, and the thermometer reading, t_i (Note 6). Take the next two readings 0.5 min and 1 min after firing because of the rapid rise. Record subsequent readings at 1-min intervals on the minute until the difference between successive readings has been constant for 5 min. If the final temperature is above the bath temperature, the temperature rises to a maximum and then begins to fall. Record the time, *f*, and the thermometer reading, t_f, after the rate of change has become uniform. The calorimeter water temperature shall be at the same temperature (±0.05°C) for every determination, at the time of firing, if the Bureau of Mines method for radiation correction is to be used. See Annex A1.5.

10.3.7 Open the cover and remove the bomb. Release the pressure at a uniform rate, such that the operation will require not less than 1 min. Open the bomb and examine the bomb interior. Discard the test if any unburned sample or sooty deposits are found. Wash the interior of the bomb with distilled water containing the titration indicator until the washings are free of acid, and titrate the washings with standard sodium carbonate solution.

10.3.8 Remove and measure, or weigh, the combined pieces of unburned ignition (firing) wire and subtract from the original length or weight to determine the wire consumed in firing. If the wire is weighed, remove the ball of oxidized metal from the end of each piece of wire before weighing.

10.4 *Calculation:*

10.4.1 *Temperature Rise*—Using data obtained as prescribed in 10.3.6, compute the corrected temperature rise, *t*, as follows:

$$t = t_f - t_i + C_e + C_s + C_r \tag{1}$$

where:

t = corrected temperature rise, °C,
t_i = initial temperature reading at time of firing,
t_f = final temperature reading, °C,
C_e = thermometer, emergent stem correction, if required (see 10.4.1.1 and Annex A1.4),
C_s = thermometer setting correction, if required (see 10.4.1.1 and Annex A1.3), and
C_r = radiation correction (see 10.4.1.1 and Annex A1.5).

10.4.1.1 With all mercury-in-glass thermometers, it is necessary to make corrections if the total calorific value is altered by 2.7 cal/g (5 Btu/lb) or more. This represents a change of 0.001°C in a calorimeter using approximately 2000 g of water. Beckmann thermometers also require a setting correction and an emergent stem correction (see Annex A1.3 and A1.4). Solid-stem ASTM Thermometer 56C does not require emergent stem corrections if all tests, including standardization, are performed within the same 5.5°C interval. If operating temperatures range beyond this limit, a differential emergent stem correction (see Annex A1.4) must be applied to the corrected temperature rise, *t*, in all tests, including standardization. A radiation correction must be made in all tests, including standardization.

10.4.2 *Thermochemical Corrections* (see Appendix X1)—Compute the following for each test:

e_1 = correction for the heat of formation of HNO_3, cal. Each millilitre of standard Na_2CO_3 is equivalent to 1.0 cal, and
e_2 = correction for heat of combustion of firing wire, cal (Note 2).
= 0.23 cal/mm (1.4 cal/mg) for 0.16-mm diameter (No. 34 B & S gage) Chromel C wire.
= 0.27 cal/mm (1.8 cal/mg) for 0.16-mm diameter (No. 34 B & S gage) iron wire.

NOTE 3—There is no correction for platinum or palladium wire provided the ignition energy is constant.

10.4.3 Compute the calorimeter energy equivalent, *E*, by substituting in the following:

$$E = [(gH) + e_1 + e_2]/t \qquad (2)$$

where:

E = calorimeter energy equivalent,
H = heat of combustion of benzoic acid, as stated in the NIST certificate, cal/g in air,
g = mass (weight in air) of benzoic acid, g,
e_1 = titration correction (10.4.2),
e_2 = fuse wire correction (10.4.2), and
t = corrected temperature rise (10.4.1).

10.5 Repeat the procedure for a total of ten determinations. Compute the standard deviation as illustrated in Table 2.

11. Restandardization

11.1 Make checks on the energy equivalent value after changing the oxygen supply, after changing any part of the calorimeter, and at least once a month otherwise.

11.1.1 If a single new determination differs from the old standard value by 4 cal/°C (6 Btu/°C) the old standard value is suspect, thereby requiring a second test.

11.1.2 The difference between the two new determinations must not exceed 5 cal/°C (8 Btu/°C), and the average of the two new determinations must not differ from the old standard by more than 3 cal/°C (4 Btu/°C). If these requirements are met, do not change the calorimeter standard.

11.1.3 If the requirements given in 11.1.2 are not met, run two more determinations. The range of the four values shall not exceed 8 cal/°C (14 Btu/°C), and the average of the four new determinations shall not differ from the old standard value by more than 2 cal/°C (3 Btu/°C). If these requirements are met, do not change the calorimeter standard.

11.1.4 If the requirements given in 11.1.3 are not met, run a fifth and sixth determination. The range of the six new determinations shall not exceed 17 Btu/°C, and the average of the six values shall not differ from the old standard value by more than 2 cal/°C (2 Btu/°C). If these requirements are met, do not change the calorimeter standard.

TABLE 3 Summary of Numerical Requirements

NOTE—Test values exceeding table limits require additional runs.[A]

Number of Runs	Maximum Range of Results	Maximum Difference between $\bar{X}_1$, and $\bar{X}_2$[B]
	cal/°C	cal/°C
1	. . .	±4
2	5	±3
4	8	±2
6	10	±2
10	12	±1

[A] $\bar{X}_1$ = average of original standard, and $\bar{X}_2$ = average of check runs.

11.1.5 If the requirements given in 11.1.4 are not met, run four more determinations to complete a series of ten runs. The range of these ten results shall not exceed 12 cal/°C (20 Btu/°C), and the average of the ten new values shall not differ from the old standard by more than 1 cal/°C (1 Btu/°C). If these requirements are met, do not change the calorimeter standard.

11.1.6 If the requirements given in 11.1.5 are not met, the average value from the ten new values shall be used for the new standard energy equivalent, provided that the standard deviation of the series does not exceed 3.6 cal/°C (6.5 Btu/°C).

11.2 The summary of the numerical requirements at each stage of restandardization is given in Table 3.

12. Procedure for Coal and Coke Samples

12.1 Thoroughly mix the analysis sample of coal or coke in the sample bottle and carefully weigh approximately 1 g ± 0.1 mg of it into the sample holder. Make each determination in accordance with the procedure described in 10.3.2 through 10.3.8.

12.2 For anthracite, coke, and coal of high ash content, that do not readily burn completely, one of the following procedures are recommended. (*1*) The inside of the sample holder is lined completely with ignited asbestos in a thin layer pressed well down into the angles, and the sample is then sprinkled evenly over the surface of the asbestos. (*2*) The mass of the sample may be varied to obtain good ignition. If the mass is varied, it will be necessary to recalibrate the calorimeter so that the water equivalent will be based on the same temperature rise as that obtained with the new sample weight. (*3*) A known amount of benzoic acid may be mixed with the sample. Proper allowance shall be made for the heat of combustion of benzoic acid when determining the calorific value of the sample.

12.3 For the calorific value of coke, it is necessary to use 3 MPa (30 atm) pressure for both standardization and analysis.

12.4 Determine the sulfur content of the sample by any of the procedures described in Test Methods D 3177 or D 4239.

13. Calculation (Note 1)

13.1 Compute the corrected temperature rise, *t*, as shown in 10.4.1.

13.2 *Thermochemical Corrections* (Appendix X1)—Compute the following for each test:

e_1 = correction for the heat of formation of HNO_3, cal. Each millilitre of standard sodium carbonate is equivalent to 1.0 cal,

e_2 = correction for heat of combustion of ignition wire, cal,
= 0.23 cal/mm (1.4 cal/mg) for 0.16-mm diameter (No. 34 B & S gage) Chromel C wire,
= 0.27 cal/mm (1.8 cal/mg) for 0.16-mm diameter (No. 34 B & S gage) iron wire (Note 3), and
e_3 = correction for difference between heat of formation of H_2SO_4 from the heat of formation HNO_3, cal,
= 13.17 times percent of sulfur in sample times weight of sample, g.

14. Calorific Value (Note 4)

14.1 *Gross Calorific Value*—Calculate the gross calorific value (gross heat of combustion at constant volume) Q_v (gross) as follows:

$$Q_v\ (\text{gross}) = [(tE) - e_1 - e_2 - e_3]/g \qquad (3)$$

where:
Q_v (gross) = gross calorific value, cal/g,
t = corrected temperature rise as calculated in 13.1,
E = energy equivalent calculated in 10.4.3,
e_1, e_2, e_3 = corrections as prescribed in 13.2, and
g = mass of sample, g.

NOTE 4—This calculation gives calorific value in calories per gram. To obtain calorific value in joules per gram or British thermal units per pound, see Appendix X2.

14.2 *Net Calorific Value*—Calculate the net calorific value (net heat of combustion at a constant pressure), Q_p (net), as follows:

$$Q_p\ (\text{net})_{ar} = Q_v\ (\text{gross})_{ar} - 5.72\ (H_{ar} \times 9) \qquad (4)$$

where:
Q_p $(\text{net})_{ar}$ = net calorific value at constant pressure, cal/g,
Q_v $(\text{gross})_{ar}$ = gross calorific value at constant volume, as-received basis, cal/g, and
H_{ar} = total hydrogen, as-received basis, where hydrogen and oxygen include hydrogen and oxygen in sample moisture, %.

NOTE 5—Example for converting from the as-determined (air-dried) sample basis to the as-received net calorific value basis:[7]

Calories per gram, as-determined (cal_{ad}) = 7506
Calories per gram, as-received (cal_{ar}) = 7056
Moisture, as-determined (M_{ad}) = 2.13
Moisture, as-received (M_{ar}) = 8.00
Hydrogen, as-determined (H_{ad}) = 5.00

To convert H_{ad} to H_{ar}:

$$H_{ar} = \left[(H_{ad} - 0.1119 M_{ad}) \times \frac{100 - M_{ar}}{100 - M_{ad}}\right] + 0.1119 M_{ar}$$

$$= \left[(5.00 - 0.1119 \times 2.13) \times \frac{100 - 8.00}{100 - 2.13}\right] + 0.1119 \times 8.00$$

$$H_{ar} = 5.37$$

$$\begin{aligned} Q_p\ (\text{net})_{ar} &= 7056 - 5.72\ (5.37 \times 9) \\ &= 7056 - 276 \\ &= 6780 \text{ cal/g (International Table Calories)} \\ &= 12204 \text{ Btu/lb} \\ &= 28382 \text{ J/g} \\ &= 28.38 \text{ MJ/kg} \end{aligned}$$

15. Report

15.1 The results of the calorific value may be reported on any of a number of bases, differing from each other in the manner that moisture is treated.

15.2 Use the percent moisture in the sample passing a 250-µm (No. 60) sieve, Test Method D 3173, to calculate the results of the analysis sample to a dry basis.

15.3 Procedures for converting the value obtained on the analysis sample to other bases are described in Practice D 3180.

16. Precision and Bias

16.1 The following criteria should be used for judging the acceptability of results (95 % probability) on split 250-µm (No. 60) samples.

16.1.1 *Repeatability*—Duplicate results by the same laboratory using the same operator and equipment, should not be considered suspect unless they differ by more than 28 cal/g (50 Btu/lb) on a dry basis.

16.1.2 *Reproducibility*—The results submitted by two or more laboratories (different equipment, operators, date of test, and different portions of the same pulp) should not be considered suspect unless the two results differ by more than 56 cal/g (100 Btu/lb) on a dry basis.

16.1.3 *Bias*—The equipment used in this test method for measuring gross calorific value has no bias because the equipment is standardized with a compound having a known heat of combustion. Since there is no acceptable reference material for determining the bias for the procedure in this test method, bias has not been determined.

17. Keywords

17.1 bomb calorimeter; calorific value; calorimeter; isoperibol bomb calorimeter

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[7] For a comprehensive derivation of calculations for converting gross calorific value at constant volume to net calorific value at constant pressure, refer to Research Report D05-1013.

ANNEX

(Mandatory Information)

A1. THERMOMETRIC CORRECTIONS

A1.1 Thermometer Corrections

A1.1.1 It is necessary to make the following individual corrections if not making the corrections would result in an equivalent change of 28 cal/g (5.0 Btu) or more.

A1.1.2 *Calibration Correction,* shall be made in accordance with the calibration certificate furnished by the calibration authority.

A1.1.3 *Setting Correction,* necessary for the Beckmann thermometer. It shall be made in accordance with the directions furnished by the calibration authority.

A1.1.4 *Differential Emergent Stem Correction,* the calculation of differential stem correction depends upon the way the thermometer was calibrated and how it is used. Two conditions are possible:

A1.1.4.1 *Thermometers Calibrated in Total Immersion and Used in Partial Immersion*—This emergent stem correction is made as follows:

$$\text{Correction} = C_e = K\,(t_f - t_i)\,(t_f + t_i - L - T) \qquad \text{(A1.1)}$$

where:

C_e = emergent stem correction,
K = 0.00016 for thermometers calibrated in °C,
L = scale reading to which the thermometer was immersed,
T = mean temperature of emergent stem, °C,
t_i = initial temperature reading, °C, and
t_f = final temperature reading, °C.

NOTE A1.1: *Example*—Assume the point L, to which the thermometer was immersed was 16°C; its initial reading, t_i, was 24.127°C, its final reading, t_f, was 27.876, the mean temperature of the emergent stem, T, was 26°C;

Differential stem correction, C_e

$$= 0.00016\,(28 - 24)\,(28 + 24 - 16 - 26)$$
$$= 0.0064\text{°C}.$$

A1.1.4.2 *Thermometers Calibrated and Used in Partial Immersion, But at a Different Temperature than the Calibrated Temperature*—This emergent stem correction is made as follows:

$$\text{Correction} = C_e = K\,(t_f - t_i)\,(t_c - t_o) \qquad \text{(A1.2)}$$

where:

C_e = emergent stem correction,
K = 0.00016 for thermometers calibrated in °C,
t_i = initial temperature reading, °C,
t_f = final temperature reading, °C,
t_o = observed stem temperature, °C, and
t_c = stem temperature at which the thermometer was calibrated, °C.

A1.1.5 *Radiation Corrections*—These are used to calculate heat loss to the water jacket. They are based on the Dickinson formula,[8] the Regnault-Pfaundler formula,[9] or the U.S. Bureau of Mines method.[10] The same method of determining the radiation correction must be used consistently in calibration and test measurements.

A1.1.5.1 *Dickinson Formula:*

$$C_r = -\,r_1\,(b - i) - r_2\,(f - b) \qquad \text{(A1.3)}$$

where:

C_r = radiation correction,
r_1 = rate of rise in temperature per minute in the preliminary period, °C,
r_2 = rate of rise of temperature per minute in the final period (if temperature is falling, r_2 is negative), °C,
t_i = firing temperature, °C,
t_f = final temperature, being the first temperature after which the rate of change is constant, °C,
i = time at temperature, t_i, min,
b = time at temperature, $t_i + 0.60\,(t_f - t_i)$, min, and
f = time at temperature, t_f, min.

A1.1.5.2 *Regnault-Pfaundler Formula:*

$$C_r = nr_1 + kS \qquad \text{(A1.4)}$$

where:

C_r = radiation correction,
n = number of minutes in the combustion period,
k = $(r_1 - r_2)/(t'' - t')$,
S = $t_n - 1 + (1/2)\,(t_i + t_f)\,nt'$,
t' = average temperature during the preliminary period, °C,
t'' = average temperature during the final period, °C,
$t_1, t_2, t_3 \ldots\ldots t_n$ = successive temperature recorded during the combustion period, °C, and
$t_n - 1$ = sum of $t_1, t_2, t_3 \ldots\ldots\ldots t_n - 1$.

A1.1.5.3 *Bureau of Mines Method*—A table of radiation correction can be established so that only the initial and final readings are required to determine the heat value of any fuel. This may be done by carrying out a series of tests utilizing the procedure described in Section 10, using the following conditions. Regulate the amount of sample burned so that a series of determinations is made in which different temperature rises are obtained. For all determinations, keep the water jacket temperature constant, fire the bomb at the same initial temperature, and have the same time, $f - i$, elapse (±2 s) between the initial and final readings. Determine the radiation corrections for each of the series of temperature rises using the Dickinson method (see A1.1.5.1), or the Regnault-Pfaundler method (see A1.1.5.2). These corrections are constant for a given temperature rise. From the

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[8] Dickinson, H. C., *Bulletin,* National Bureau of Standards, Vol 11, 1951, p. 189.

[9] Pfaundler, L., *Annalen der Physik* (Leipzig), Vol 129, 1866, p. 102.

[10] "Methods of Analyzing and Testing Coal and Coke" *Bulletin 638,* U.S. Bureau of Mines, 1967, pp. 16–17.

series of readings a table or graph is plotted to show radiation correction versus temperature rise. Once the table or graph is established, the radiation corrections can be obtained from it until there is a major change in the equipment.

APPENDIXES

(Nonmandatory Information)

X1. THERMOCHEMICAL CORRECTIONS

X1.1 *Energy of Formation of Nitric Acid*—A correction, e_1, (10.4.2 and 13.2) is applied for the acid titration. This correction is based on the assumptions (*1*) that all the acid titrated is HNO_3 formed by the following reaction: ½ N_2 (gas) + $\frac{5}{4}$ O_2 (gas) + ½ H_2O (liquid) = HNO_3 (in 500 mol H_2O), and (*2*) that the energy of formation of HNO_3 in approximately 500 mol of water under bomb conditions is −59.0 kJ/mol.[11]

X1.1.1 A convenient concentration of Na_2CO_3 is 3.76 g Na_2CO_3/1000 mL which gives $e_1 = V$, where V is the volume of Na_2CO_3 in millilitres. (One millilitre of this solution is equivalent to 1.0 cal in the acid titration.) This value (V = mL) is to be used for calculating calorific value in calories per gram. For other units see Table X2.1. When H_2SO_4 is also present, a part of the correction for H_2SO_4 is contained in the e_1 correction and the remainder in the e_3 correction.

X1.2 *Energy of Formation of Sulfuric Acid*—By definition (see Terminology D 121) the gross calorific value is obtained when the product of the combustion of sulfur in the sample is SO_2 (in grams). However, in actual bomb combustion processes, all the sulfur is found as H_2SO_4 in the bomb washings. A correction e_3 (see 13.2) is applied for the sulfur that is converted to H_2SO_4. This correction is based upon the energy of formation of H_2SO_4 in solutions, such as will be present in the bomb at the end of a combustion. This energy is taken as −295.0 kJ/mol.[12] A correction of 2 times 59.0 kJ/mol of sulfur was applied in the e_1 correction, so the additional correction necessary is 295.0 − (2 times 59.0) = 177 kJ/mol, or 5.52 kJ/g of sulfur in the sample (55.2 J times weight of sample in grams times percent sulfur in sample). This causes e_3 to be 23.7 times weight of samples in grams times percent sulfur in sample for calculating calorific value in British thermal units per pound. The factor 13.17 for e_e (see 13.2) is to be used for calculating calorific value in calories per gram. For other units, see Appendix X2. The values above are based on a coal containing about 5 % sulfur and about 5 % hydrogen. The assumption is also made that the H_2SO_4 is dissolved entirely in the water condensed during combustion of the sample.[13]

X1.2.1 If a 1-g sample of such a fuel is burned, the resulting H_2SO_4 condensed with water formed on the walls of the bomb will have a ratio of about 15 mol of water to 1 mol of H_2SO_4. For this concentration the energy of the reaction SO_2 (gas) + ½ O_2 (gas) + H_2O (liquid) = H_2SO_4 (in 15 mol of H_2O) under the conditions of the bomb process is −295 kJ/mol.[12] Basing the calculation upon a sample of comparatively large sulfur content reduces the possible overall errors, because, for small percents of sulfur, the correction is smaller.

X1.3 *Fuse (Ignition) Wire*—Calculate the energy contributed by burning the fuse wire in accordance with the directions furnished by the supplier of the wire. For example, the energy of the combustion of No. 34 B & S gage Chromel C wire is 6.0 J/mg or approximately 0.95 J/mm. For calculating e_2 for use in Eqs 2 and 3, these give $e_2 = 0.41$ times length (mm) of wire or $e_2 = 2.6$ times weight (mg) of wire. The energy required to melt a platinum wire is constant for each experiment if the same amount of platinum wire is used. As the energy is small, its effect is essentially cancelled out in the relationship between the standardization experiments and the calorific value determinations, and it can be neglected. The factors listed above for e_2 (10.4.2 and 13.2) are suitable for calculating calorific value in calories per gram. For other units, see Appendix X2.

X2. REPORTING RESULTS IN OTHER UNITS

X2.1 *Reporting Results in Joules per Gram:*

X2.1.1 The gross calorific value can be expressed in joules per gram, calories per gram, or British thermal units per pound. The relationships between these units are given in Table 1.

X2.1.2 Because the energy of combustion of the reference material is measured and certified by NIST in joules per gram, the most straightforward usage of the reference material would lead to the calorific value of the fuel in joules per gram. To carry out this procedure, make the changes outlined in X2.1.3 through X2.1.5.

X2.1.3 For calculating energy equivalent, substitute Eq X2.1 for Eq 2:

$$E' = [(gH') + e_1' + e_2']/t \qquad \text{(X2.1)}$$

where the meanings of the symbols in Eq X2.1 are the same as in Eq 2 except that:

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[11] Calculated from data in National Bureau of Standards Technical Note 270-3.

[12] Calculated from data in National Bureau of Standards Circular 500.

[13] Mott, R. A., and Parker, C., "Studies in Bomb Calorimetry IX—Formation of Sulfuric Acid," *Fuel*, FUELB, Vol 37, 1958, p. 371.

E' = energy equivalent, with units of joules per temperature unit,
H' = heat of combustion of reference material, with units of joules per gram weight in air (J/g from the certificate for the NIST benzoic acid),
g = mass (weight in air) of benzoic acid, g,
t = corrected temperature rise (see 10.4.1), and
e_1', e_2', and e_3' = corrections, with units of joules (see Table X2.1).

X2.1.4 For calculating gross calorific value, substitute Eq X2.2 for Eq 3:

$$Q_v\ (\text{gross}) = [(tE') - e_1' - e_2' - e_3')]/g \qquad (X2.2)$$

where the meanings of the symbols in Eq X2.2 are the same as in Eq 3 except that:

Q_v (gross) = gross calorific value with units of joules per gram (weight in air),
E' = energy equivalent, with units of joules per temperature unit, and
e_1', e_2', and e_3' = corrections, with units of joules (see Table X2.1).

X2.1.5 *Precision:*

TABLE X2.1 Alternative Thermochemical Correction Factors (Units in Joules)[A]

Correction	Multiplication Factor	Multiply By
e_1' (HNO_3)	20 J/mL	mL of 0.34 *N* Na_2CO_3
e_3' (H_2SO_4)	55.2 J/cgS	percent of sulfur in sample times mass of sample in grams
e_2' (fuse wire)	0.95 J/mm	length (mm) of 0.16-mm diameter (No. 34 B & S gage) Chromel C wire
or		
e_2' (fuse wire)	1.14 J/mm	length (mm) of 0.16-mm diameter (No. 34 B & S gage) iron wire
e_2' (fuse wire)	6.0 J/mg	mass (mg) of Chromel C wire
or		
e_2' (fuse wire)	7.4 J/mg	mass (mg) of iron wire

[A] To be used in Eqs X2.1 and X2.2 only.

X2.1.5.1 *Repeatability*—Duplicate results by the same laboratory, using the same operator and equipment, should not be considered suspect unless they differ by more than 120 J/g.

X2.1.5.2 *Reproducibility*—The results submitted by two or more laboratories (different equipment, operators, date of test, and different portions of the same pulp) should not be considered suspect unless the results differ by more than 240 J/g.

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Document Name: ASTM D3371: Standard Test Method for Nitriles in Aqueous Solution by Gas-Liquid Chromatography

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Designation: D 3371 – 95

Standard Test Method for Nitriles in Aqueous Solution by Gas-Liquid Chromatography[1]

This standard is issued under the fixed designation D 3371; 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 nitriles that can be separated and detected quantitatively at a limit of approximately 1 mg/L by aqueous injection on a selected gas-liquid chromatographic column.

1.2 This test method utilizes the procedures and precautions as described in Practice D 2908.

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 1129 Terminology Relating to Water[2]

D 2908 Practice for Measuring Volatile Organic Matter in Water by Aqueous-Injection Gas Chromatography[3]

3. Terminology

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

4. Significance and Use

4.1 Nitriles at concentrations of a few milligrams per litre are potentially toxic to aquatic life. Nitriles in waste water discharges should be detected and controlled.

4.2 Gas-liquid chromatography (GLC) can detect and determine mixtures of nitriles at levels where wet chemical procedures are not applicable.

5. Special Comments

5.1 It is recommended that samples that cannot be analyzed immediately, be quick frozen for preservation. Samples should be neutralized to pH 7 at the time of collection to minimize hydrolysis of the nitrile groups.

5.2 Samples of nitriles to be employed as standards should be considered to be unstable. Storage in a freezer is recommended.

5.3 It is not always practical to translate operating conditions directly from one GLC instrument to another. An operator should optimize his instrument to a particular procedure, for example, injection and detection temperature, flow rates, etc.

6. Typical Chromatograms

6.1 The following instrument parameters were used to obtain the typical chromatograms (See Fig. 1 and Fig. 2).

6.1.1 *Column*—⅛ in. outside diameter stainless steel, 8 ft long packed with a porous styrene divinylbenzene polymer.

NOTE 1—"Chromosorb" 101, 50/60 mesh, was used for the typical chromatograms.

6.1.2 *Detector*, flame ionization.

6.1.3 *Temperatures*:

Injection port	240°C
Detector	240°C
Oven, isothermal	130°C
Oven, programmed at 10°C/min	110°C to max of 200°C

6.1.4 *Carrier Gas*, helium at 25 mL/min.

6.1.5 *Sample Size*:

isothermal 5 μL

programmed 3 μL

6.1.6 *Recorder*, ¾ in./min chart speed and 1 mV full-scale response.

6.2 *Kovats Index Values:*[4]

Compounds	Relative Retention	Kovats Index
Acetonitrile	1.00	470
Acrylonitrile	1.25	512
Proprionitrile	1.67	570
Methoxyacetonitrile	2.21	635[5]
Butyronitrile	2.50	678
Isovaleronitrile	3.04	740[5]
Valeronitrile	3.38	783
Hexanenitrile	4.25	905[5]
Benzonitrile	5.42	990

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[1] This test method is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D 19.06 on Methods for Analysis for Organic Substances in Water.

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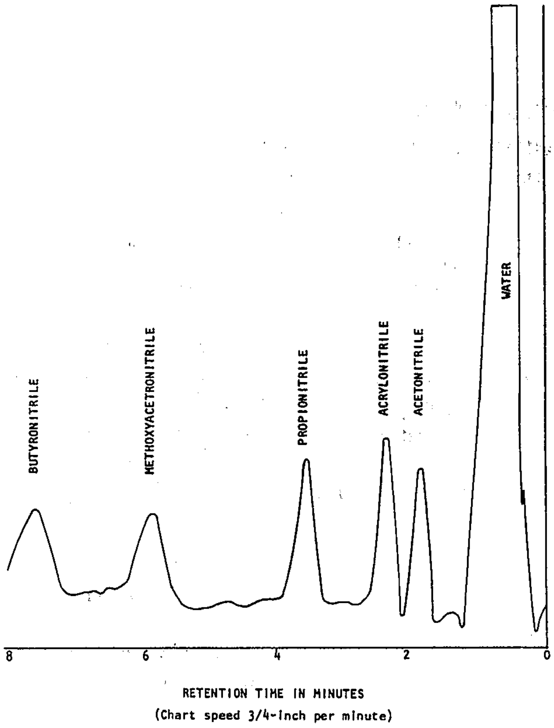
[2] *Annual Book of ASTM Standards*, Vol 11.01.

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

[4] *Gas Chromatographic Data Compilation, ASTM AMD25A*, 1967.



Column Packing - Chromosorb 101, 50/60 mesh
Carrier Gas - Helium at 25 mL/min
Temperature - Isothermal operation of the column at 130°C
Sample Size - 5 microlitres containing 10 mg/L of each nitrile

FIG. 1 Isothermal Chromatographic Analysis of Nitriles in Aqueous Solution

7. Precision and Bias

7.1 An interlaboratory study was conducted in 1972 with participation from four laboratories and seven operators. Triplicate analyses of three concentrations in distilled water were contributed by all operators; see Table 1 for statistics from distilled water data. Three operators also did triplicate recoveries of three concentrations spiked into a river water of their choice; see Table 2 for the statistics from the river water recovery data.

7.2 The precision of this test method within the range from 10 to 60 mg of standards/L in distilled water may be expressed as follows:

Compound	
Acetonitrile	$S_t = 0.182x + 0.194$
	$S_o = 0.023x + 0.038$
Proprionitrile	$S_t = 0.100x - 0.817$
	$S_o = 0.020x + 0.348$
Methoxyacetonitrile	$S_t = 0.260x + 0.263$
	$S_o = 0.026x + 0.671$
Butyronitrile	$S_t = 0.107x - 0.457$
	$S_o = 0.036x + 0.202$

where:

S_t = overall precision,
S_o = single operator precision, and
x = concentration of the specification compound, mg/L.

8. Keywords

8.1 flame ionization; gas-liquid chromatography; GLC; isothermal chromatographic analysis; Kovats index

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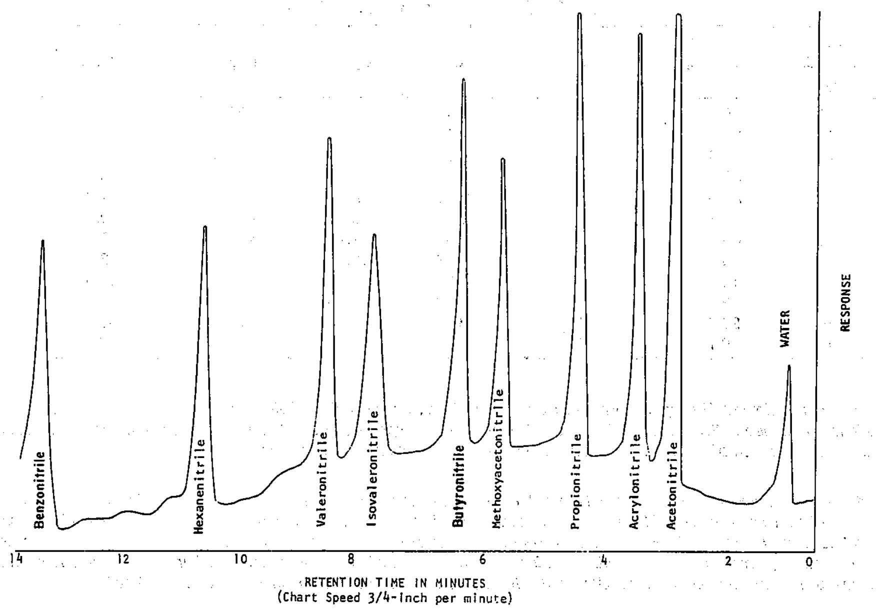
[5] Kovats index values estimated from relative retention data because standard compound was not readily available.



Column Packing - Chromosorb 101, 50/60 mesh
Carrier Gas - Helium at 25 mL/min
Temperature - Programmed operation at 10°C/min from 110°C to a maximum of 200°C
Sample Size - 3 microlitres containing 1 500 mg/L of each nitrile

FIG. 2 Proposed Temperature Chromatographic Analysis of Nitriles in Aqueous Solution

TABLE 1 Recovery for Reagent Water

Compound	Amount Added, mg/L	Amount Found, mg/L	*n*	S_o	S_t	Bias	% Bias	Statistical Significance, 95 % CL
Acetonitrile	60	50.7	21	1.37	11.0	−9.3	−15.5	yes
	30	24.4	21	1.10	5.90	−5.6	−18.7	yes
	10	8.42	21	0.57	1.86	−1.58	−15.8	yes
Proprionitrile	60	56.6	15	1.54	5.20	−3.4	−5.7	yes
	30	28.8	15	0.96	1.35	−1.2	−4.0	yes
	10	9.66	15	0.54	0.56	−0.34	−3.4	yes
Methoxyacetonitrile	60	62.8	18	2.21	15.6	2.8	4.7	no
	30	31.6	18	1.48	8.65	1.6	5.3	no
	10	9.88	18	0.91	2.50	−0.12	−1.2	no
Butyronitrile	60	57.9	21	2.43	6.08	−2.1	−3.5	no
	30	28.9	21	1.12	2.48	−1.1	−3.7	no
	10	9.31	21	0.66	0.78	−0.69	−6.9	yes

TABLE 2 Recovery for River Water

Compound	Amount Added, mg/L	Amount Found, mg/L	n	S_o	S_t	Bias	% Bias	Statistical Significance, 95 % CL
Acetonitrile	60	38.7	9	2.83	17.4	−21.3	−35.5	yes
	30	16.3	9	1.59	9.94	−13.7	−45.7	yes
	10	4.32	9	1.12	4.58	−5.68	−56.8	yes
Proprionitrile	60	57.8	9	1.25	3.11	−2.2	−3.7	no
	30	29.6	9	0.64	2.67	−0.4	−1.3	no
	10	9.77	9	0.24	0.45	−0.23	−2.3	no
Methoxyacetonitrile	60	85.4	9	1.63	21.7	25.4	42.3	yes
	30	44.4	9	1.83	12.65	14.4	46.7	yes
	10	14.3	9	0.88	5.36	4.3	43.0	yes
Butyronitrile	60	62.5	9	1.68	5.73	2.5	4.2	yes
	30	29.9	9	0.76	1.38	−0.1	−0.3	yes
	10	9.75	9	0.64	0.90	−0.25	−2.5	yes

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Document Name:	ASTM D3454: Standard Test Method for Radium-226 in Water
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Standards Body:	American Society for Testing and Materials

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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

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[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.

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.

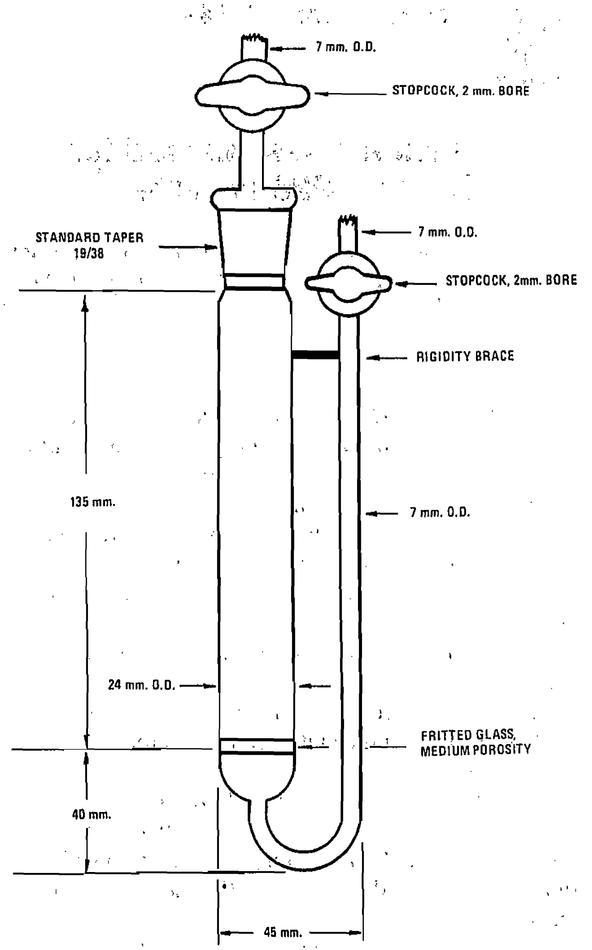

FIG. 1 Radon Bubbler

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

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[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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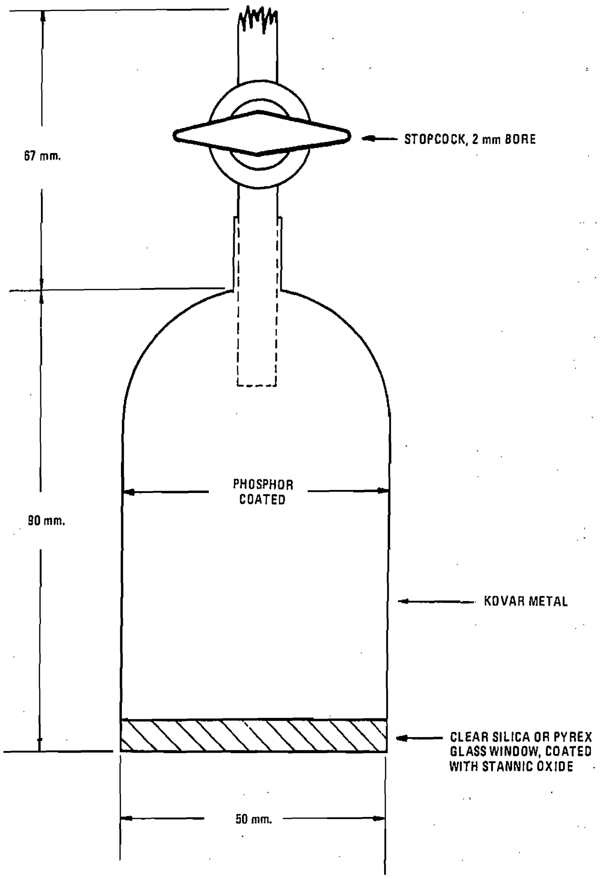

FIG. 2 Radon Scintillation Chamber

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).

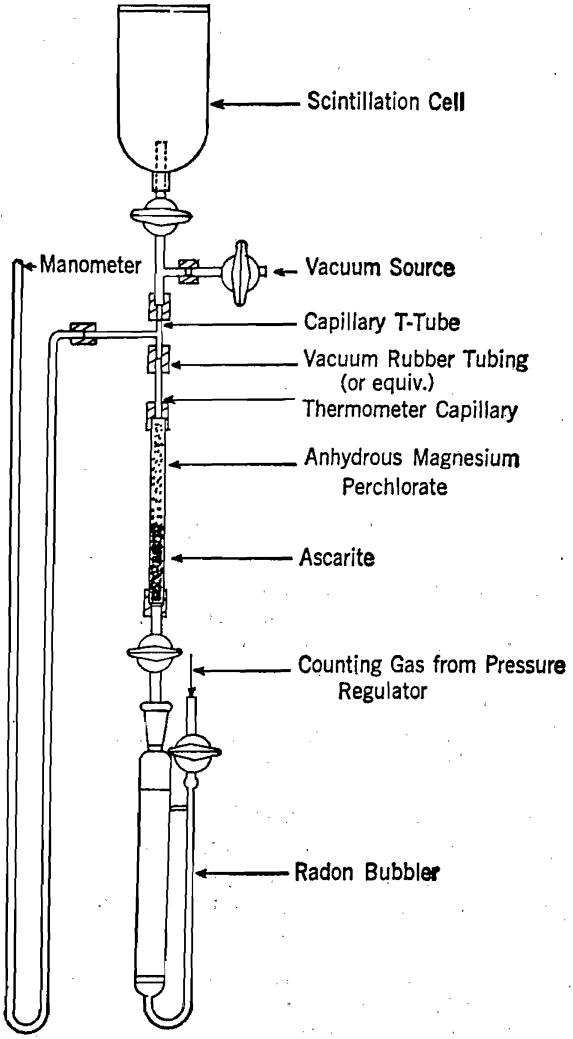

FIG. 3 De-emanation Assembly

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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[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.

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 ⅔to 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

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[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.

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.

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:

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

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:

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

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;

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

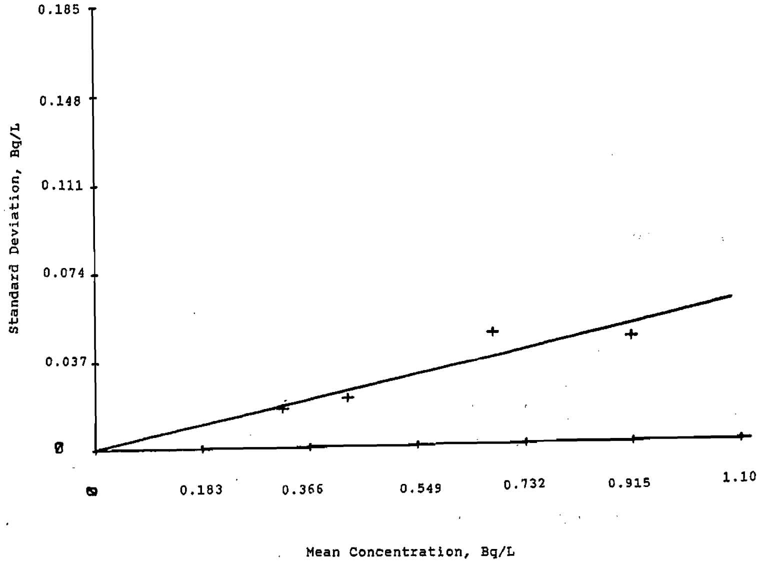

FIG. 4 Overall Standard Deviation versus Mean Concentration

radon-222; water

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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

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[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.

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.

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:

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

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 $H_w^v - H_w^{l\,\prime}$.

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] H_n^{id}, kJ · mol^{-1}	Ideal Gross Heating Value[D] H_m^{id}, Btu · lbm^{-1}	Ideal Gross Heating Value[D] H_v^{id}, Btu · ft^{-3}	Ideal Net Heating Value h_n^{id}, kJ · mol^{-1}	Ideal Net Heating Value h_m^{id}, Btu · lbm^{-1}	Ideal Net Heating Value h_v^{id}, Btu · ft^{-3}	Summation Factor, b_i, psia^{-1}
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.

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

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:

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

where: M is the molar mass of the mixture,

$$M = \sum_{j=1}^{n} x_j M_j \tag{4}$$

P is the base pressure in absolute units (psia), R is the gas constant, 10.7316 psia.ft³/(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:

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

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}:

$$H_v^{id} = \rho^{id}\, H_m^{id} = \sum_{j=1}^{n} x_j H_{vj}^{id} \tag{6}$$

$H_{v,j}^{id}$ 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:

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

7.5 *Real Gas Values—Compressibility Factor*:

7.5.1 The compressibility factor is:

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

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:

$$Z(T,P) = 1 + BP/RT \tag{9}$$

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

$$B = x_1^2 B_{11} + x_2^2 B_{22} + \cdots + x_n^2 B_{nn} + 2x_1 x_2 B_{12} + \cdots + 2x_{n-1} x_n B_{n-i,n}$$

$$= \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j B_{ij} \tag{10}$$

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:

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

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:

$$\rho = \rho^{id}/Z \tag{12}$$

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:

$$d = \rho/\rho_a = MZ_a/M_a Z \tag{13}$$

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:

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

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:

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

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:

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

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

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_ib_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 $\mathrm{Btu{\cdot}ft^{-3}}$
Hv^{id} (sat gas, dry air) = $1179.7(0.9826) = 1159.1$ $\mathrm{Btu{\cdot}ft^{-3}}$
$l - x_w = 0.9826$
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) = $1179.7/0.9968 = 1183.5$ $\mathrm{Btu{\cdot}ft^{-3}}$
$\{Hv^{id}/Z\}$ (sat gas, dry air) = $1159.1/(0.9964) = 1163.3$ $\mathrm{Btu{\cdot}ft^{-3}}$

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 $\dot{m}$ is the mass flow rate. For an ideal gas, the mass flow rate is related to the volumetric flow rate, $\dot{V}^{id}$, 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.

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_ib_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^{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:

$$\begin{aligned} &C_\alpha H_\beta S_\gamma(id) + (\alpha + \beta/4 + \gamma)(1 + \epsilon)O_2(id) \\ &+ 0.043\,83(\alpha + \beta/4 + \gamma)(1 + \epsilon)\mathrm{Ar}\,(id) \qquad (X1.1) \\ &+ [0.001\,62(\alpha + \beta/4 + \gamma)(1 + \epsilon) + x_c/(1 - x_N - x_C)]CO_2(id) \end{aligned}$$

TABLE X1.1 Example Calculation of Precision

Compound	Composition, x_j	$H_v^{id} - H_{vi}^{id}$ Btu•ft^{-3}	Repeatability δx_j	Repeatability $[(H_v^{id} - H_{vi}^{id})\delta x_j]^2$ (Btu•ft^{-3})^2	Reproducibility $\delta x'_j$	Reproducibility $[(H_v^{id} - H_{vi}^{id})\delta x'_j]^2$ (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

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

$$= [\alpha + 0.001\,62(\alpha + \beta/4 + \gamma)(1 + \epsilon) + x_C/(1 - x_N - x_C)]\mathrm{CO_2}(id)$$

$$+ n_w^v\mathrm{H_2O}\,(id) + n_w^1\mathrm{H_2O}\,(1) + \gamma\mathrm{SO_2}(id)$$

$$+ [3.728\,73(\alpha + \beta/4 + \gamma)(1 + \epsilon) + x_N/(1 - x_N - x_C)]\mathrm{N_2}(id)$$

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

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^1 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:

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

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:

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

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:

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

where:

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

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

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

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:

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

(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:

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

The corrected mole fractions then become:

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

and the heating value becomes:

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

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:

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

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.

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

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

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

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

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

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

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

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

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

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:

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

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

$$(1 - x_n - x_c) + (\alpha + \beta/4 + \gamma)(3.774\,18 + 4.774\,18\,\epsilon)]$$

$$\times (P_w^\sigma/P)/(1 - P_w^\sigma)\}H_w^{id}]$$

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:

$$Hn - Hn^{id} = \int_O^P \left\{\left[\left(\frac{\partial H}{\partial P}\right)_T\right]_{r'} - \left[\left(\frac{\partial H}{\partial P}\right)_T\right]_r\right\} dP \qquad \text{(X3.1)}$$

where:

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

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 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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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-

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[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.

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[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.

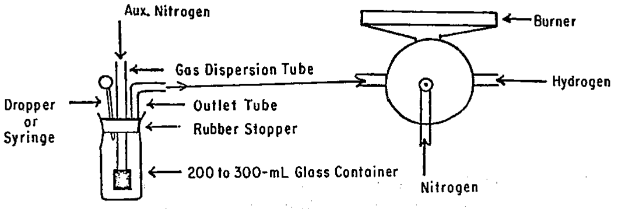

FIG. 1 Stibine Vapor Analyzer

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.

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[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.

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	$S_T = 0.451 + 0.104\,\overline{X}$
			7.0	6.42	0.88	0.78	−8.3^y		0.89	$S_o = 0.255 + 0.109\,\overline{X}$
			12.0	11.16	1.71	1.54	−7.0			
	WOC	4	3.0	2.74	0.66	0.66	−8.7		0.98	$S_T = 0.346 + 0.132\,\overline{X}$
			7.0	6.00	1.22	0.95	−14.3^y		1.00	$S_o = 0.386 + 0.0967\,\overline{X}$
			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:

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

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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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

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[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.

Current edition approved Nov. 10, 1995. Published January 1996. Originally published as D 4177 – 82. Last previous edition D 4177 – 82 (1990)$^{\epsilon 1}$.

[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.

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

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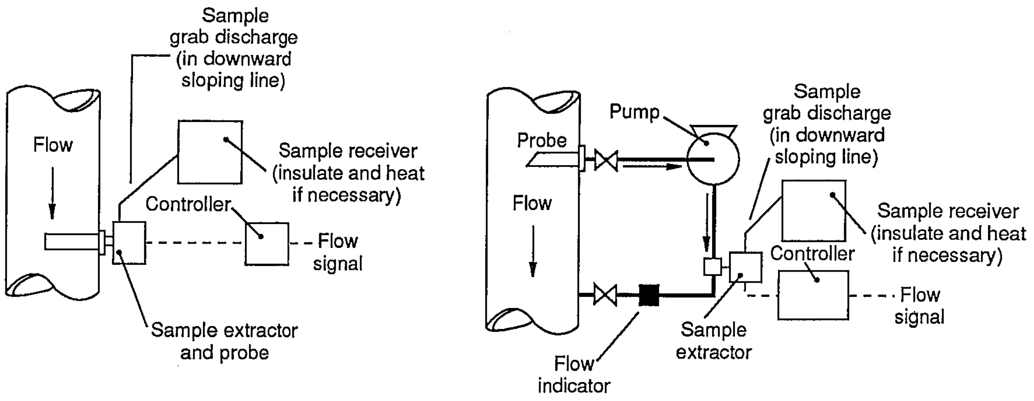
[9] Available from The Institute of Petroleum, 61 New Cavendish St., London WIM 8AR, England.

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



Automatic Sampling-in-Line

Automatic Sampling With a Fast Loop

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:

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

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

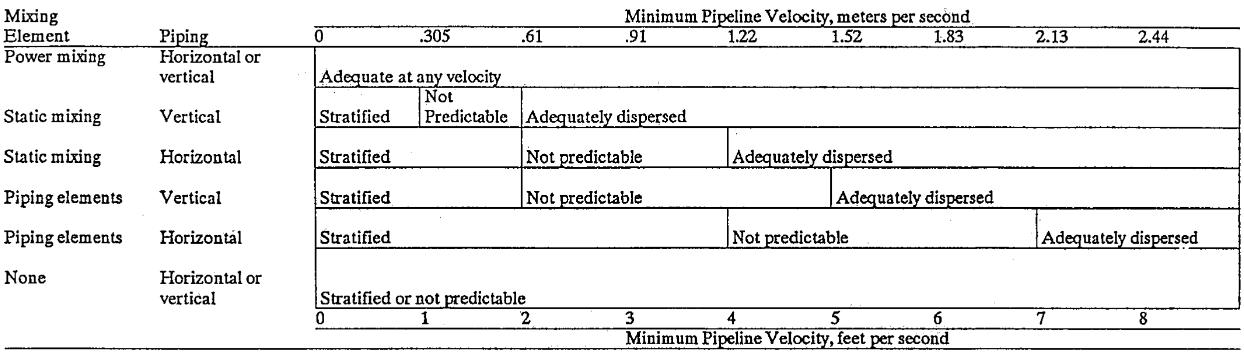


FIG. 2 General Guidelines for Minimum Velocities Versus Mixing Elements

(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.

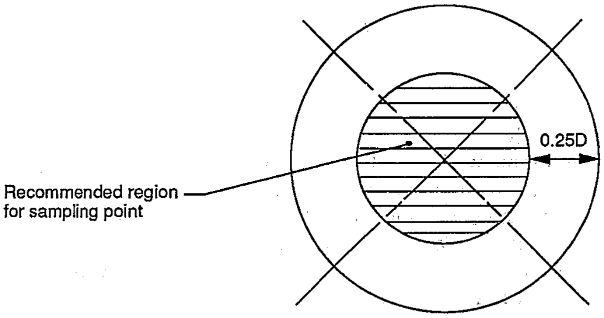


FIG. 3 Recommended Sampling Area

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)

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

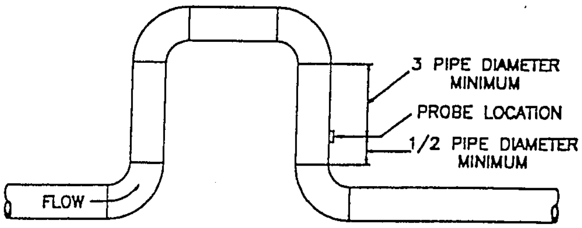


FIG. 4 General Vertical Piping Loop Configuration

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

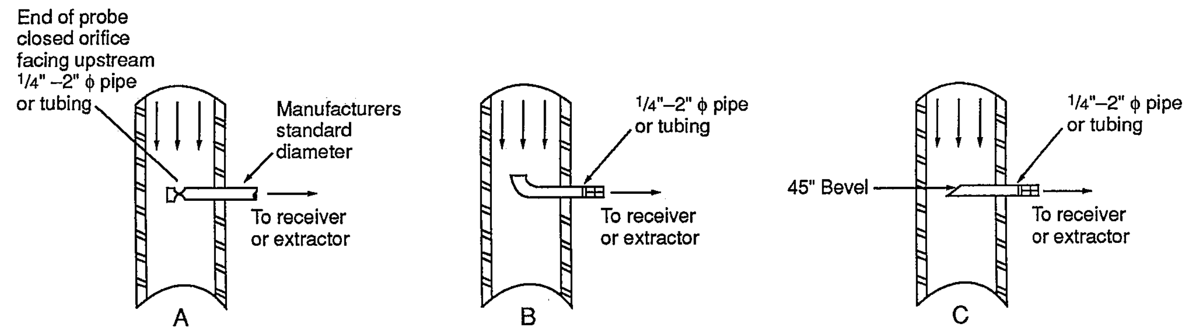
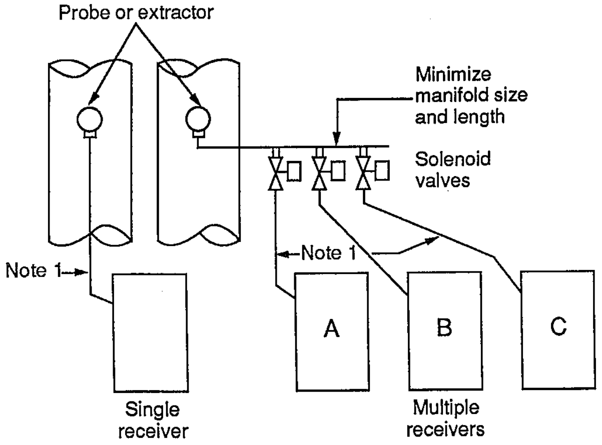
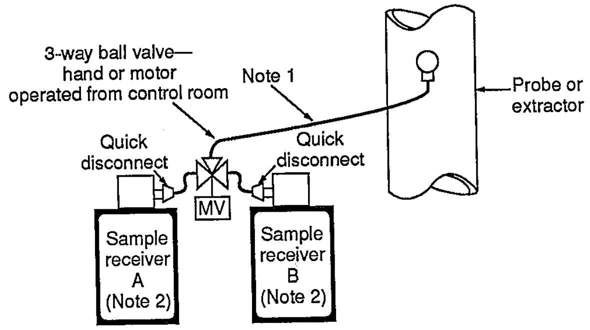


FIG. 5 Probe Designs



NOTE—6.4 or 9.5 mm (1/4 or 3/8 in.) tubing, as short as possible and sloping continuously toward the sample receiver, should be used. 9.5 mm (3/8 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 (3/8 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

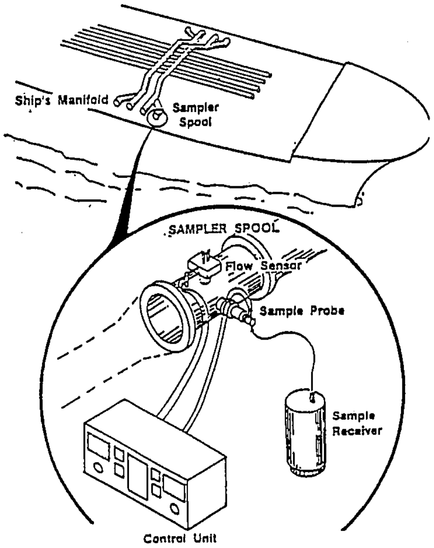


FIG. 8 Typical Portable Marine Installation

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.

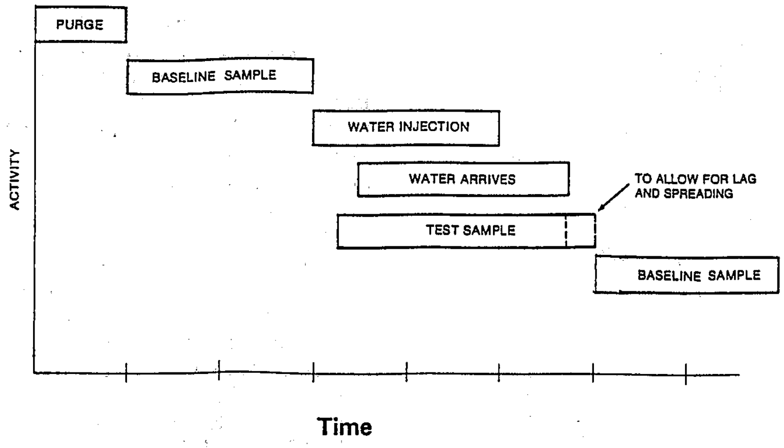
16.4 *Requirements for Acceptability*—Testing by either the component or total system method requires that two out of three consecutive sets of test data repeat within the limits shown in Annex A3.

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.



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.

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

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:

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

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.

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

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.

$$E = \frac{\Delta PV}{\Delta X_\rho} \qquad (3)$$

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 m²/s = 10^6 cSt = 10^6 mm²/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	m³/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	m²/s
θ	turn angle	degrees
ν	kinematic viscosity	m²/s (2)
σ	surface tension	N/m (3)
ρ	crude oil density	kg/m³
ρ_d	water density	kg/m³
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

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	$K = 0.5\,(1 - \gamma^2)$	$(0 \leq K \leq 0.5)$
Enlargement	$K = \frac{(1 - \gamma^2)^2}{\gamma^4}$	$(0 \leq K \leq 0.5)$
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	$(0 \leq K \leq 1.2)$
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 mm²/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/m³ 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

TABLE A2.5 Dissipation Energy Relationships

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

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.

$$W = \frac{\epsilon/D}{G} \qquad (12)$$

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.

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

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.

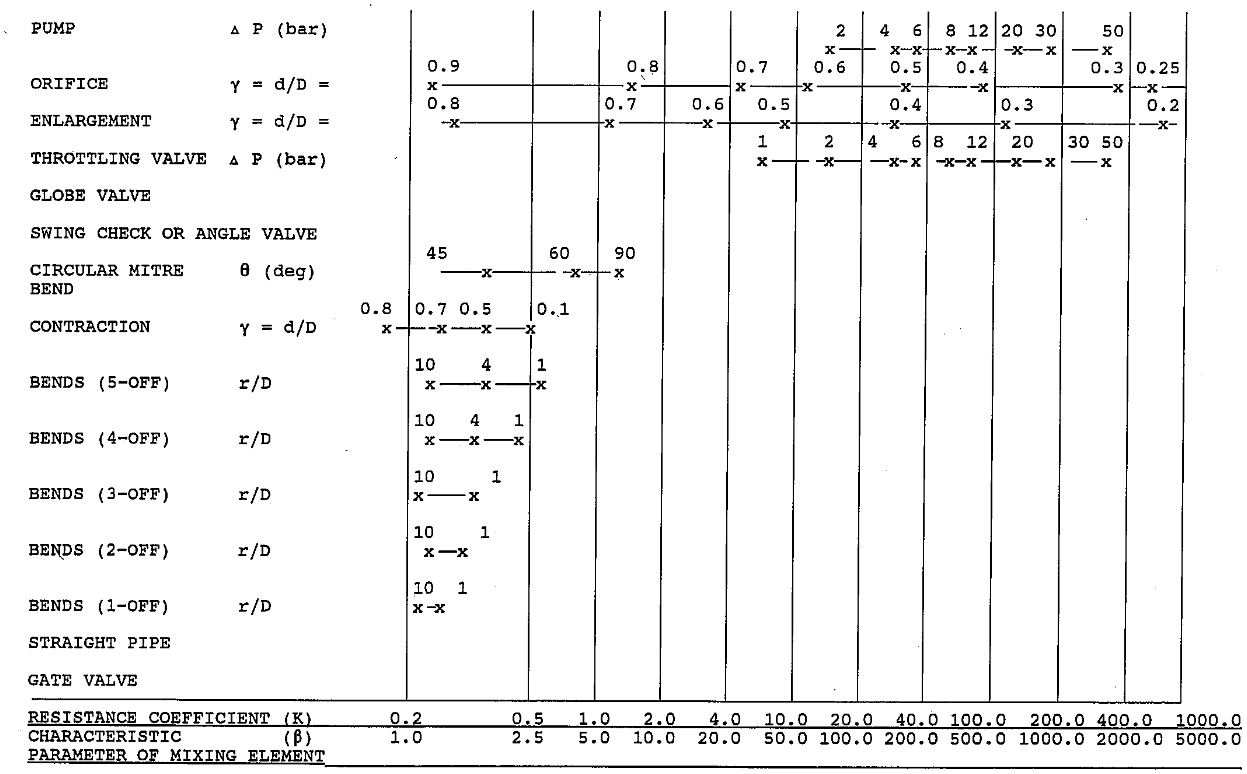
A2.11.7 Compare E_r with E to determine if an acceptable profile can be achieved. If for any piping element $E > E_r$, then a satisfactory profile can be achieved using that element. If $E < E_r$ for all piping elements, then additional dissipation energy must be provided. This can be done by reducing 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_0 and the following typical values—$D = 0.4$ m; $\nu = 16$ cSt; $\rho = 900$ kg/m^3; V = 5.6 m/s.

FIG. A2.1 Comparison of Mixing Devices

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:

$$E = \frac{\Delta PV}{\Delta xp} \; W/\text{kg} \qquad (3)$$

or as:

$$\Delta P = \frac{K\rho V^2}{2} \; W/\text{kg} \qquad (4)$$

then:

$$E = \frac{KV^3}{2\Delta X} \; W/\text{kg} \qquad (12)$$

and using $\Delta X = 10D$

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

A2.12.1.4

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

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

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

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

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

and

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

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

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

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:

$$E = \beta E_0 \; W/\text{kg} \qquad (17)$$

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

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

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

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

A2.12.1.8

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

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

as calculated for Method A:

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

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

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

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

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:

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

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

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

A2.12.2.4 The water droplet settling velocity is:

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

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

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

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

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

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

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.

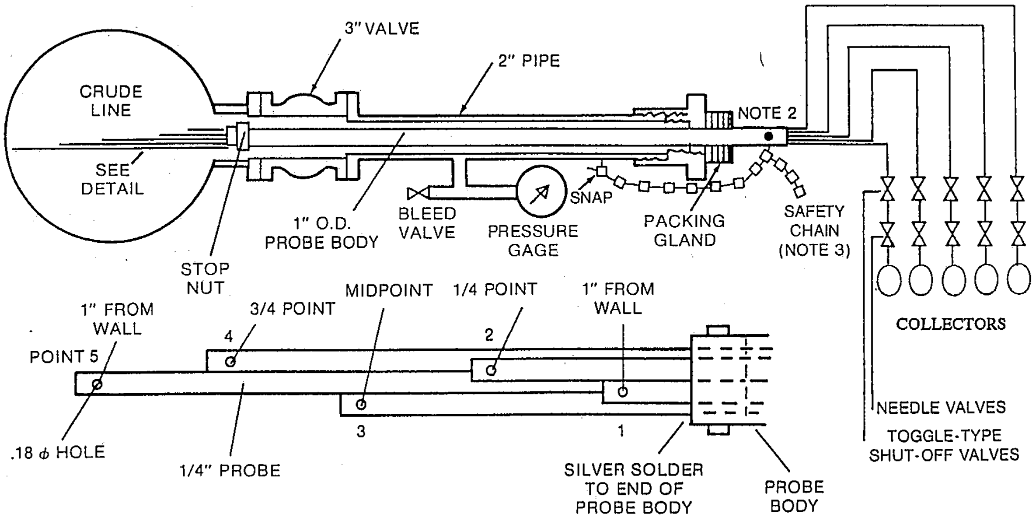
A3.4 *Single Sampler—Acceptance Test:*

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



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

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.

$$\text{Dev} = (W_{\text{test}} - W_{\text{bl}}) - W_{\text{inj}} \qquad (35)$$

where:

Dev = deviation, vol %,

W_{test} = water in test sample, vol %,

W_{bl} = baseline water adjusted to test conditions, vol %

$$= W_{\text{avg}} \times \frac{TOV - V}{TOV}, \qquad (36)$$

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 %

$$= \frac{V}{TOV} \times 100 \qquad (37)$$

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

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.

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).

$$SA = \frac{N \times B}{PV_{co}} = 1 \pm 0.10 \tag{46}$$

VESSEL _____ LOCATION _____

LOADING _____ DISCHARGE _____ TIME PUMPING BEGINS ____ ENDS ____

DATE PUMPING BEGINS _____

		Probe ID (1)		Line No. (1)		Parcel	Calculation (2)	
Date	Time	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):*

$$\text{Sampling Factor} = \frac{\text{Total sampling time}}{\text{Total parcel time}} = 1 \text{ at } \pm 0.05 \qquad (44)$$

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.

VESSEL ______ LOCATION ______ DATE ______

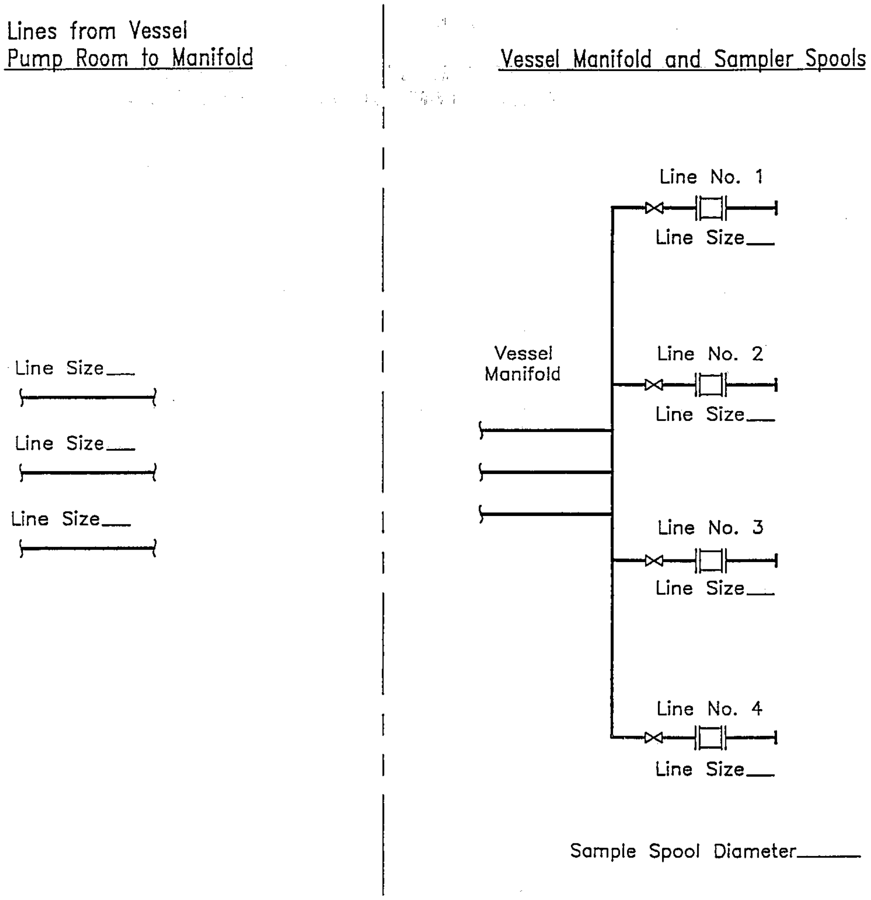
TABLE G2 PORTABLE SAMPLER OPERATIONAL DATA CONFIRMATION OF MIXING AND FLOW SENSOR VELOCITY

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.

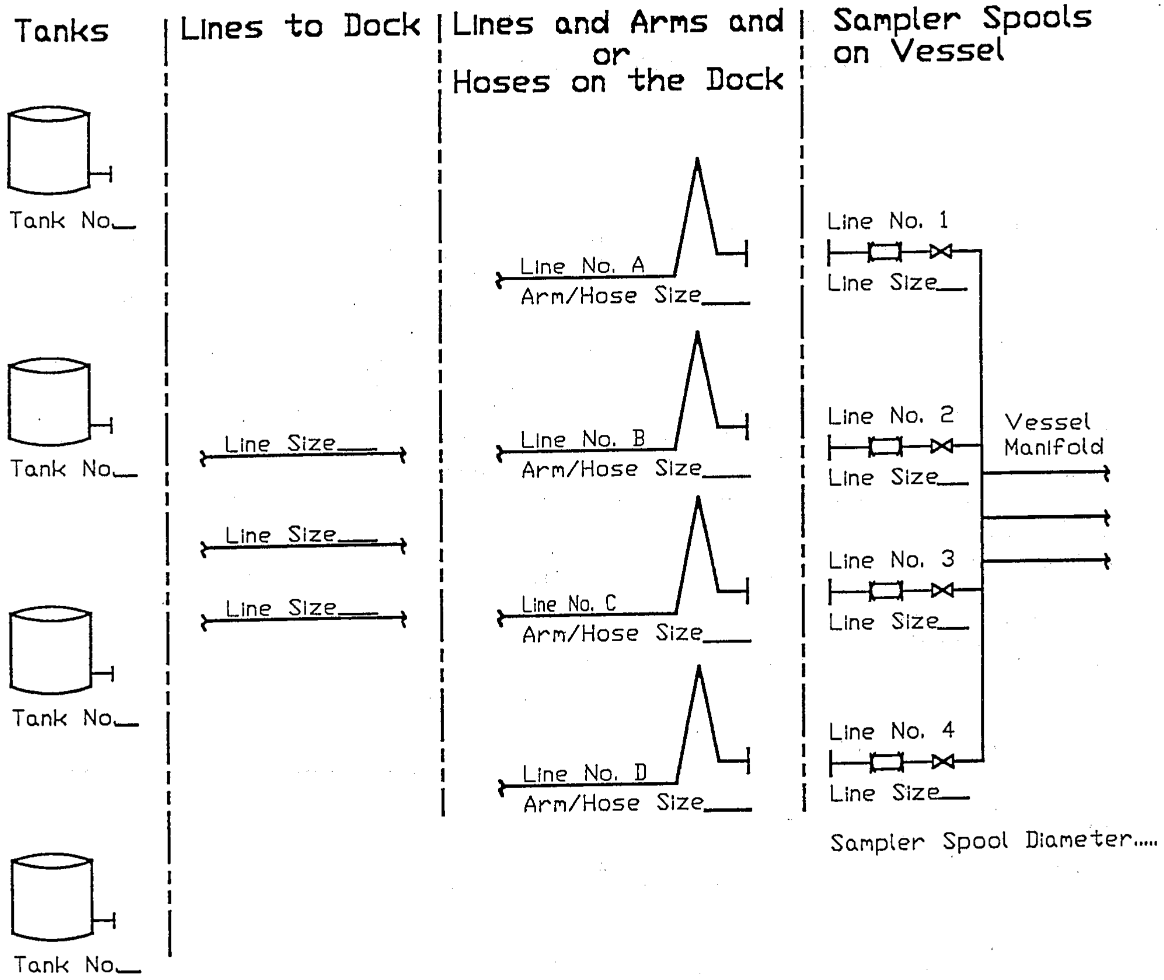
NOTE 2—A sample cannot be judged representative if more than 10 % of the water found in the total parcel after the operation is complete is pumped as free water and the velocity in the piping ahead of the sampler at the time of pumping is less than 2.44 m/s (8 ft/s).

FIG. A5.2 Portable Sampler Operational Data Confirmation of Free Water Sampled



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



NOTE—In the spaces provided, enter the line sizes used during discharge.

FIG. A5.4 Typical Piping Schematic to be Recorded for Discharges

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: ____ Meter ____ Tank Tank Increment Vol. ______ bbls/m3 Sample Receiver Volume: ____ gal/l Test Sample Volume ____ gal/l	Probe Design: ____ Isokinetic ____ Ell ____ Beveled ____ Plain ____ Other ____ Grab Size(ml)	Probe Orientation: ____ Top ____ Side ____ Bottom ____ Sample Loop	Stream Conditioning: ____ Power Mixing ____ Static Mixer–Vertical ____ Static Mixer–Horizontal ____ Piping Element–Vertical ____ Piping Element–Horizontal ____ None	Laboratory Analysis: ____ Centrifuge ____ Distillation ____ Karl Fischer ____ Mass ____ Volume

Test Water: ____ Fresh; ____ Brackish; ____ 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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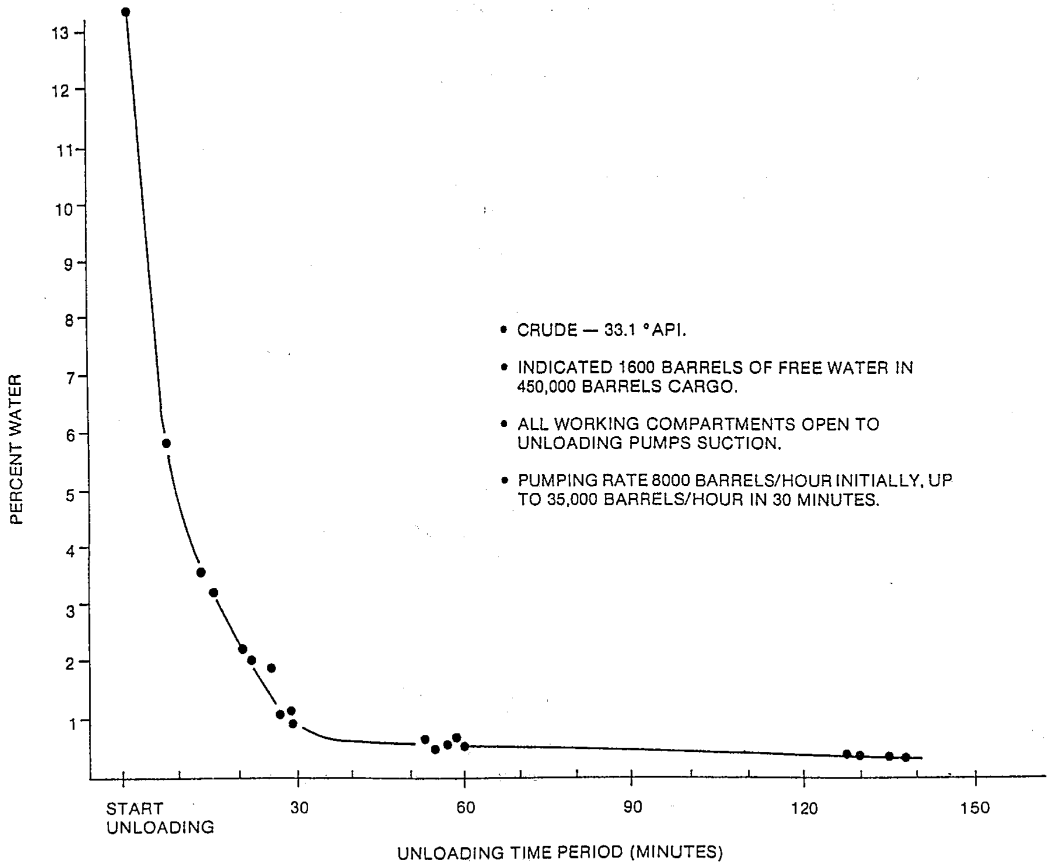
FIG. X1.1 Design Data Sheet for Automatic Sampling System

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.



- CRUDE — 33.1 °API.
- INDICATED 1600 BARRELS OF FREE WATER IN 450,000 BARRELS CARGO.
- ALL WORKING COMPARTMENTS OPEN TO UNLOADING PUMPS SUCTION.
- PUMPING RATE 8000 BARRELS/HOUR INITIALLY, UP TO 35,000 BARRELS/HOUR IN 30 MINUTES.

FIG. X2.1 Comparison of Percent Sediment and Water Versus Unloading Time Period

CERTIFICATE

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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.

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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

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[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.

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

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[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.

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

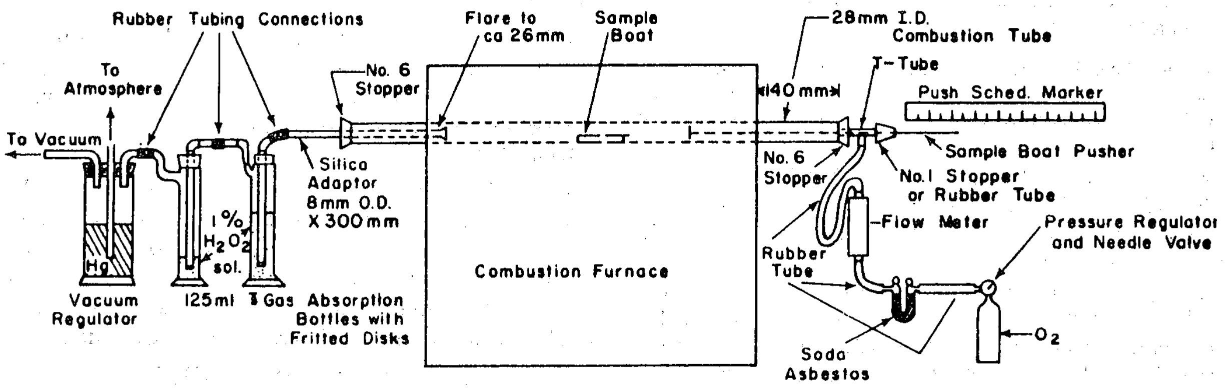

FIG. 1 Apparatus for the Determination of Sulfur Using Acid-Base Titration

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[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.

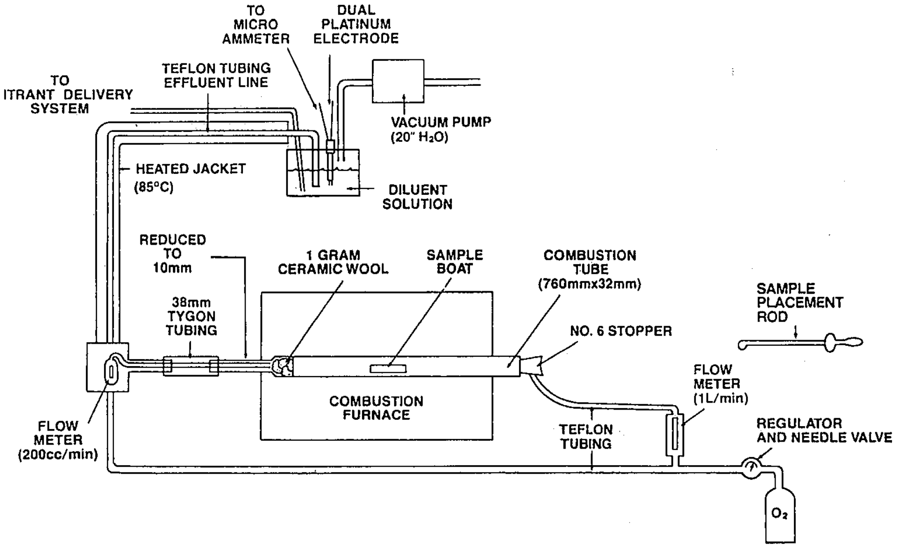

FIG. 2 Apparatus for the Determination of Sulfur by the Iodimetric Detection Method

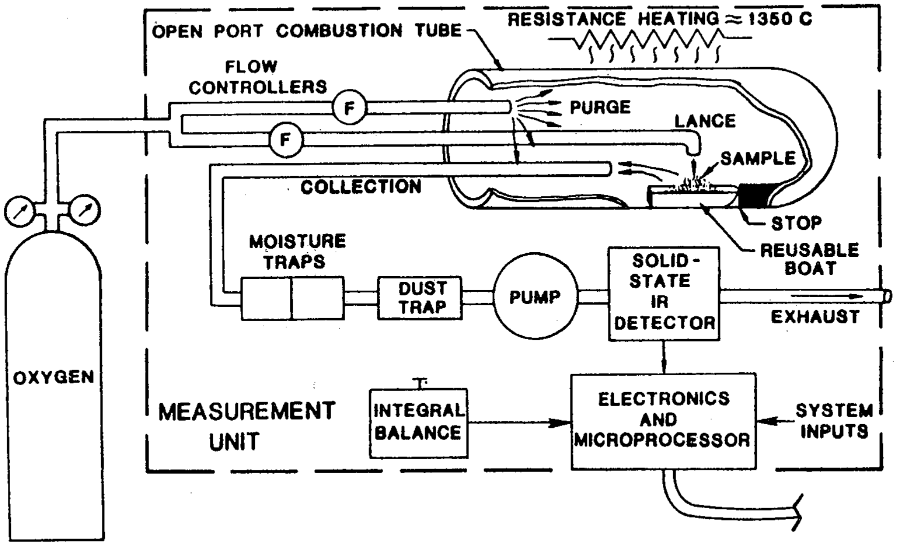

FIG. 3 Apparatus for the Determination of Sulfur by the Infrared Detection Method

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.

$$F = \frac{\text{Actual Sulfur in Standard, Dry Basis}}{\text{Analyzed Sulfur in Standard, Dry Basis}} \quad (1)$$

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 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:

$$S_c = 1.603\,(S_b/1.603 \times F - \text{Cl},\,\%/3.546) \qquad (2)$$

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:

$$S_c = 1.603\,[(S_b \times N_1 \times F \times 10) - \text{Cl},\,\%/3.546]/W \qquad (3)$$

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:

$$S_c = 1.603\,[(V_1 \times N_1 \times F) - \text{Cl},\,\%/3.546]/W \qquad (4)$$

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) 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:

$$T = S_s \times W/100 \times V_t \qquad (5)$$

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:

$$S = 100\,(T \times V_t)/W \qquad (6)$$

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

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[7] Available from the Office of Standard Reference Materials, Room B314, Chemistry Bldg., National Institute of Standards and Technology, Washington, DC 20234.

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:

$$I(r) = 0.06 + 0.03\,\bar{x} \qquad (7)$$

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:

$$I(R) = 0.03 + 0.11\,\bar{x} \qquad (8)$$

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:

$$I(r) = 0.08\,\bar{x} \quad (9)$$

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

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[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.

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.

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 ($\frac{1}{32}$ 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 ($\frac{1}{32}$ 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 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.

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.

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.

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

CERTIFICATE

By Authority Of
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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.

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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 (e) 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

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[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.

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

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[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.

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:

$$S=[DBS \times S_{DBS})+(MO \times S_{MO})]/(DBS + MO) \quad (1)$$

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.

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	

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 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:

$$0.02894(X + 0.1691) \tag{2}$$

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:

$$0.1215\ (X + 0.05555) \tag{3}$$

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.

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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[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.

16. Keywords

16.1 analysis; energy dispersive; petroleum; spectrometry; sulfur, X-ray

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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

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[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.

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:

$$Q_n\ (\text{net, }25°\text{C}) = Q_g\ (\text{gross, }25°\text{C}) - 0.2122 \times H \qquad (1)$$

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).

$$1\ \text{MJ/kg} = 1000\ \text{J/g} \qquad (2)$$

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

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[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.

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:

$$W = (Q_b \times m + e_1)/\Delta t \qquad (3)$$

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]

$$1 + 10^{-6}[197\,(P - 3.04) + 42((m/V) - 3) + 30((M_w/V) - 3) - 45(t - 25)] \qquad (5)$$

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:

$$Q_{pst} = (\Delta t \times W - e_1)/a \qquad (6)$$

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.

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[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.

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:

$$V = (W \times 0.0032)/(Q \times D) \qquad (7)$$

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

$$V = (W \times 1.3)/(Q \times D) \qquad (8)$$

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 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:

$$\Delta t = t_f - t_i - r_1(b - a) - r_2(c - b) \tag{9}$$

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:

$$\Delta t = t_f - t_i \tag{10}$$

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.

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:

$$Q_g\ (\text{gross}\ t°\text{C}) = (\Delta t \times W - e_1 - e_2 - e_3 - e_4)/1000\ M \qquad Q_g\ (\text{gross, }25°\text{C}) = Q_g\ (\text{gross, }t°\text{C}) + A(t - 25) \tag{11}$$

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:

$$Q_n(\text{net, }25°\text{C}) = Q_g(\text{gross, }25°\text{C}) - 0.2122 \times H \tag{12}$$

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.

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		

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.

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

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[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.

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

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[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.

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.

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[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 × 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 (l) − $H_2SO_4 \cdot 650\ H_2O$ (l) 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.

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.

CERTIFICATE

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Standard Test Method for Heating Value of Gases in Natural Gas Range by Stoichiometric Combustion[1]

$^{\epsilon 1}$ 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

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[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.

Current edition approved Jan. 27, 1989. Published March 1989.

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

[3] *Annual Book of ASTM Standards*, Vol 14.02.

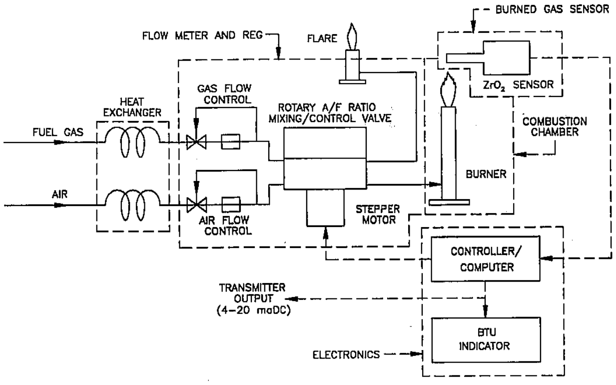

FIG. 1 Gas Btu Transmitter (Functional Overview)

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.

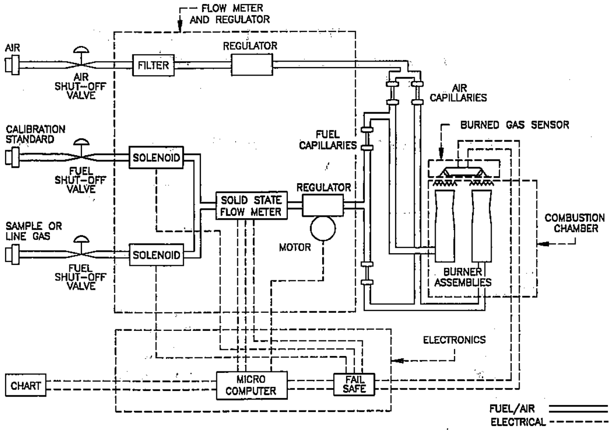

FIG. 2 Stoichiometric Combustion Apparatus

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 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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Designation: D 5257 – 97

Standard Test Method for Dissolved Hexavalent Chromium in Water by Ion Chromatography[1]

This standard is issued under the fixed designation D 5257; 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 procedures for the determination of dissolved hexavalent chromium in waste water, surface water, and drinking water.

1.2 The precision and bias of this test method has been tested in reagent water and industrial waste water and has been found suitable over the range of approximately 1 to 1000 µg/L. See Table 1 for details. Higher levels can be determined by appropriate dilution.

1.3 Samples containing very high levels of anionic species (that is, chloride, sulfate, etc.) may cause column overload. Samples containing high levels of reducing species (that is, sulfides, sulfites, etc.) may cause reduction of Cr(VI) to Cr(III). This can be minimized by buffering the sample to a pH of 9 to 9.5, filtering it, storing it at 4°C and analyzing it within 24 h.

1.4 The values stated in SI units are to be regarded as the standard.

1.5 *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 1066 Practice for Sampling Steam [2]
D 1129 Terminology Relating to Water[2]
D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits[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]
D3370 Practices for Sampling Water from Closed Conduits

2.2 *EPA Standard:*

EPA Method 218.6 Determination of Dissolved Hexavalent Chromium in Drinking Water, Groundwater and Industrial Wastewater Effluents by Ion Chromatography[3]

TABLE 1 Determination of Precision and Bias for Hexavalent Chromium

Water Matrix	Amount Added, µg/L	Amount Found, µg/L	S_t	S_o[A]	Bias, %
Reagent	1.2	1.40	0.16	0.15	+ 16.6
	1.6	1.87	0.65	...	+ 16.9
	6.0	6.68	1.03	0.53	+ 11.3
	8.0	8.64	1.10	...	+ 8.0
	16.0	17.4	2.25	0.77	+ 8.8
	20.0	21.4	2.31	...	+ 7.0
	100	101	1.91	3.76	+ 1.0
	140	143	5.52	...	+ 2.1
	800	819	24.3	12.7	+ 2.4
	960	966	18.5	...	+ 7.3
Waste	6.0	5.63	1.17	0.55	–6.2
	8.0	7.31	1.91	...	–8.6
	16.0	15.1	2.70	1.85	–5.6
	20.0	19.8	1.01	...	–1.0
	100	98.9	4.36	3.31	–1.1
	140	138	8.39	...	–1.4
	800	796	60.6	27.1	–0.5
	960	944	72.1	...	–1.7

[A] Each Youden pair was used to calculate one lab data point, S_o.

3. Terminology

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

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *eluant*— the ionic mobile phase used to transport the sample through the ion exchange column.

3.2.2 *resolution*—the ability of a column to separate constituents under specified test conditions.

4. Summary of Test Method

4.1 A fixed volume of buffered and filtered sample, typically 100 µL, is injected into the eluant flow path and separated by anion exchange using an ammonium sulfate based eluant.

4.2 After separation, the sample is reacted with an acidic solution of diphenylcarbohydrazide. Hexavalent chromium reacts selectively with this reagent to form the characteristic violet colored complex.

4.3 The eluant stream passes through a photometric detector

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[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.

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

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

for detection of the chromium diphenylcarbohydrazide complex by visible absorbance at 530 nm. Absorbance is proportional to the hexavalent chromium concentration.

5. Significance and Use

5.1 Hexavalent chromium salts are used extensively in the metal finishing and plating industries, in the leather industry as a tanning agent, and in the manufacture of paints, dyes, explosives, and ceramics. Trivalent chromium salts are used as mordants in textile dying, in the ceramic and glass industry, and in photography. Chromium, in either oxidation state, may be present in waste water from these industries and may also be discharged from chromate-treated cooling waters.

5.2 Hexavalent chromium is toxic to humans, animals, and aquatic life. It can produce lung tumors when inhaled and readily induces skin sensitization. It is not known whether cancer will result from ingestion of chromium in any of its valence states.

5.3 Ion chromatography provides a means of separating the hexavalent chromium from other species present in the sample, many of which interfere with other detection methods. The combination of this separation with a sensitive colorimetric detection method provides a selective and sensitive analytical method for hexavalent chromium with minimal sample preparation.

6. Interferences

6.1 By virtue of the chromatographic separation essentially all interfering species are removed from the hexavalent chromium before detection.

6.2 Interferences may result from overloading of the analytical column capacity with high concentrations of anionic species in the sample. Concentrations of chloride ion or sulfate ion up to the equivalent of 1 % NaCl and 3 % Na_2SO_4 do not affect the separation or detection when using an anion exchange column and a 100 µL sample loop.

6.3 The response of 1 mg/L of hexavalent chromium is not affected by 1 g/L of chromic ion.

6.4 Reducing species may reduce hexavalent chromium in acidic matrices. Preservation at a pH 9 to 9.5 will minimize the effect of these species.

6.5 Trace amounts of Cr are sometimes found in reagent grade salts. Since a concentrated buffer solution is used in this test method to adjust the pH of samples, reagent blanks should be analyzed to assess the potential for Cr(VI) contamination. Contamination can also come from improperly cleaned glassware or contact with caustic or acidic reagents with chromium containing stainless steel or pigmented materials.

7. Apparatus

7.1 *Ion Chromatograph*—An ion chromatograph having the following components configured as shown in Fig. 1.

7.1.1 *Pump*, capable of delivering a constant flow in the range of 1 to 5 mL/min at a pressure of 200 to 2000 psi.

7.1.2 *Injection Valve*— A high pressure, low dead volume valve that allows introduction of 50 to 250 µL of sample into the eluant stream at up to 2000 psi.

7.1.3 *Guard Column*— A column placed before the separator column to protect the separator column from fouling by particles or strongly absorbed organic constituents.

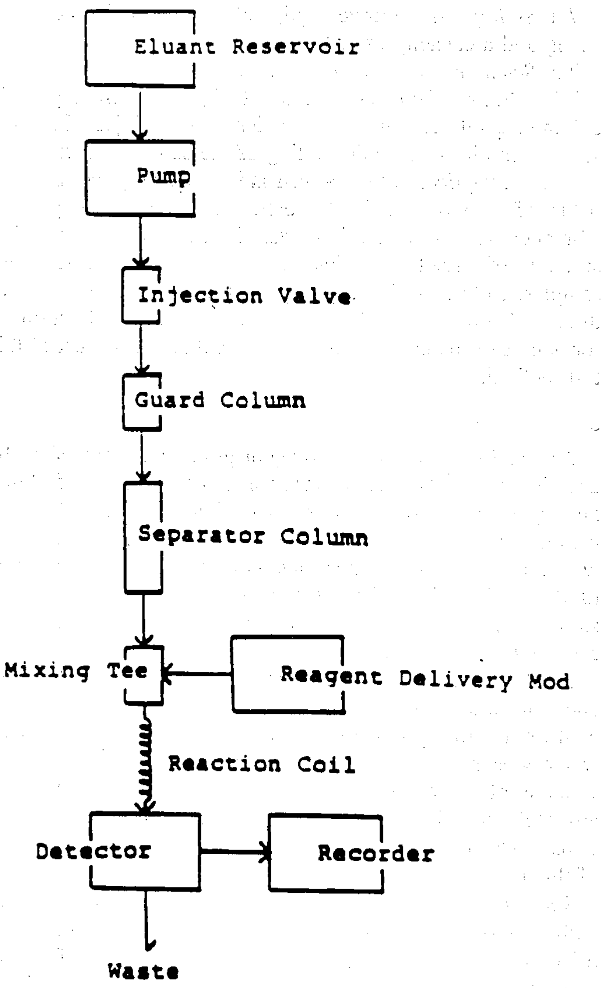

FIG. 1 Diagram of an Ion Chromatograph Using Post-Column Reagent Addition and Photometric Detection

7.1.4 *Analytical Column*—A liquid chromatographic column packed with a polymeric anion exchange resin capable of separating chromate from other anions in a sample containing high total dissolved solids (for example 3 % Na_2SO_4).

7.1.5 *Reagent Delivery Module*—A device capable of delivering 0 to 2 mL/min of reagent against a backpressure of up to 60 psi.

7.1.6 *Mixing Tee and Reaction Coil*—A device capable of mixing two flowing streams providing a sufficient reaction time for post column reaction with minimal band spreading.

7.1.7 *Detector*—A low-volume, flow-through UV-visible absorbance detector with a non-metallic flow path. The recommended detection wavelength for hexavalent chromium is 530 nm.

7.2 *Recorder, Integrator, Computer*—A device compatible with detector output, capable of recording detector response as a function of time for the purpose of measuring peak height or area.

7.3 *Eluant Reservoir*— A container suitable for storing eluant.

7.4 *Syringe*—A syringe equipped with a male luer type fitting and a capacity of at least 1 mL.

7.5 *Summary of Column Requirements*:

7.5.1 *Guard Column*— A short liquid chromatographic column capable of removing organics from the injected sample so as to minimize organic fouling of the separator column.

7.5.2 *Analytical Column*—An anion exchange column capable of providing suitable retention and chromatographic efficiency for chromate ion even in the presence of high amounts of dissolved solids that can occur in waste water samples. Note that high capacity columns will tolerate higher dissolved solids before becoming overloaded. See Section 13 for details of the columns used in the collaborative test of this test method.

8. Reagents

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 of the Committee on Analytical Reagents of the American Chemical 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. Other reagent water types may be used provided it is first ascertained that the water is of sufficiently high purity to permit its use without adversely affecting the bias and precision of the test method. Type II water was specified at the time of round robin testing of this test method.

8.3 *Chromium Solution, Stock* (1000 mg Cr/L)—Dissolve 0.2828 g of potassium dichromate ($K_2Cr_2O_7$ that has been dried at 105°C for 1 h) in water. Add 0.1 mL of eluant concentrate (8.6) to ensure analyte stability. Dilute to 100 mL in a volumetric flask.

8.4 *Chromium Solution, Standard* (1000 µg Cr/L)—Pipet 1.00 mL of chromium stock solution (see 8.3) and 1 mL of eluant concentrate into a 1 L volumetric flask. Dilute to volume with water.

8.5 *Reagent Blank*— Add 1 mL of eluant concentrate (8.6) to a 1 L flask and dilute to volume with the water used to prepare the chromium standards.

8.6 *Eluant Concentrate* (2.5 *M* $(NH_4)_2SO_4$, 1.0 *M* NH_4OH)—Dissolve 330 g of ammonium sulfate $(NH_4)_2SO_4$ in about 500 mL of water. Add 65 mL of concentrated ammonium hydroxide (NH_4OH to sp gr 0.90). Mix well and dilute to 1 L in a volumetric flask.

8.7 *Eluant*—Two different analytical anion exchange columns proved satisfactory in the collaborative test that is summarized in Section 13. Accordingly, the eluant appropriate for each column is described in 8.7.1 and 8.7.2. Eluants should be filtered through a 0.45-µm filter and degassed.

8.7.1 *Eluant for IonPac AS7 Column* (0.250 *M* $(NH_4)_2SO_4$, 0.1 *M* NH_4OH)—Add 100 mL of eluant concentrate (8.6) to a 1 L volumetric flask and dilute to volume with water.

8.7.2 *Eluant for IC Pac Anion HC Column* (0.025 *M* $(NH_4)_2SO_4$, 0.01 *M* NH_4OH)—Add 10 mL of eluant concentrate (8.6) to a 1 L volumetric flask and dilute to volume with water.

8.8 *Diphenylcarbohydrazide Reagent*—Dissolve 0.5 g of 1,5-diphenylcarbohydrazide in 100 mL of reagent grade methanol. Add to about 500 mL of water containing 28 mL of concentrated sulfuric acid. Dilute with water, while stirring, to 1 L in a volumetric flask. Filter and degas if necessary to ensure reliable delivery.

9. Sampling

9.1 Collect the sample in accordance with the applicable ASTM Standards as follows: Practice D 1066, Specification D 1192, or Practices D 3370.

9.2 Filter samples and adjust pH immediately upon sampling to minimize any interconversion between Cr III and Cr VI species. Filter the sample through a 0.45 µm filter. Collect the filtrate and adjust its pH to 9 to 9.5 using the eluant concentrate (see 8.6). Ship and store samples at 4°C. Bring to ambient temperature prior to analysis. Analyze this stabilized filtrate within 24 h. Adjust final calculations to account for sample dilution.

10. Calibration

10.1 Prepare at least three levels of standards for each decade of the concentration range of interest. For standards of 1 to 1000 µg/L, prepare by diluting measured volumes of the standard chromium solution (see 8.4) with water in separate volumetric flasks.

10.2 Determine the chromium response for each of the standards and blank using the procedure defined in Section 11.

10.3 Prepare a calibration curve by using a linear plot of the peak height or area as a function of standard concentration. Do not force the calibration curve through zero. The response of the reagent blank should be less than 0.1 µg/L hexavalent chromium.

10.4 Prepare a new calibration curve when new reagents are made or the hardware is altered.

11. Procedure

11.1 Set up the ion chromatograph in accordance with the manufacturer's instructions.

11.2 Adjust the eluant flow rate to 1.5 mL/min. Increase the flow of the post-column reagent until the flow rate from the detector outlet line is 2.0 mL/min. so as to have a reagent flow of 0.5 mL/min under operating conditions. Measure the pH of the detector effluent to confirm it is 2 or lower.

11.3 After the flow rates are adjusted, allow the system to equilibrate for about 15 min.

11.4 If using a fixed volume sample loop (typically 100 µL), load at least 1 mL of sample through the sample port using an appropriate syringe. Inject the sample into the eluant stream and record the chromatogram (see Fig. 2). If using a variable volume injector, inject the desired sample volume into the eluant stream and record the chromatogram.

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[4] "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 Chemicals," BDH Ltd., Poole, Dorset, U.K., and the "United States Pharmacopeia."

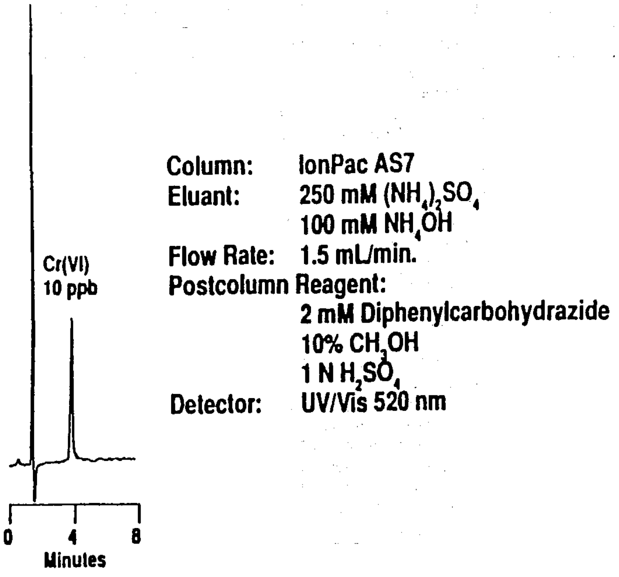

FIGURE 2 ION CHROMATOGRAPHIC DETERMINATION OF HEXAVALENT CHROMIUM

FIG. 2 Ion Chromatographic Determination of Hexavalent Chromium

12. Calculation

12.1 Refer the hexavalent chromium peak height or peak area to the calibration curve to determine the hexavalent chromium concentration of the injected sample in µg/L.

12.2 For samples that have been diluted, calculate the original hexavalent chromium concentration in µg/L by:

$$\mu g\ Cr(VI)/L = C \times F / V.$$

where:

C = µg Cr(VI)/L read from the calibration curve,
F = volume of diluted sample, in mL, and
V = volume of undiluted sample in mL.

13. Precision and Bias

13.1 The precision and bias data presented in this test method meet the requirements of Practice D 2777 (see Annex A1 for details).

13.2 The following separator columns were used in the collaborative test high capacity separator column[5] and low capacity separator column.[6]

13.3 The collaborative test of this test method was performed in reagent water and waste water by fifteen laboratories using one operator each. For reagent water the test used ten levels of concentration comprised of five Youden pairs ranging from 1.2 to 960 µg/L of hexavalent chromium. For waste water the test used eight levels of concentration comprised of four Youden pairs ranging from 6 to 960 µg/L of hexavalent chromium. The precision and bias data are presented in Table 1. See the Annex for a detailed description of the collaborative test.

13.4 The results of this collaborative test can also be summarized as follows:

Number of laboratories: 15
Range tested: 1.2 to 960 µg/L
Matrix: Reagent Water:
S_o = $0.033x + 0.106$
S_t = $0.050x + 0.559$
Mean Recovery = $1.04x + 0.183$
Matrix: Wastewater:
S_o = $0.041x + 0.039$
S_t = $0.059x + 1.05$
Mean Recovery = $0.989x + -0.41$

14. Keywords

14.1 analysis; hexavalent chromium; ion chromatography; wastewater; water

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[5] Model IonPac A57 column, available from Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94088, has been found suitable for this purpose.

[6] Model IC Pac Anion HC, available from Millipore Corporation (Waters Division), 34 Maple Street, Milford, MA 01757.

ANNEX

(Mandatory Information)

A1. DUPLICATION OF QUALITY CONTROL MEASURES

A1.1 The precision and bias data cited in this test method were the result of a collaborative test designed and executed jointly by ASTM Committee D-19 on Water and the U.S. EPA Environmental Monitoring and Support Laboratory (Cincinnati). Participants were required to use this method or EPA Method 218.6, or both. These two methods are technically equivalent. The eleven reagent water samples consisted of a reagent water blank and five Youden pairs. The nine wastewater samples consisted of a waste-water blank and four Youden pairs. The following is a duplication of the test instructions that included the quality control measures that were part of this test method:

A1.2 Preparation

A1.2.1 *Calibration Standard Preparation*:

A1.2.1.1 A standard concentrate (green label) has been furnished with this study to minimize calibration standard biases. The Cr(VI) concentration contained within the standard concentrate ampul and the study range are listed in Table A1.1.

A1.2.1.2 Prepare a calibration curve according to 9.1 of

TABLE A1.1 Standard Ampul Concentration and Study Range

Analyte	MDL, µg/L	STANDARD Ampul, µg/L	Study Range, µg/L
Cr(VI)	0.4	100,000	1–1000

EPA Method 218.6, revision 3.2 using a series of calibration standards prepared from the standard concentrate. The calibration curve must range from 1.0 µg/L to 1000 µg/L.

A1.2.2 *Matrix Blanks*:

A1.2.2.1 An analysis of each matrix water is required to determine potential background concentrations of Cr(VI). These blanks are referred to as *reagent water blank* and *wastewater blank*. The wastewater blank should be adjusted to pH 9.0 to 9.5 with the buffer solution (section 7.9, EPA Method 218.6) and passed through a 0.45 µm filter before analysis. Analyze a portion of the wastewater solution prepared in A1.2.4.2 as the blank.

A1.2.3 *Quality Control Sample Preparation*:

A1.2.3.1 Prepare the QC sample (laboratory fortified blank (LFB) as described in section 10.3.2, Method 218.6, revision 3.2) by pipetting a 1.0 mL aliquot from the QC sample concentrate ampul (blue label) and diluting to 100 mL with reagent water. The Cr(VI) concentration in the QC sample and the acceptance limits that are to be used for this study are presented in Table A1.2.

A1.2.4 *Sample Preparation*:

A1.2.4.1 *Reagent Water Samples*:

(a) Prepare the reagent water samples by transferring a 1.0 mL aliquot from each ampul labelled reagent water (yellow labels) to individual 100 mL volumetric flasks and dilute to volume with reagent water. These samples are now ready for analysis.

A1.2.4.2 *Wastewater Samples*:

(a) Collect at least 1 liter of a wastewater of your choice. Filter the wastewater matrix through a 0.45 µm filter then adjust the pH of the filtrate to 9.0 to 9.5 by adding dropwise a solution of the buffer (8.2, EPA Method 218.6). Prepare the individual wastewater samples by transferring a 1.0 mL aliquot from each ampul labelled wastewater (orange labels) to individual 100 mL volumetric flasks and dilute to volume with the pH adjusted wastewater. These samples are now ready for analysis. The wastewater matrix is not to be diluted prior to spiking regardless of the Cr(VI) background concentration.

A1.3 Sample Analyses

A1.3.1 Analyze each prepared sample in the order defined in Table A1.3. The sample names and numbers in Table A1.3 are the same as those on the data report forms. Be certain that the sample data is entered under the correct sample name.

TABLE A1.2 Quality Control Sample Acceptance Limits

Analyte	True Value (T.V.) µg/L	Acceptance Limits [A] µg/L
Cr(VI)	40.0	36–44

[A] Defined as T.V. ± 10 %.

TABLE A1.3 EPA Method Study 218.6 Injection Order

Sample Name and Sample Order
QC Sample
Reagent Water Blank
Reagent Water—Sample #1
Reagent Water—Sample #2
Reagent Water—Sample #3
Reagent Water—Sample #4
Reagent Water—Sample #5
Reagent Water—Sample #6
Reagent Water—Sample #7
Reagent Water—Sample #8
Reagent Water—Sample #9
Reagent Water—Sample #10
QC Sample
Wastewater Blank
Wastewater—Sample #11
Wastewater—Sample #12
Wastewater—Sample #13
Wastewater—Sample #14
Wastewater—Sample #15
Wastewater—Sample #16
Wastewater—Sample #17
Wastewater—Sample #18
QC Sample

A1.4 Quality Control (QC)

A1.4.1 The QC sample is used to perform regular checks on the calibration curve. Only one QC sample need be prepared. However, three analyses of this QC sample will be required; one immediately following the last calibration standard, another immediately following the reagent water sample series, and the third immediately following the wastewater sample series. If the Cr(VI) concentration in the QC sample falls outside of the acceptance limits found in Table A1.2, the analyst should reanalyze the QC sample. If the Cr(VI) concentration falls within the acceptance limits, continue with the sample analyses. If the Cr(VI) concentration is still outside of the acceptance limits, a new calibration curve is required and must be confirmed by a successful QC analysis before sample analyses can continue.

A1.5 Data Report Forms

A1.5.1 Analytical values reported on the data report forms must not be corrected for matrix background concentrations. Report measured concentrations of Cr(VI) as µg/L to three significant figures (that is, 2.35, 23.5, or 235).

A1.6 Questionnaire

A1.6.1 Operate your ion chromatograph according to manufacturer specifications and recommendations found in EPA Method 218.6 (revision 3.2) and the equivalent Test Method D 5257. A questionnaire is enclosed to record your specific operating conditions and equipment type.