EXHIBIT 150
PART 7

CERTIFICATE

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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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THE EXECUTIVE DIRECTOR
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Designation: D 1890 – 96

Standard Test Method for Beta Particle Radioactivity of Water[1]

This standard is issued under the fixed designation D 1890; 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 measurement of beta particle activity of water, as referenced to the beta energy of ^{137}Cs, not corrected for conversion electrons. It is applicable to beta emitters having maximum energies above 0.1 MeV and at activity levels above 0.02 Bq/mL of radioactive homogeneous water for most counting systems. This test method is not applicable to samples containing radionuclides that are volatile under conditions of the analysis.

1.2 This test method can be used for either absolute or relative determinations. In tracer work, the results may be expressed by comparison with a standard which is defined to be 100 %. For radioassay, data may be expressed in terms of a known radionuclide standard if the radionuclides of concern are known and no fractionation occurred during processing, or may be expressed arbitrarily in terms of some other standard such as cesium-137. General information on radioactivity and measurement of radiation may be found in the literature [2] and Practice D 3648.

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[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 3648 Practice for the Measurement of Radioactivity[4]

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *Becquerel*—a unit of radioactivity equivalent to 1 nuclear transformation per second.

3.1.2 *beta energy, maximum*—the maximum energy of the beta-particle energy spectrum produced during beta decay of a given radioactive species.

NOTE 1—Since a given beta-particle emitter may decay to several different quantum states of the product nucleus, more than one maximum energy may be listed for a given radioactive species.

3.1.3 *counter background—in the measurement of radioactivity*, the counting rate resulting from factors other than the radioactivity of the sample and reagents used.

NOTE 2—Counter background varies with the location, shielding of the detector, and the electronics; it includes cosmic rays, contaminating radioactivity and electrical noise.

3.1.4 *counter beta-particle efficiency—in the measurement of radioactivity*, that fraction of beta particles emitted by a source which is detected by the counter.

3.1.5 *counter efficiency—in the measurement of radioactivity*, that fraction of the disintegrations occurring in a source which is detected by the counter.

3.1.6 *radioactive homogeneous water*—water in which the radioactive material is uniformly dispersed throughout the volume of water sample and remains so until the measurement is completed or until the sample is evaporated or precipitating reagents are added to the sample.

3.1.7 *reagent background—in the measurement of radioactivity of water samples*, the counting rate observed when a sample is replaced by mock sample salts or by reagent chemicals used for chemical separations that contain no analyte.

NOTE 3—Reagent background varies with the reagent chemicals and analytical methods used and may vary with reagents from different

[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] Friedlander, G., et al., *Nuclear and Radiochemistry*, 3rd Ed., John Wiley and Sons, Inc., New York, NY, 1981.

Price, W. J., *Nuclear Radiation Detection*, 2nd Ed., McGraw-Hill Book Co., Inc., New York, NY, 1964.

Lapp, R. E., and Andrews, H. L., *Nuclear Radiation Physics*, 4th Ed., Prentice-Hall Inc., New York, NY, 1972.

Overman, R. T., and Clark, H. M., *Radioisotope Techniques*, McGraw-Hill Book Co., Inc., New York, NY, 1960.

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

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

manufacturers and from different processing lots.

3.2 *Definitions*—For terms not defined in this test method or in Terminology D 1129, reference may be made to other published glossaries.[5]

4. Summary of Test Method

4.1 Beta radioactivity may be measured by one of several types of instruments composed of a detecting device and combined amplifier, power supply, and scaler—the most widely used being proportional or Geiger-Müller counters. Where a wide range of counting rates is encountered (0.1 to 1300 counts per seconds), the proportional-type counter is preferable due to a shorter resolving time and greater stability of the instrument. The test sample is reduced to the minimum weight of solid material having measurable beta activity by precipitation, ion exchange resin, or evaporation techniques. Beta particles entering the sensitive region of the detector produce ionization of the counting gas. The negative ion of the original ion pair is accelerated towards the anode, producing additional ionization of the counting gas and developing a voltage pulse at the anode. By use of suitable electronic apparatus, the pulse is amplified to a voltage sufficient for operation of the counter scaler. The number of pulses per unit of time is related to the disintegration rate of the test sample. The beta-particle efficiency of the system can be determined by use of prepared standards having the same radionuclide composition as the test specimen and equivalent residual plated solids. An arbitrary efficiency factor can be defined in terms of some other standard such as cesium-137.

5. Significance and Use

5.1 This test method was developed for the purpose of measuring the gross beta radioactivity in water. It is used for the analysis of both process and environmental water to determine gross beta activity.

6. Measurement Variables

6.1 The relatively high absorption of beta particles in the sample media and any material interposed between source and sensitive volume of the counter results in an interplay of many variables which affect the counting rate of the measurement. Thus, for reliable relative measurements, hold all variables constant while counting all test samples and standards. For absolute measurements, appropriate correction factors are applied. The effects of geometry, backscatter radiation, source diameter, self-scatter and self-absorption, absorption in air and detector window for external counters, and counting coincidence losses have been discussed[2] and may be described by the following relation:

$$cps = Bq_b (G_p)(f_{bs})(f_{aw})(f_d)(f_{ssa})(f_c) \quad (1)$$

where:

cps = recorded counts per second corrected for background,

Bq_b = disintegrations per second yielding beta particles,

G_p = point source geometry (defined by the solid angle subtended by the sensitive area of the detector),

f_{bs} = backscatter factor or ratio of *cps* with backing to *cps* without backing,

f_{aw} = factor to correct for losses due to absorption in the air and window of external detectors. It is equal to the ratio of the actual counting rate to that which would be obtained if there were no absorption by the air and window between the source and sensitive volume of the detector. Expressed in terms of absorption coefficient and density of absorber, $f_{aw} = e^{-\mu x}$, where μ = absorption coefficient, in square centimetres per milligram, and x = absorber density in milligrams per square centimetre.

f_d = factor to correct a spread source counting rate to the counting rate of the same activity as a point source on the same axis of the system,

f_{ssa} = factor to correct for the absorption and scatter of beta particles within the material accompanying the radioactive element, and

f_c = factor for coincident events to correct the counting rate for instrument resolving time losses and defined by the simplified equation, $f_c = 1 - nr$, where, n = the observed counts per second, and r = instrument resolving time in seconds. Generally, the sample size or source to detector distance is varied to obtain a counting rate that precludes coincident losses. Information on the effect of random disintegration and instrument resolving time on the sample count rate as well as methods for determining the resolving time of the counting system may be found in the literature.

For most applications, a detector system is calibrated using a single beta emitting radionuclide and an efficiency of detection, f_o, response curve generated for various sample residue weights. The efficiency of detection for each sample residual weight incorporates all the factors mentioned above so that:

$$f_o = cps/Bq = (G_p)(f_{bs})(f_{aw})(f_d)(f_{ssa})(f_c) \quad (2)$$

6.1.1 In tracer studies or tests requiring only relative measurements in which the data are expressed as being equivalent to a defined standard, the above correction factors can be simply combined into a counting efficiency factor. The use of a counting efficiency factor requires that sample mounting, density of mounting dish, weight of residue in milligrams per square centimetre, and radionuclide composition, in addition to conditions affecting the above described factors, remain constant throughout the duration of the test and that the comparative standard be prepared for counting in the same manner as the test samples. The data from comparative studies between independent laboratories, when not expressed in absolute units, are more meaningful when expressed as percentage relationships or as the equivalent of a defined standard. Expressing the data in either of these two ways minimizes the differences in counters and other equipment and in techniques used by the laboratories conducting the tests.

6.2 The limit of sensitivity for both Geiger-Muller and proportional counters is a function of the background counting rate. Massive shielding or anti-coincidence detectors and

[5] American National Standard Glossary of Terms in Nuclear Science and Technology (ANSI N1.1).

circuitry, or both, are generally used to reduce the background counting rate to increase the sensitivity.

7. Interferences

7.1 Material interposed between the test sample and the instrument detector, as well as increasing density in the sample containing the beta emitter, produces significant losses in sample counting rates. Liquid samples are evaporated to dryness in dishes that allow the sample to be counted directly by the detector. Since the absorption of beta particles in the sample solids increases with increasing density and varies inversely with the maximum beta energy, plated solids shall remain constant between related test samples and should duplicate the density of the solids of the plated standard.

7.2 Most beta radiation counters are sensitive to alpha, gamma, and X-ray radiations, with the degree of efficiency dependent upon the type of detector.[2] The effect of interfering radiations on the beta counting rate is more easily evaluated with external-type counters where appropriate absorbers can be used to evaluate the effects of interfering radiation.

8. Apparatus

8.1 *Beta Particle Counter*, consisting of the following components:

8.1.1 *Detector*—The end-window Geiger-Muller tube and the internal or external sample gas-flow proportional chambers are the two most prevalent commercially available detector types. The material used in the construction of the detector should be free from detectable radioactivity. When detectors contain windows, the manufacturer shall supply the window density expressed in milligrams per square centimetre. To establish freedom from undesirable characteristics, the manufacturer shall supply voltage plateau and background counting rate data. Voltage plateau data shall show the threshold voltage, slope, and length of plateau. Detectors requiring external positioning of the test sample are mounted on a tube support of low-density material (aluminum or plastic) and positioned so the center of the window is directly above the center of the test sample. The distance between the detector window and test sample plays an important part in determining the geometry of the system and can be varied for external counters to correspond more favorably with such factors as activity level, source size, sensitivity requirements, energy of beta particles, etc. A convenient arrangement is to combine the tube mount with a sample holder containing slots for positioning the sample at three or four distances from the detector window, varying from approximately 5 to 100 mm from tube flange.

8.1.2 *Detector Shield*—The detector assembly is surrounded by an external radiation shield of massive metal equivalent to approximately 51 mm of lead and lined with 3.2-mm thick aluminum. The material of construction should be free from detectable radioactivity. The shield has a door or port for inserting or removing specimens. Detectors having other than completely opaque windows are light sensitive. The design of the shield and its openings shall eliminate direct light paths to the detector window; beveling of door and opening is generally satisfactory. The percentage of the beta particles scattered from the walls of the shield into the detector can be reduced by increasing the internal diameter of the shield. The use of a detector without a shield will significantly increase the background and the detection capability.

8.1.3 *Scaler*—Normally the scaler, mechanical register, power supply, and amplifier are contained in a single chassis, generally termed the scaler. The power supply and amplifier sections are matched by the manufacturer with the type of detector to produce satisfactory operating characteristics and to provide sufficient range in adjustments to maintain controlled conditions. The manufacturer shall provide resolving time information for the counting system. The scaler shall have capacity for storing and visually displaying at least 10^6 counts and with a resolving time no greater than 250μ s for use with Geiger Muller detectors or 5 μs for use with proportional detectors. The instrument shall have an adjustable input sensitivity matched and set by the manufacturer to that of the detector, and a variable high-voltage power supply with indicating meter.

8.2 *Sample Mounting*—Sample mounting shall utilize dishes having a flat bottom of a diameter no greater than that of the detector window preferably having 3.2-mm high side walls with the angle between dish bottom and side equal to or greater than 120° to reduce side-wall scattering (Note 4). Dishes shall be of a material that will not corrode under the plating conditions and should be of uniform surface density preferably great enough to reach backscatter saturation. [2]

NOTE 4—Sample dishes with vertical side walls may be used but the exact positioning of these dishes relative to the detector is very important. This factor becomes critical for dishes having the same diameter as the detector. Dishes having side walls more than 3.2 mm in height are not recommended. Stainless steel has been found to be satisfactory for this purpose.

8.3 *Alpha Particle Absorber*—Aluminum or plastic, having a uniform density such that total absorbing medium (air plus window plus absorber) between sample and sensitive volume of detector is approximately equal to 7 mg/cm ^{2} of aluminum. The absorber diameter shall be equal to or greater than the detector window and should be placed against the window to minimize scattering of the beta particles by the absorber. This absorber is not used when counting beta particles with maximum energies below 0.35 MeV due to the high-count rate loss by absorption (about 48 % at 0.35 MeV in 7 mg/cm ^{2}, of aluminum). The alpha particle absorber is not recommended for use with internal beta particle detectors, especially when either the composition or activity ratios of the radionuclides or radioactivity level might vary significantly between samples. Chemical separation of the alpha and beta particle emitters produces a higher degree of accuracy for internal detector measurements. Use published information [2] on beta particle absorption as a guide.

9. Reagents

9.1 *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 increasing the background of the measurement.

NOTE 5—Some chemicals, even of high purity, contain naturally occurring radioactive elements, for example, rare earths and potassium compounds. Also, some chemical reagents, including organic compounds, have been found to be contaminated with artificially produced radionuclides. Consequently, when carrier chemicals are used in the analysis of low-radioactivity samples, the radioactivity of the carriers shall be determined under identical analytical conditions as used for the sample, including amounts of residual solids in the dish. The radioactivity of the reagents may be considered as background and subtracted from the test sample counting rate. This increased background reduces the sensitivity of the measurement.

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

9.3 *Cesium-137 Solution*—A ^{137}Cs solution containing approximately 200 Bq/mL with a calibration that is traceable to National Institute of Standards and Technology (NIST).

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

10. Sampling

10.1 Collect the sample in accordance with Practices D 3370.

10.2 Preserve the sample in a radioactively homogeneous state.

NOTE 6—A sample may be made homogeneous by addition of a reagent in which the radionuclides or compounds of the radionuclides present in the sample would be soluble in large concentrations. Addition of acids, complexing agents, or chemically similar stable carriers may be used to obtain homogeneity. Consideration of the chemical nature of the radionuclides and compounds present and the subsequent chemistry of the method will indicate the action to be taken. The addition of chemicals (HCl) corrosive to the mounting dish shall be avoided to prevent increased absorption of beta particles by the increased residual solids.

11. Establishing Gas Proportional Counter Operating Plateau

11.1 Put the instrument into operation according to the manufacturer's instructions. Place the counter's quality control standard (Note 7) having an approximate disintegration rate of 170 Bq in the counting position closest to the detector and begin counting. Slowly increase the high voltage until the first counts are observed and record the" threshold" voltage. Raise the voltage 20 to 25 V (or some other convenient unit) above threshold, stop counting, reset the scaler to zero, and determine the count rate. Advance the voltage in small equal increments of 20 or 25 V, determining the count rate at each voltage. The count rate should rise initially, reach an approximately constant value (plateau), and then increase rapidly at the end of the plateau. The operating time at voltages above the plateau shall be minimized to avoid extensive arcing of the detector. If the plateau is 150 V in length, additional measurements are not necessary. Some newer computer controlled gas proportional counters (commercially available) have software that automatically measures the detector plateau through the use of an algorithm that controls the high voltage and scaler units of the system.

NOTE 7—The counter's quality control standard may be any available radionuclide having a high percentage of beta particle emission, a half-life sufficiently long to minimize decay corrections, and a maximum beta particle energy above 0.5 MeV. Knowledge of its true beta disintegration rate is not essential. The radionuclide shall be fixed permanently to the dish and distributed uniformly over an area preferably smaller than the dish bottom; electrodeposition and flaming of a salt-free solution are the two methods most generally used. The standard may be covered by thin aluminum or plastic of sufficient thickness to exclude any alpha particles originating from the source and to protect against damage. The dish shall be securely mounted for reproducible positioning. Any loss of activity in the control standard, other than by natural decay, requires establishment of a new control chart (see Section 12). For external counters, the ratio of control standard source diameter to detector window diameter should not exceed 0.33 to avoid the effect of a spread source on the counting geometry.

11.2 Plot the counting rate of the control standard against the indicated voltage. The voltage setting that corresponds to a value approximately 75 V above the "knee" of the curve shall be used as the operating voltage, provided this voltage is 50 V below the highest voltage on the plateau; otherwise the operating voltage shall be that at approximately the mid-point of the plateau (Note 8). A plateau slope of less than 3 %/100 V is desirable, but slopes between 3 and 6 %/100 V can be tolerated if a stable power supply is used. Refer to Practice D 3648 for additional details relative to operating voltage plateaus for gas proportional counters. Check the voltage plateau and operating voltage of the instrument on a regular schedule determined by experience and after any repair or major adjustment of the instrument. Shortening of the plateau length or an increase in slope are indications of a deteriorating detector.

NOTE 8—The counting life of the detector may be shortened by operation at a voltage higher than required for reliable performance. Consequently, the lowest voltage that meets the above conditions and will provide reproducible data should be chosen as the operating voltage.

12. Control of Instrument Operation

12.1 Tolerance or statistical control charts are used to assure that the instrument is operating to within pre-specified limits of the initial calibration. Repetitive measurements of a quality control source are taken to develop the tolerance or statistical control chart. The QC source is then used on a daily or prior to use basis to ensure proper operation. Refer to Practice D 3648 for the preparation of a tolerance or statistical control chart.

13. Calibration and Standardization for General Measurements

13.1 Place a known amount of cesium-137 standard (approximately 200 Bq) into a volume of water having a dissolved salts content equivalent to those of the test samples and prepare for counting as directed in Section 15. Throughout the experiment, the evaporation, mounting, counting, and density of plate

[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.

solids of this reference standard shall be identical with those of the test samples. Count for a length of time required to produce the desired statistical precision (typically 1 %; refer to Practice D 3648). The combined efficiency factor, f_o, for each dissolved salt weight is then expressed as a fraction of the disintegration rate, Bq, of the reference standard according to Eq. 2.

14. Calibration and Standardization for Tracer Experiments

14.1 Add a known quantity of activity of a reference solution of the tracer (approximately 200 Bq) to a radioactivity-free standard test sample and process in accordance with Section 15.

15. Procedure

15.1 Place an appropriate volume of the test specimen in a glass beaker, make 0.5 *M* with HNO_3, and evaporate to 1 to 2 mL. Quantitatively transfer to the mounting dish and evaporate to dryness. Adjust the heat carefully to prevent spattering or boiling. A ring heater having a continuously variable voltage control, or adjustable infrared heat lamps, is the preferable heat source for the final evaporation and drying. Uniform spreading of the residual salts is necessary for reliable comparative data. The salts shall be thoroughly mixed to assure uniform and homogeneous distribution of the radioactive nuclides in the deposit. Inhomogeneity may result in poor reproducibility. Cool hygroscopic solids in a dry atmosphere and store in a desiccator until the start of counting. Place the sample in the counter and count for a time interval sufficient to obtain the desired statistical uncertainty. Record the scaler reading. Transfer of large volume samples to smaller beakers as evaporation nears completion makes for easier transfer of the test specimen to the mounting dish. All transfers shall be made with reagent water. The sample size shall be chosen with consideration for the absorption of beta particles in the residual solids. Information[2] on the range energy relationship of beta particles in aluminum should be used as a guide to obtain the desired results.

15.2 Precipitation methods may be used to expediently concentrate the radioactive material into small amounts of precipitate. The precipitate is separated and washed free of precipitant by centrifugation or filtration. Choose the method of separation that will produce a uniform deposit of precipitate after quantitatively transferring to the mounting dish or filter paper for counting. Calibrate the instrument under counting conditions identical to those used for the samples. More detailed information on the techniques and equipment for separation and mounting of the precipitate may be found in the literature.[2]

16. Calculation

16.1 Results may be expressed in observed counts per second per millilitre or Bq/mL. This test method is useful for comparing activities of a group of samples, as in tracer experiments. Results may also be reported in terms of equivalent cesium-137 activity or other standard radionuclide activity, using the empirical efficiency determined by use of a reference standard. If it is known that only one nuclide is present, its disintegration rate may be determined by use of the efficiency factor determined from a reference standard of that nuclide obtained from the National Institute of Standards and Technology (NIST) or from a NIST-traceable standard. Calculate the results as follows:

$$beta\ concentration\ (Bq/mL) = C_{net} / (f_o \times V) \quad (3)$$

where:

C_{net} = net count rate (s^{-1}),
V = test specimen, mL, and
f_o = detector efficiency factor.

The total propagated uncertainty of the beta concentration is calculated as:

$$\sigma_{Bq/mL} = Bq/mL \times [(\sigma_{C_{net}} / C_{net})^2 + (\sigma_{fo}/f_o)^2 + (\sigma_V / V)^2]^{1/2} \quad (4)$$

where:

$\sigma_{C_{net}}/C_{net}$ = relative counting uncertainty,
σ_{fo}/f_o = relative detector efficiency uncertainty, and
σ_V/V = relative uncertainty in the sample volume measurement.

The net count rate and counting uncertainty, $\sigma_{C_{net}}$, are defined as:

$$C_{net} = CR_S - CR_B = C_s / t_s - C_B / t_B \quad (5)$$

$$\sigma_{C_{net}} = (C_s / t_s^2 + C_B / t_B^2)2½ \quad (6)$$

where:

CR_s = sample count rate (s^{-1}),
CR_B = background count rate (s^{-1}),
C_s = sample counts,
C_B = background counts,
t_s = counting time of sample(s), and
t_B = counting time of background(s).

The *a priori* minimum detectable concentration (*MDC*) is calculated using the equation:

$$MDC = 2.71/(t_s \times k) + 4.65 \times \sigma_B / k \quad (7)$$

where:

σ_B = $(CR_B/t_s)^{½}$, and
k = $f_o \times V$.

A more detailed discussion on the minimum detectable concentration concept can be found in Practice D 3648.

17. Precision and Bias

17.1 The overall precision and bias of this test method within its designated range varies with the quantity being tested according to Table 1.

17.2 This collaborative test for the determination of gross beta activity in water was conducted by six laboratories at three concentration levels ranging from 4.6 to 46.5 Bq/mL and containing 8 mg, 19.5 mg, and 40 mg of solids, respectively. Each laboratory processed three replicates per level.

TABLE 1 Determination of Precision and Bias

Amount Added, Bq/mL	Average Calculated Amount, Bq/mL	± Bias	± % Bias	Statistically Significant (5 % C.I.)	Precision	
					S_t	S_o
4.60 ± 0.12	4.6 ± 1.0	s0.0	0.0	No	0.997	0.288
18.55 ± 0.50	20.0 ± 1.0	+1.5	+7.8	Yes	1.04	0.617
46.5 ± 1.2	50.6 ± 2.6	+4.1	+8.8	Yes	2.63	1.50

17.3 The precision and bias statements for this test method were obtained using Practice D 2777 – 86.

17.4 These test data were obtained using select water matrices. For other matrices these data may not apply.

18. Quality Control

18.1 Before this test method is utilized for the analysis of samples, a counter quality control or tolerance chart shall be established to ensure that the counting system is operating within prescribed limits. The quality control or tolerance chart shall be established at the time the counting system is calibrated.

18.2 Prepare a quality control or tolerance chart as recommended in Practice D 3648. The counting system shall be checked by analyzing a QC source daily or prior to use. The result of the QC analysis shall be tabulated or plotted on the control or tolerance chart and evaluated according to Practice D 3648.

18.3 Evaluate the counting system's background periodically. The background data shall be maintained in a logbook or plotted on a trend chart.

18.4 Precision and bias can be assessed in the following manner: the precision of an individual measurement can be approximated by the total propagated uncertainty and bias can be assessed by the analysis of NIST traceable spiked samples with known quantities of radioactivity.

19. Keywords

19.1 gross beta radioactivity; gross radioactivity measurement; proportional counter; water

CERTIFICATE

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

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Standard Test Method for Alpha Particle Radioactivity of Water[1]

This standard is issued under the fixed designation D 1943; 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 measurement of alpha particle activity of water. It is applicable to alpha emitters having maximum energies above 3.9 MeV and at activity levels above 0.02 Bq/mL of radioactive homogeneous water. This test method is not applicable to samples containing alpha-emitting radionuclides that are volatile under conditions of the analysis.

1.2 This test method can be used for either absolute or relative determinations. In tracer work, the results may be expressed by comparison with a standard that is defined to be 100 %. For radioassay, data may be expressed in terms of alpha disintegration rates after calibration with a suitable standard. General information on radioactivity and measurement of radiation has been published[2] and summarized in Practice D 3648.

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[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[3]

D 3648 Practice for the Measurement of Radioactivity[4]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D 1129. For terms not defined in this test method or in Terminology D 1129, reference may be made to other published glossaries.[5]

4. Summary of Test Method

4.1 The test sample is reduced by evaporation or a suitable chemical method to the minimum weight of material having measurable alpha activity. Alpha radioactivity is measured by an instrument composed of a detecting device, amplifier, power supply, and scaler—the most widely used being proportional and scintillation counters. In the proportional counter, which may be of the windowless or thin window type, alpha particles entering the sensitive region of the detector produce ionization of the counting gas. The negative ion of the original ion pair is accelerated towards the anode, producing additional ionization of the counting gas and developing a voltage pulse at the anode. In the scintillation detector, alpha particles interact with the material of the phosphor, transferring some of their energy to electrons. These electrons subsequently lose part of their energy by excitation rather than ionization of atoms, and the excited atoms revert to the ground state by re-emitting energy in the form of light quanta. A suitable light-sensitive device, usually a multiplier phototube, transforms the resulting flashes of light into voltage impulses. By use of suitable electronic apparatus, the pulse is amplified to a voltage sufficient for operation of the counting scaler. The number of pulses per unit time is related to the disintegration rate of the test sample. The efficiency of the system can be determined by use of a suitable alpha standard having equivalent residual plated solids.

5. Significance and Use

5.1 This test method was developed for the purpose of measuring gross alpha radioactivity in water. It is used for the analysis of both process and environmental water to determine

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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] Friedlander, G., et al., *Nuclear and Radiochemistry*, 3rd Ed., John Wiley and Sons, Inc., New York, NY, 1981.

Price, W. J., *Nuclear Radiation Detection*, 2nd Ed., McGraw-Hill Book Co., Inc., New York, NY, 1964.

Lapp, R. E., and Andrews, H. L., *Nuclear Radiation Physics*, 4th Ed., Prentice-Hall Inc., New York, NY, 1972.

Overman, R. T., and Clark, H. M., *Radioisotope Techniques*, McGraw-Hill Book Co., Inc., New York, NY, 1960.

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

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

[5] American National Standard Glossary of Terms in Nuclear Science and Technology (ANSI N1.1) available from the American National Standards Institute, 1430 Broadway, New York, NY 10018.

gross alpha activity which is often a result of natural radioactivity present in minerals.

6. Measurement Variables

6.1 The relatively high absorption of alpha particles in the sample media affects the counting rate of the measurement. Effects of geometry, back-scatter, source diameter, as well as the purity, pressure variation, and type of counting gas used shall also be considered. Thus, for reliable relative measurements, the variables shall be held constant while counting all test samples and standards. For absolute measurements, appropriate efficiency factors shall be applied. If a windowless proportional counter is employed, the sample mount shall be electrically conducting.

6.1.1 In tracer studies or tests requiring only relative measurements, in which the data are expressed as being equivalent to a defined standard, the above correction factors can be simply combined into a counting efficiency factor. The use of a counting efficiency factor requires that sample mounting, material of mounting dish, and weight of residue (milligrams per square centimetre), in addition to conditions affecting the above described factors, remain constant throughout the duration of the test and that the comparative standard be prepared for counting in the same manner as the test samples. The data from comparative studies between independent laboratories when not expressed in absolute units are more meaningful when expressed as percentage relationships or as equivalent of a defined standard.

6.2 The limit of sensitivity for both scintillation and proportional counters is a function of the background counting rate which should be as low as is feasible. Massive shielding is not used for alpha counters. The maximum activity for this test method is 1600 Bq.

7. Interferences

7.1 Solids content in the sample containing the alpha emitter produces significant losses in sample counting rates of about 10 to 15 % loss at 1 mg/cm^2. Liquid samples shall be evaporated to dryness onto dishes that allow the sample to be counted directly by the detector. Solids on the dish shall remain constant in amount between related test samples, and should duplicate the density of the solids of the plated standard.

7.2 Most alpha counters are insensitive to beta, gamma, and X radiations.[2]

8. Apparatus

8.1 *Alpha Particle Counter*, consisting of either a proportional detector or a scintillation detector, and a scaler conforming to the following requirements:

8.1.1 *Proportional Detector*—This may be one of several types commercially available. The material used in the construction of the detector should contain a minimal amount of detectable radioactivity. To establish freedom from undesirable characteristics, the manufacturer shall supply voltage plateau and background counting rate data. Voltage plateau data shall show the threshold voltage, slope, and length of plateau for a particular input sensitivity.

8.1.2 *Scintillation Detector*—This may be one of several types commercially available. It shall consist of an "activated" zinc sulfide phosphor having a minimum effective diameter of 36.5 mm and a superficial density of 10 to 15 mg/cm^2. The phosphor shall be mounted so that it can be attached and optically coupled to a multiplier phototube. Extraneous light shall be excluded from the phosphor either by its being covered with a thin (less than 1 mg/cm^2) opaque window or by enclosing the assembly in a lightproof sample changer. The material used in the construction of the detector shall be free from detectable radioactivity. To establish freedom from undesirable characteristics, the manufacturer shall supply voltage plateau and background counting rate data. Voltage plateau data shall show the threshold voltage, slope, and length of a plateau for a specified scaler sensitivity.

8.1.3 *Scaler*—Often the scaler, mechanical register, power supply, and amplifier are contained in a single chassis, generally termed the scaler. The power supply and amplifier sections shall be matched with the type of detector to produce satisfactory operating characteristics and to provide sufficient range in adjustments to maintain controlled conditions. The manufacturer shall provide resolving time information for the counting system. The scaler shall have capacity for storing and visually displaying at least 10^6 counts with a resolving time no greater than 5 μs. The instrument shall have an adjustable input sensitivity that can be matched to the detector and a variable high voltage power supply with indicating meter.

8.2 *Sample Mounting Dish*—Dishes having a flat bottom of a diameter slightly less than the inside diameter of the detector. Flat dishes are preferred, but dishes may be used that have 3.2-mm high side walls with the angle between dish bottom and side equal to or greater than 120°. Dishes shall be of a material that will not corrode under the plating conditions and shall be of uniform surface density; platinum and stainless steel have been used for this purpose.

9. Reagents

9.1 *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 and free from radioactivity to preclude detrimental effects. Some chemicals, even of high purity, contain naturally occurring radioactive elements, for example, uranium, actinium, and thorium. Consequently, when carrier chemicals are used in the analysis of low-radioactivity samples, the radioactivity of the carriers shall be determined under identical analytical conditions of the sample including residual dish solids. The radioactivity of the reagents shall be considered as background and subtracted from the test sample counting rate.

9.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming

[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.

to Specification D 1193, Type HI.

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

9.4 *Nitric Acid* (1 + 30)—Mix 1 volume of concentrated HNO_3(sp gr 1.42) with 30 volumes of water.

9.5 *Alpha-Emitting Radioactive Standard Solution* (~200 Bq/mL), traceable to the National Institute of Standards and Technology (NIST).

10. Sampling

10.1 Collect the sample in accordance with Practices D 3370.

10.2 Preserve the sample in a radioactive homogeneous state. A sample shall be made radioactive homogeneous by addition of a reagent in which the radionuclides or compounds of the radionuclides present would be soluble in large concentrations. Addition of acids, complexing agents, or stable chemically similar carriers may be used to obtain homogeneity. Consideration of the chemical nature of the radionuclides and compounds present and the subsequent chemistry of the method shall indicate the action to be taken.

11. Establishing Gas Proportional Counter Operating Plateau

11.1 Put the instrument into operation according to the manufacturer's instructions. Place a quality control (QC) source in the detector, set the sensitivity control near its maximum and turn the "count" switch to "count" position. Slowly increase the high voltage until the first counts are observed and record the "threshold" voltage. Advance the voltage in increments of convenient magnitude (approximately 25 V) and determine the counting rate at four or more settings of the sensitivity control at each voltage setting. Measure the background counting rate at each of the settings using an empty sample mounting dish in place of the standard.

11.1.1 The QC source may be any available alpha-emitting radionuclide having a half life sufficiently long to eliminate decay corrections. Knowledge of its true disintegration rate is not essential. The radionuclide shall be permanently fixed to the dish and uniformly distributed over an area preferably smaller than the dish bottom; electro-deposition and flaming of a salt-flee solution are the two methods most generally used. Quality control sources are commercially available.

11.2 Plot the gross counting rate of the standard against the voltage. The counting rate should rise initially as the voltage is increased, then, for at least some of the settings of the sensitivity control, reach an approximate constant value, and finally rise again. The" plateau" of the curve should be at least 100 V in length and have a slope less than 2 %/100 V; however, shorter plateaus or one with greater slope shall be acceptable if a well regulated high voltage power supply is available.

11.3 Plot the ratio of the square of the net counting rate of the standard to the background counting rate against the voltage for each of the settings of the sensitivity control.

11.4 Determine the optimum conditions for operation of the instrument by selecting values for the high-voltage and sensitivity adjustments that correspond to some point lying on the plateau of the counting-rate-versus-voltage plot and near the maximum value of the ratio of the sample-squared-to-background counting rates.

12. Control of Instrument Operation

12.1 Tolerance or statistical control charts are used to assure that the instrument is operating to within pre-specified limits of the initial calibration. Repetitive measurements of a quality control source are taken to develop the tolerance or statistical control chart. The QC source is then used on a daily or prior-to-use basis to ensure proper operation. Refer to Practice D 3648 for the preparation of a tolerance or statistical control chart.

13. Calibration and Standardization for General Measurements

13.1 Place a known amount of a NIST-traceable alpha standard (approximately 200 Bq) into a volume of water sufficient to dissolve salts (or into a volume of water containing dissolved salts) equivalent to those of the test samples and prepare for counting as directed in Section 15. Throughout the experiment, the evaporation, mounting, counting, and density of plate solids of this reference standard shall be identical with those of the test samples. Count for a length of time required to produce the desired statistical reliability (typically 1 %). The efficiency factor for each dissolved salt weight, f_o, is then expressed as a fraction of the disintegration rate (Bq) of the reference standard and is calculated according to the following equation:

$$f_o = cps / Bq \quad (1)$$

where:

cps = the measured counts per second.

The alpha emitting standard should have approximately the same alpha particle energy as the nuclides of interest so that mass attenuation effects can be estimated appropriately.

13.1.1 Purified natural uranium, of which the specific activity is 0.25 Bq per microgram, has been found satisfactory for this purpose. Other alpha-emitter preparations of known disintegration rate, for example, ^{241}Am or ^{237}Np, may also be used. When available, all calibration solutions shall be NIST traceable.

14. Calibration and Standardization for Tracer Experiments

14.1 Add a known quantity of activity from a reference solution of the tracer (approximately 180 Bq) to a radioactivity-free standard test sample and process as directed in Section 15.

15. Procedure

15.1 Place an appropriate volume of the test solution in a glass beaker, add 3 mL of concentrated HNO_3(sp gr 1.42) for each 100 mL of solution, and evaporate to 1 to 2 mL. Quantitatively transfer to the mounting dish and evaporate to dryness. Adjust the heat carefully to prevent spattering or boiling. A ring heater having a continuously variable voltage control or adjustable infrared heat lamps are the preferable heat sources for the final evaporation and drying. Uniform spreading of the residual salts is necessary for reliable comparative data. After drying, heat the dish to dull redness for a few

seconds using a burner. Cool hygroscopic solids in a dry atmosphere and store in a desiccator until the start of counting. Place the sample in the counter and count for a time interval sufficient to attain the desired statistical reliability. Record the reading of the register. Transfer of large volume samples to smaller beakers as evaporation nears completion makes for easier transfer of the test specimen to the mounting dish. Make all transfers with HNO_3(1 + 30). Choose the sample size with consideration for the absorption of alpha particles in the residual solids. The size should be such that the density of the deposit on the plate shall not exceed 5 mg/cm^2.

15.2 Precipitation methods may be used expediently to concentrate the radioactive material into small amounts of precipitate. The precipitate is separated and washed free of precipitant by centrifugation or filtration. Choose the method of separation that will produce a uniform deposit of precipitate after quantitatively transferring to the mounting dish for counting. Calibrate the instrument under counting conditions identical to those used for the samples. More detailed information is published[2] on the techniques and equipment for separation and mounting of the precipitate.

16. Calculation

16.1 Results may be expressed in observed counts per second per millilitre or Bq/mL. This test method is useful for comparing activities of a group of samples, as in tracer experiments. Results may also be reported in terms of equivalent americium-241 activity or other standard radionuclide activity using the empirical efficiency determined by use of a reference standard. If it is known that only one nuclide is present, its disintegration rate may be determined by use of the efficiency factor determined from a reference standard of that nuclide obtained from the National Institute of Standards and Technology (NIST) or from a NIST-traceable standard. Calculate the results as follows:

$$\textit{alpha concentration } (Bq/mL) = C_{net} / (f_o \times V) \quad (2)$$

where:

C_{net} = net count rate (s^{-1}),
V = test specimen, mL, and
f_o = detector efficiency factor.

The total propagated uncertainty of the alpha concentration is calculated as:

$$\sigma_{Bq/mL} = Bq/mL \times [(\sigma_{Cnet\,/\,Cnet})^2 + (\sigma_{fo}/f_o)^2 + (\sigma_V / V)^2]^{1/2} \quad (3)$$

where:

$\sigma_{Cnet/Cnet}$ = relative counting uncertainty,
σ_{fo}/f_o = relative detector efficiency uncertainty, and
σ_V/V = relative uncertainty in the sample volume measurement.

The net count rate and counting uncertainty, σ_{Cnet}, are defined as:

$$C_{net} = CR_S - CR_B = C_S / t_S - C_B / t_B \quad (4)$$

$$^{\sigma}C_{net} = (C_S / t_S^2 + C_B / t_B^2)^{1/2} \quad (5)$$

where:

CR_s = sample count rate (s^{-1}),
CR_B = background count rate (s^{-1}),
C_s = sample counts,
C_B = background counts,
t_s = counting time of sample(s), and
t_B = counting time of background(s).

The *a priori* minimum detectable concentration (*MDC*) is calculated using the equation:

$$MDC = 2.71 / (t_s \times k) + 4.65 \times \sigma_B / k \quad (6)$$

where:

σ_B = $(CR_B / t_s)^{1/2}$, and
k = $f_o \times V$.

A more detailed discussion on the minimum detectable concentration concept can be found in Practice D 3648.

17. Precision and Bias

17.1 The overall precision and bias of this test method within its designated range varies with the quantity being tested according to Table 1.

17.2 This collaborative test for the determination of gross alpha activity in water was conducted by six laboratories at three concentration levels ranging from 1.03 to 4.17 Bq/mL and containing 8 mg, 19.5 mg, and 40 mg of solids, respectively. Each laboratory processed three replicates per level.

17.3 The precision and bias statements for this test method were obtained using Practice D 2777 – 86.

18. Quality Control

18.1 Before this test method is utilized for the analysis of samples, a counter quality control or tolerance chart shall be established to ensure that the counting system is operating within prescribed limits. The quality control or tolerance chart shall be established at the time the counting system is calibrated.

18.2 Prepare a quality control or tolerance chart as recommended in Practice D 3648. The counting system shall be checked by analyzing a QC source daily or prior to use. The result of the QC analysis shall be tabulated or plotted on the control or tolerance chart and evaluated according to Practice D 3648.

18.3 Evaluate the counting system background periodically. The background data shall be maintained in a logbook or plotted on a trend chart.

18.4 Precision and bias can be assessed in the following manner: the precision of an individual measurement can be approximated by the total propagated uncertainty and bias can be assessed by the analysis of NIST traceable spiked samples with known quantities of radioactivity.

19. Keywords

19.1 gross alpha radioactivity; gross radioactivity measurement; proportional counter; water

TABLE 1 Determination of Precision and Bias

Amount Added, Bq/mL	Average Calculated Amount, Bq/mL	± Bias	± % Bias	Statistically Significant (5 % C.I.)	Precision	
					S_t	S_o
1.03 ± 0.01	0.98 ± 0.20	−0.05	−4.9	No	0.195	0.058
2.08 ± 0.02	2.08 ± 0.46	+ 0.00	+ 0.0	No	0.458	0.137
4.17 ± 0.05	3.97 ± 0.83	−0.20	−4.8	No	0.828	0.347

CERTIFICATE

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

Document Name: ASTM D1945: Standard Test Method for Analysis of Natural Gas By Gas Chromatography

CFR Section(s): 40 CFR 60.45(f)(5)(i)

Standards Body: American Society for Testing and Materials

APPROVED

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

Designation: D 1945 – 96

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

[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.

Current edition approved Nov. 10, 1996. Published January 1997. Originally published as D 1945 – 62 T. Last previous edition D 1945 – 91.

[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:

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

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

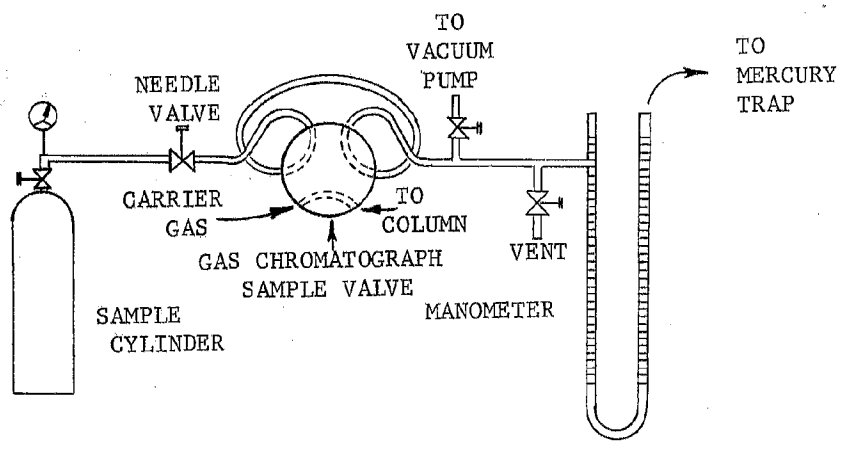

FIG. 1 Suggested Manifold Arrangement for Entering Vacuum Samples

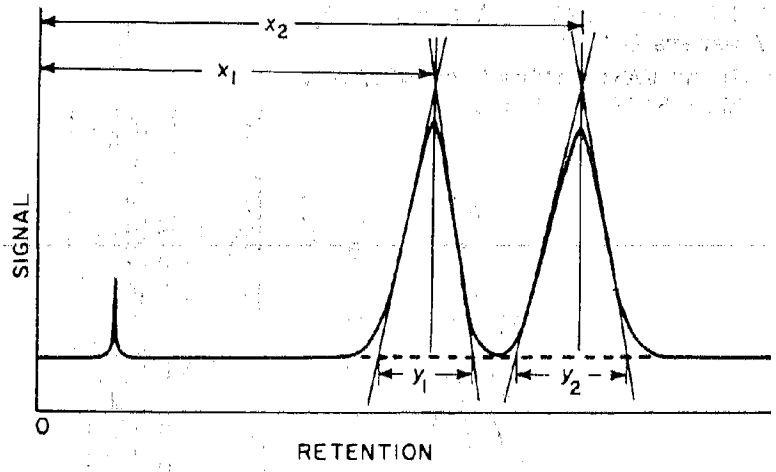

FIG. 2 Calculation for Resolution

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

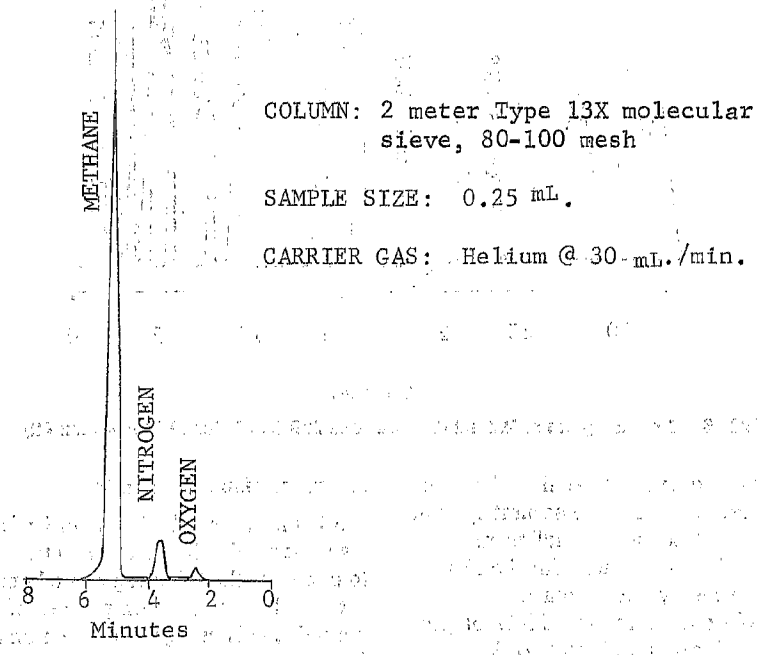

FIG. 3 Separation Column for Oxygen, Nitrogen, and Methane (See Annex A2)

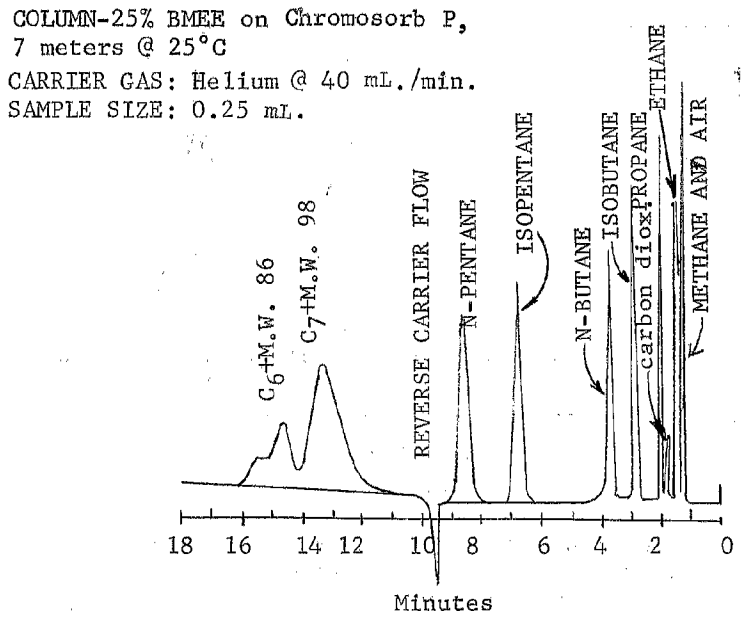

FIG. 4 Chromatogram of Natural Gas (BMEE Column) (See Annex A2)

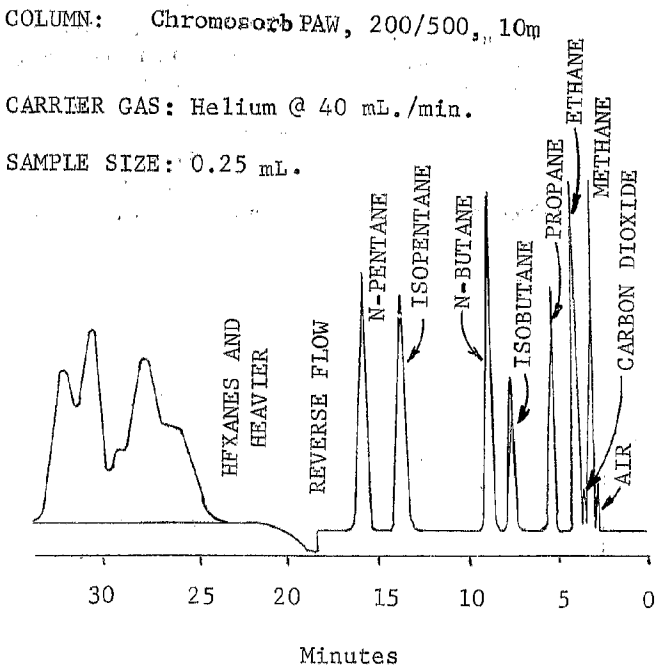

FIG. 5 Chromatogram of Natural Gas (Silicone 200/500 Column) (See Annex A2)

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

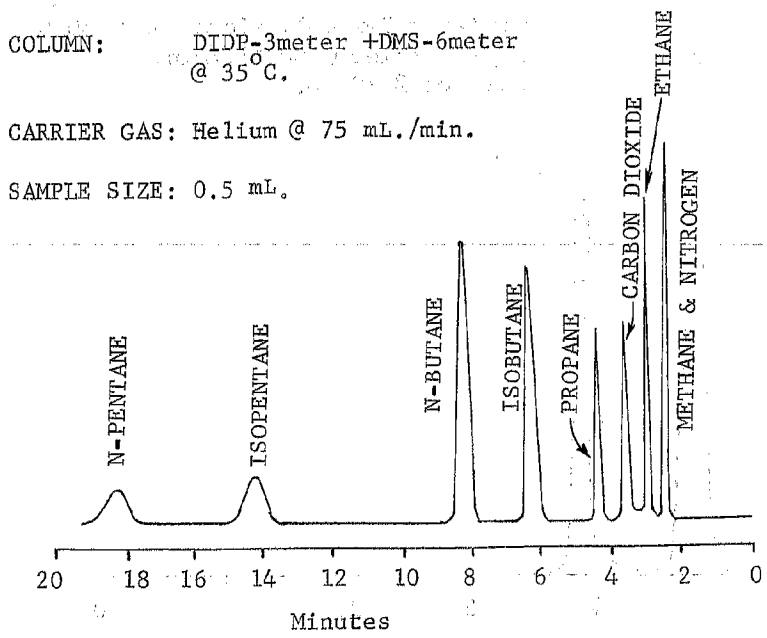

FIG. 6 Chromatogram of Natural Gas (See Annex A2)

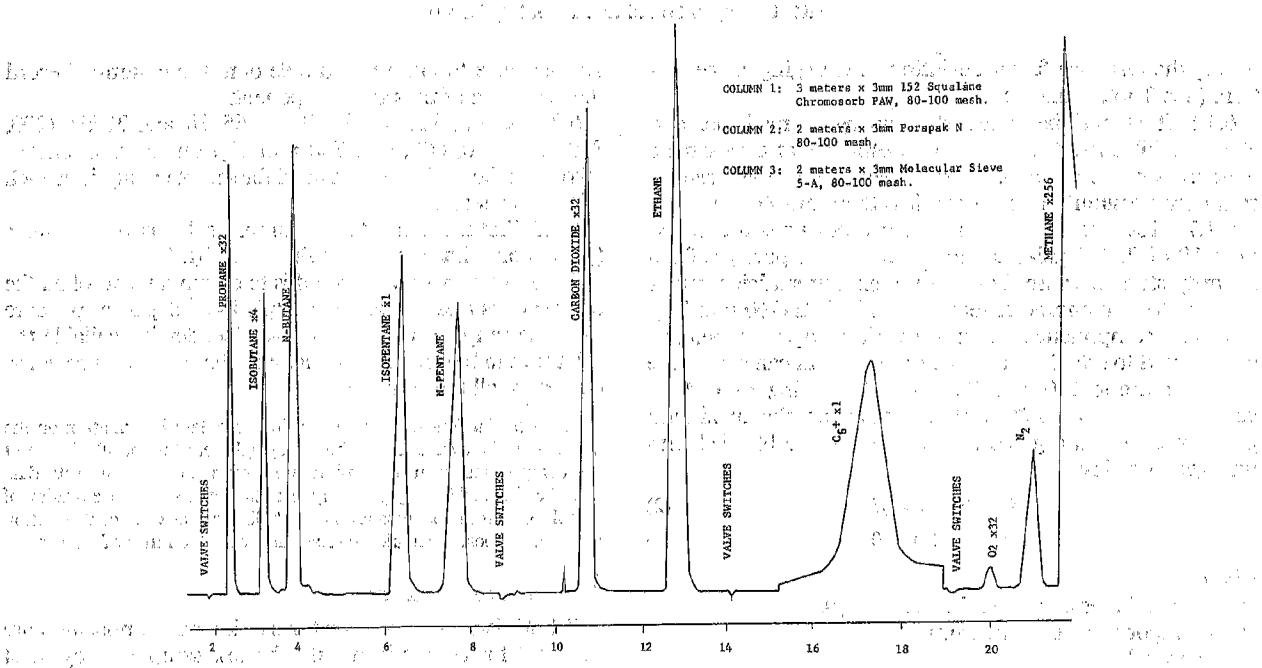

FIG. 7 Chromatogram of Natural Gas (Multi-Column Application) (See Annex A2)

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

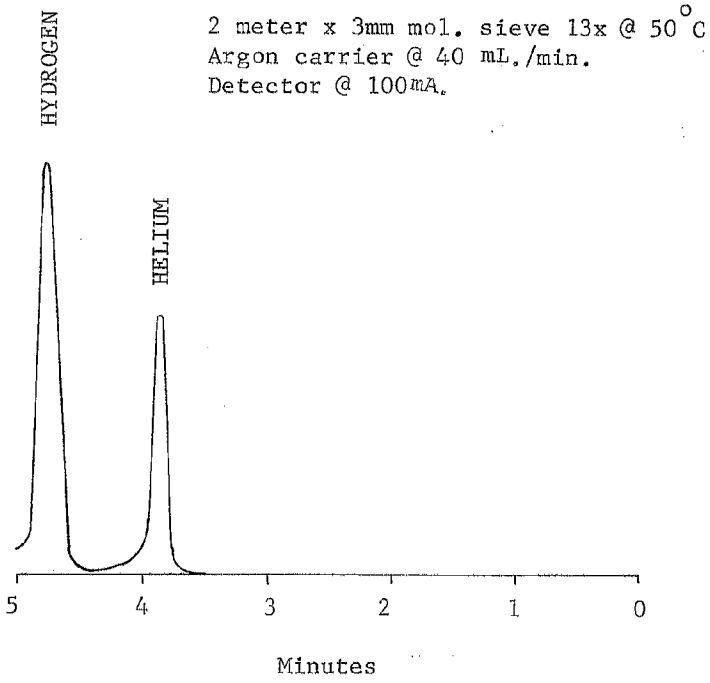

FIG. 8 Separation of Helium and Hydrogen

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.

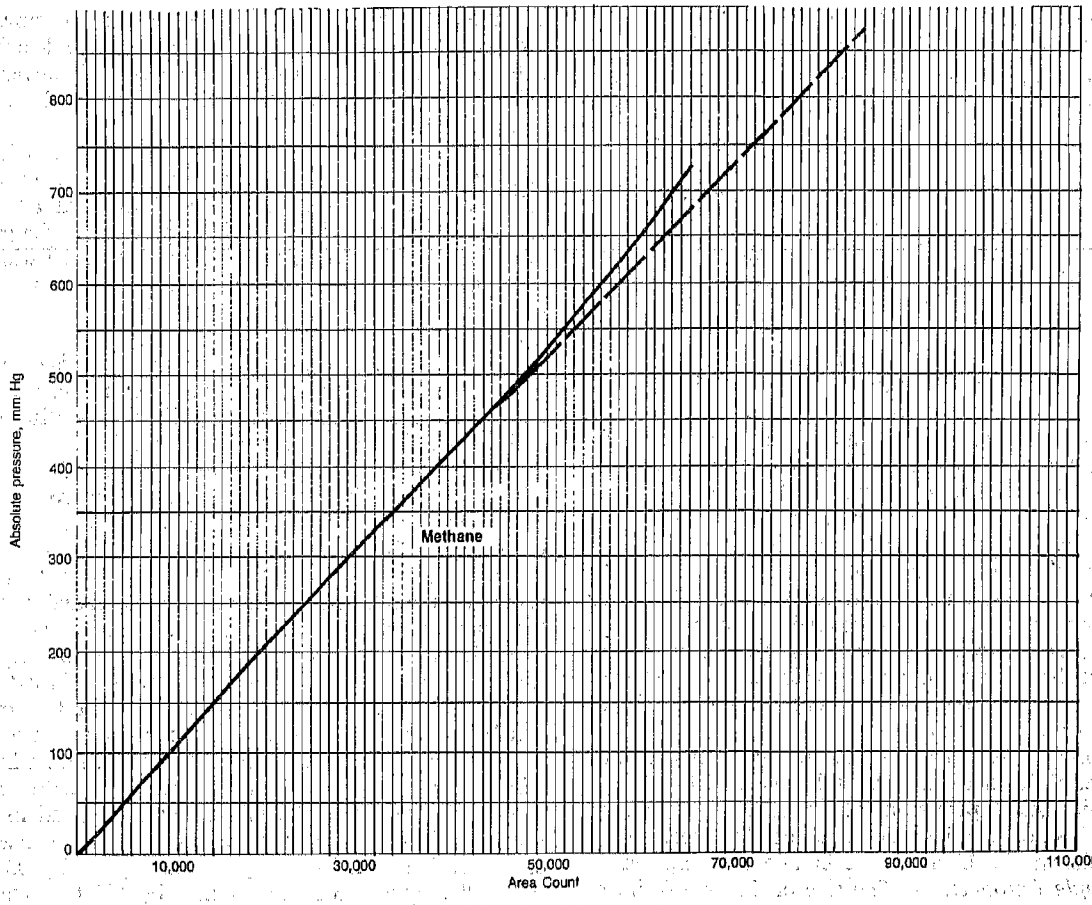

FIG. 9 Linearity of Detector Response

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

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

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.

[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:

$$C = S \times (A/B) \quad (4)$$

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:

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

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:

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

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

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:

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

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

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/m³ (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.

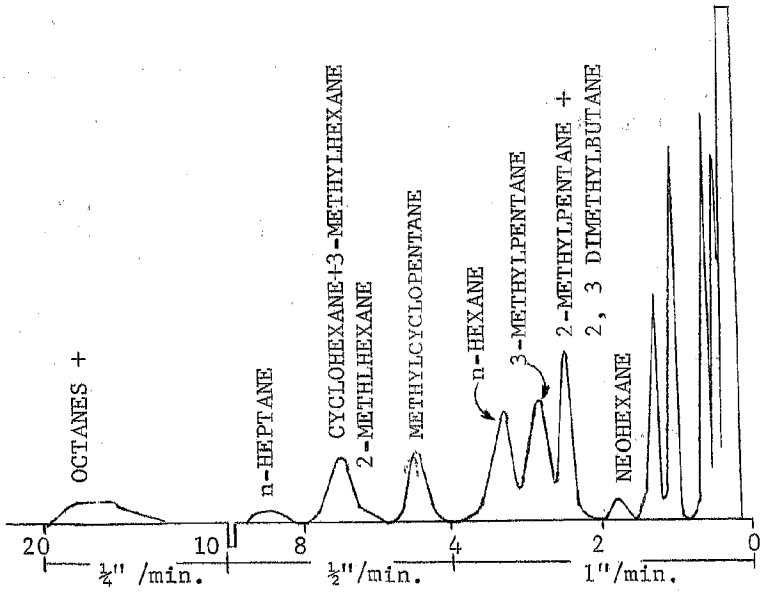

FIG. A1.1 Composition of Hexanes and Heavier Fraction

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

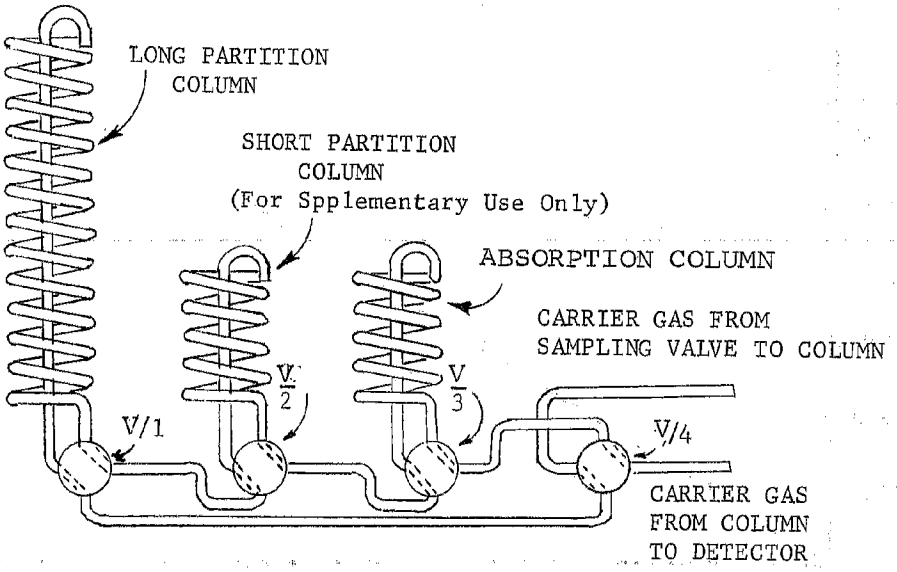

FIG. A2.1 Column Arrangement

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

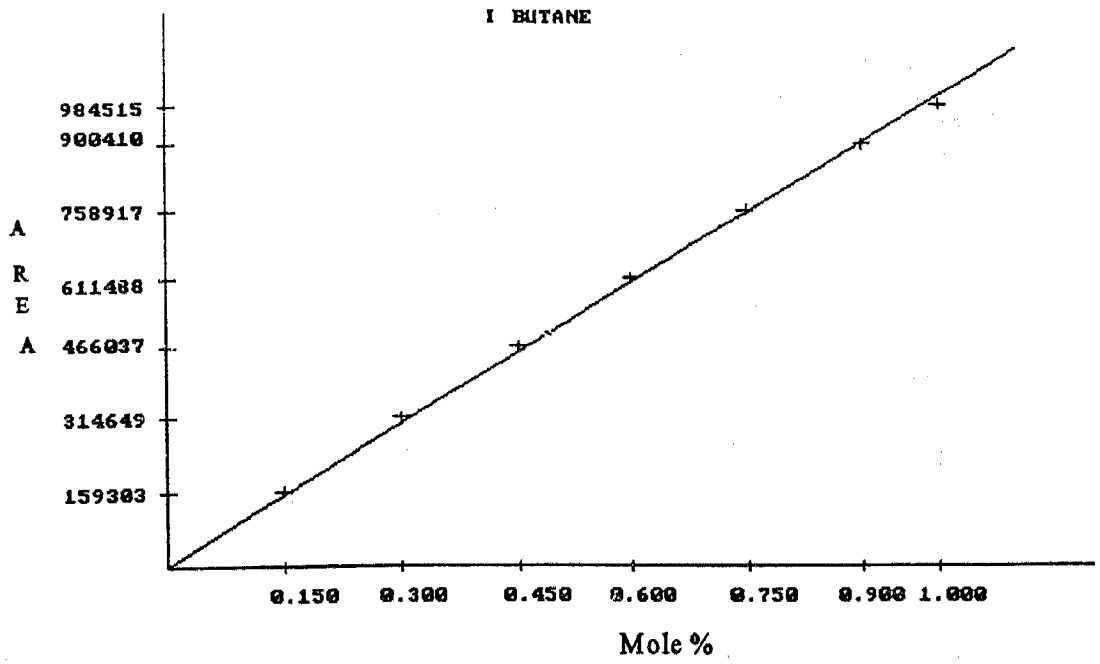

FIG. X1.1 Example of Deriving a Relative Molar Response Factor

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

	area Y	mole % X	XY	Y^2
	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 =	$\Sigma XY/\Sigma Y^2$	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:

$$RMR_{ic_4} = (\text{slope}/c_4)/(Kc_3) = 9.9594E\text{-}7\ 1.1315E\text{-}6 = 0.72958$$

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:

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

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).

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

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

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

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 × 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
Isobutane	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
neopentane	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.

CERTIFICATE

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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.

ε1 NOTE—Section 12 was added in December 1994.

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

[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

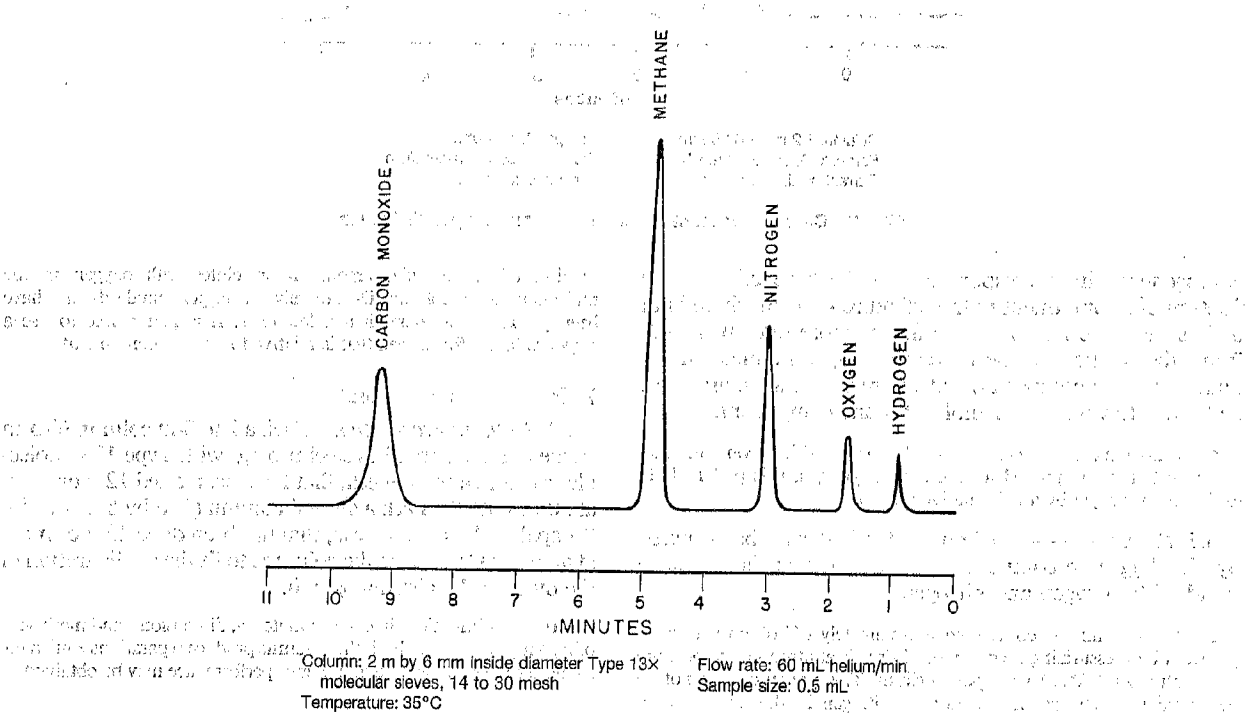

FIG. 1 Chromatogram of Reformed Gas on Molecular Sieve Column

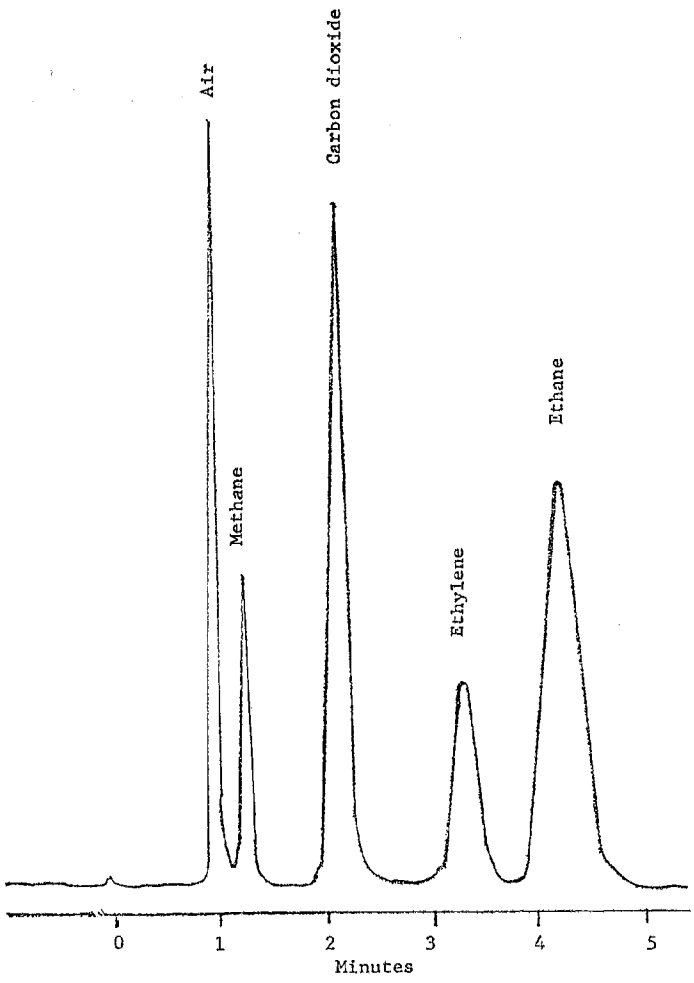

FIG. 2 Chromatogram of Reformed Gas on Porapak Q Column

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

[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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WASHINGTON, D.C.

Designation: D 2013 – 86 (Reapproved 1994)

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)[ε1].

[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.

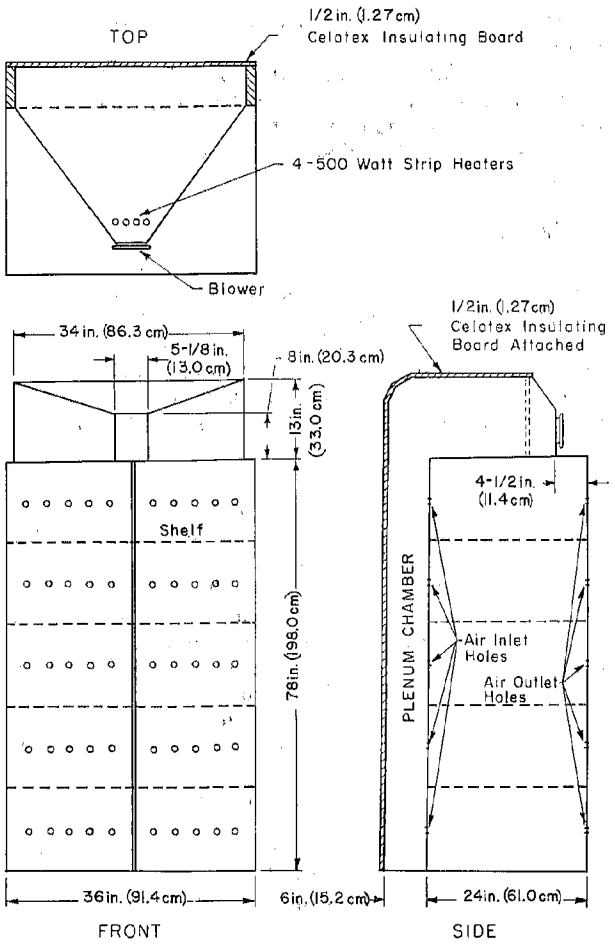
6.3 *Pulverizer or Mill*—For final reduction of laboratory sample to pass the No. 60 (250-μm) sieve, the following equipment may be used:

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.

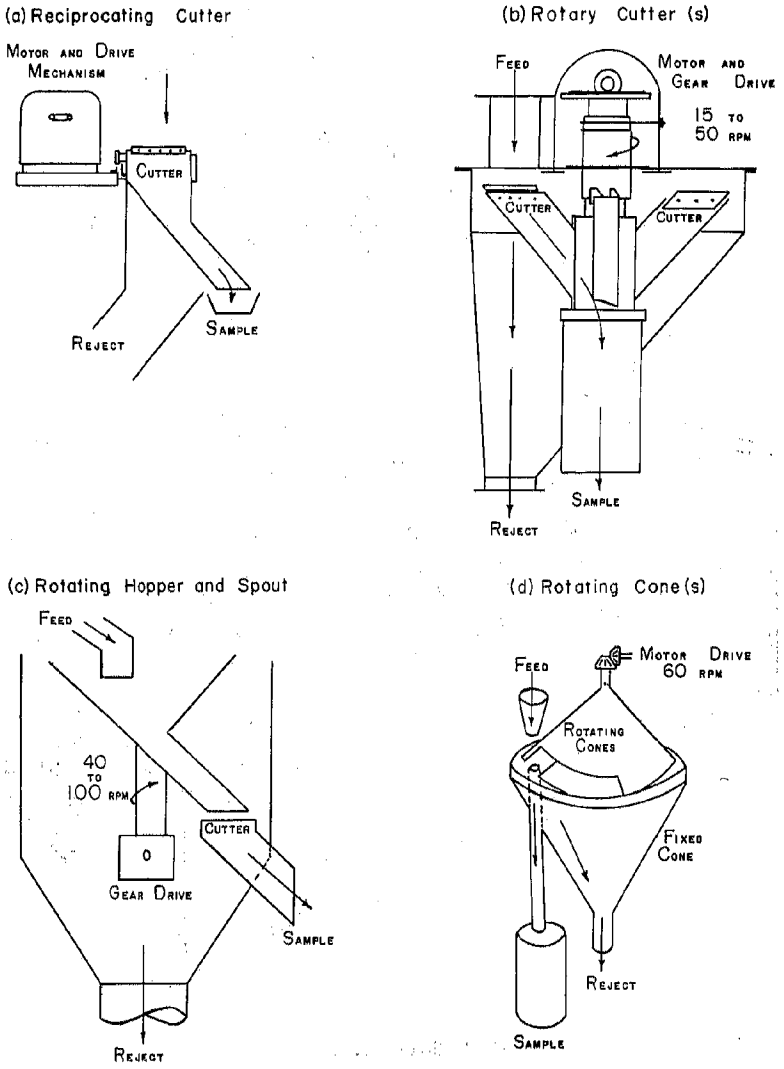
7.2 *Number of Tests*—Before preparing the gross or divided sample, the number and nature of the analysis and tests should be considered. A separate moisture laboratory sample may be required, and portions may be required for grindability and other tests. Also, a reserve sample may be desired in case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

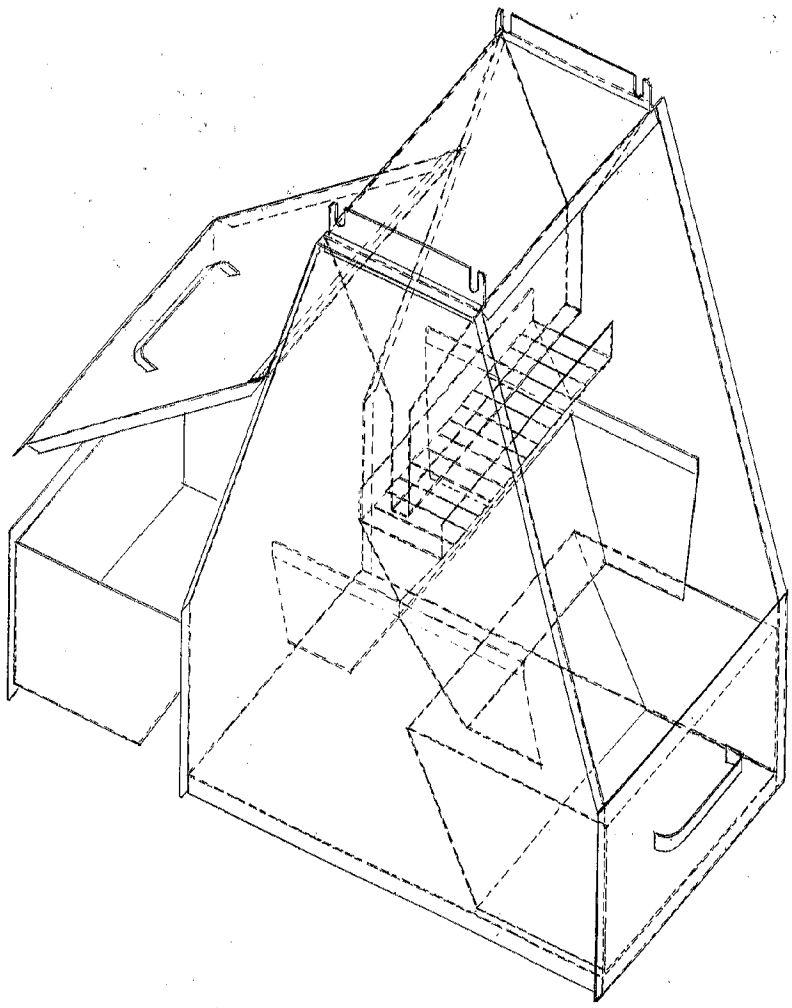


FIG. 3 Sample Divider (Riffle)

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.

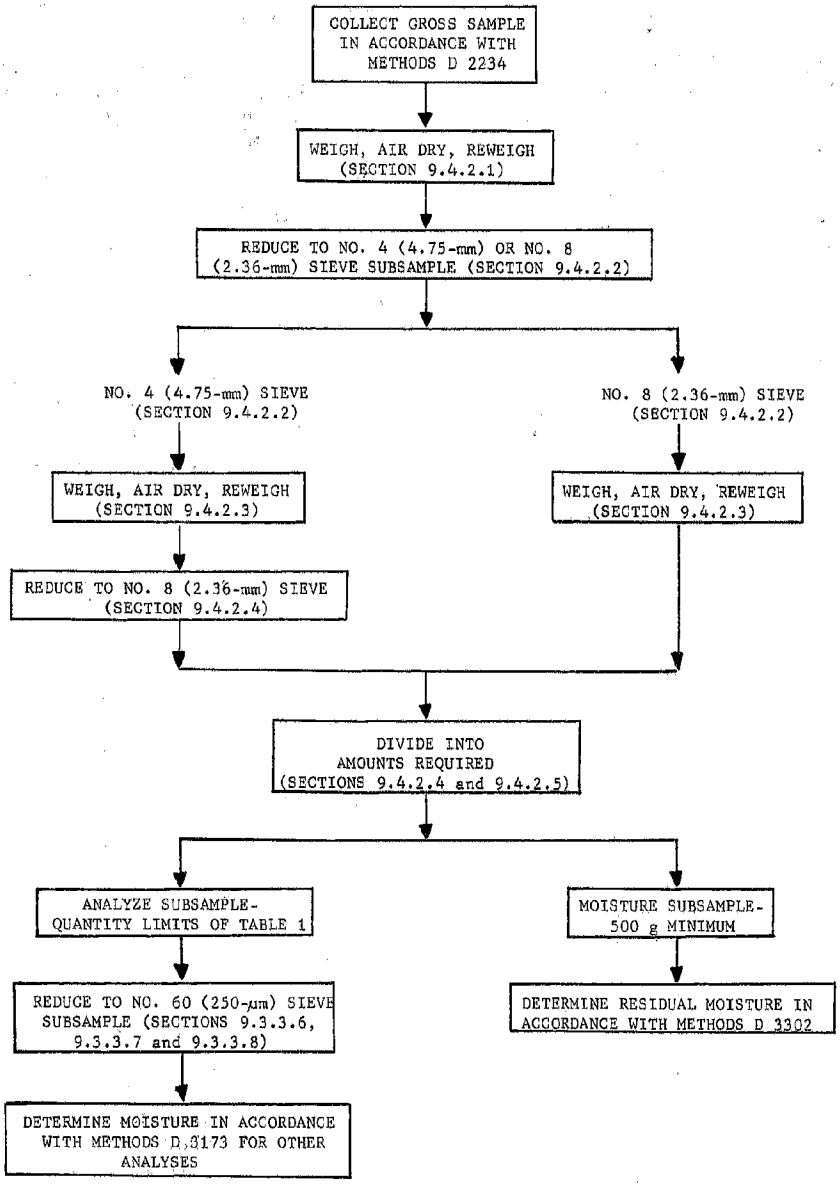


FIG. 4 Gross Sample Preparation for Moisture Determination (Referee Method)

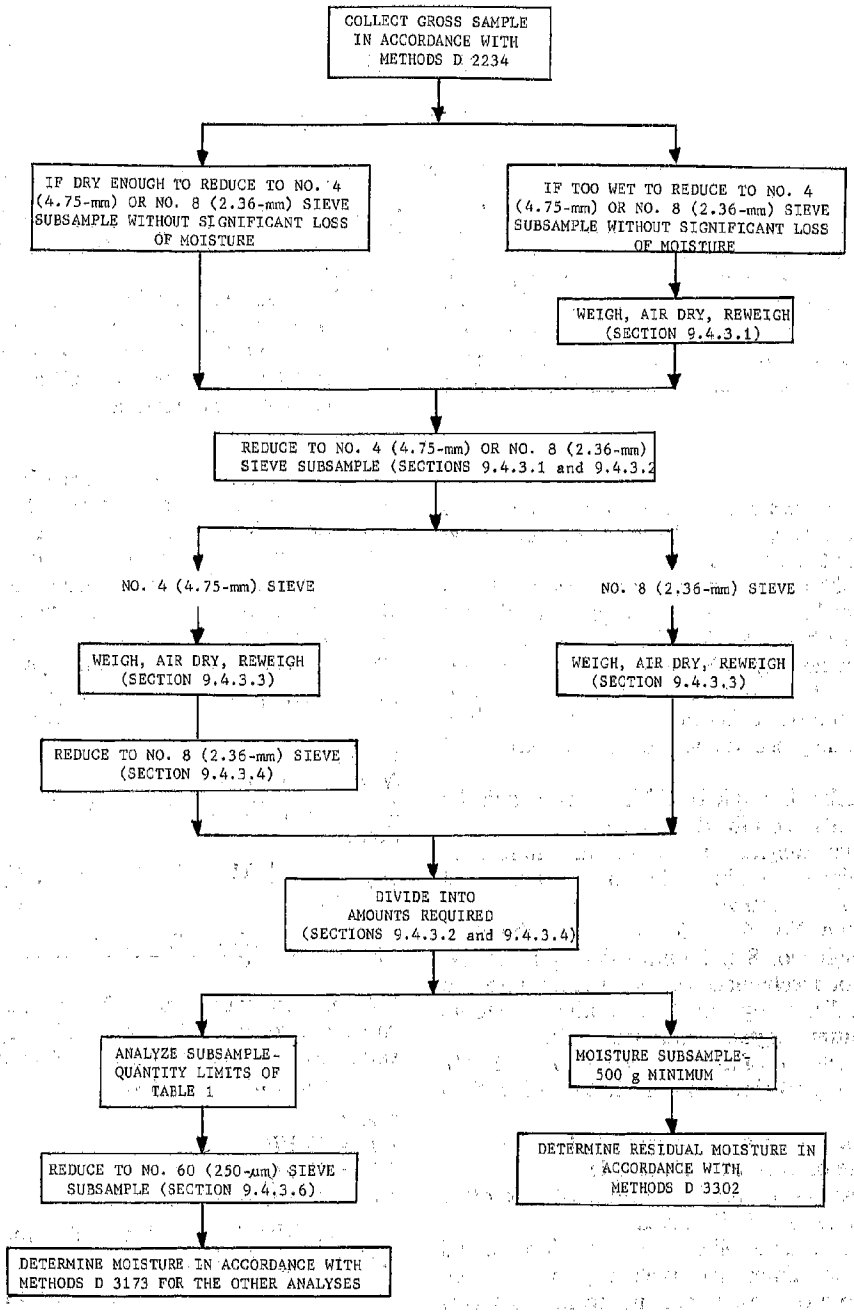


FIG. 5 Gross Sample Preparation for Moisture Determination (Nonreferee Method)

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.	X1	X2	Difference	Difference^2	X3	X4	Difference	Difference^2
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.	Y1	Y2	Difference	Difference^2	Y3	Y4	Difference	Difference^2
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	Difference^2	Y(1 + 2)/2	Y(3 + 4)/2	Difference	Difference^2
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	Difference^2
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 = 1/40 (0.0874 + 0.0691 + 0.0456 + 0.0840) = 0.0071
VQ = 1/20 (0.5491 + 0.0969) = 0.0323
VR = 1/10 (0.2932) = 0.0293
Then:
Va = 1/2 (0.0071) = 0.0035
V_2 = 1/2 (0.0323) − 1/4 (0.0071) = 0.0144
V_1 = 1/2 (0.0293) − 1/4 (0.0323) = 0.0066
S_{de}^2 = = 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:

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

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_l [A]	C_l [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.

CERTIFICATE

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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

[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

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

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_i, 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:

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

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:

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

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:

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

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:

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

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}:

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

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

$$H_{ar} = 5.37$$

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

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)

[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:

Differential stem correction, C_e
= 0.00016 (28 − 24) (28 + 24 − 16 − 26)
= + 0.0064°C.

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:

Differential stem correction
= 0.00009 (86 − 80) (82 − 72)
= 0.005°F

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.

[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:

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

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:

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

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.

CERTIFICATE

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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,

[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 equivalent.

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,

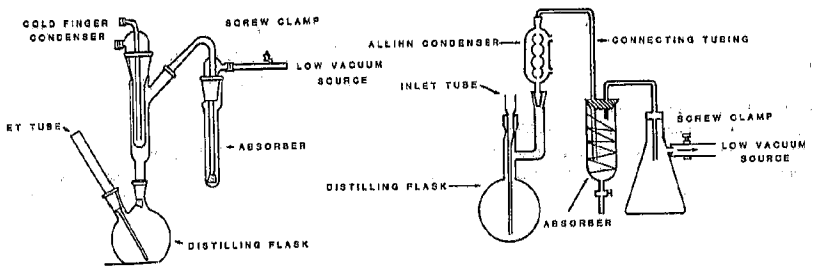

FIG. 1 Cyanide Distillation Apparatus

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

[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:

$$\text{mg CN/L} = [(A - B) \times N\,AgNO_3 \times 0.052/\text{mL original sample}] \times (250/\text{mL aliquot used}) \times 10^6 \quad (1)$$

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:

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

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.

[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:

$$\text{CN, mg/L} = G - H \tag{6}$$

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

[9] Supporting data are available from ASTM Headquarters. Request RR: D19 – 1074.

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

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 Rs 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

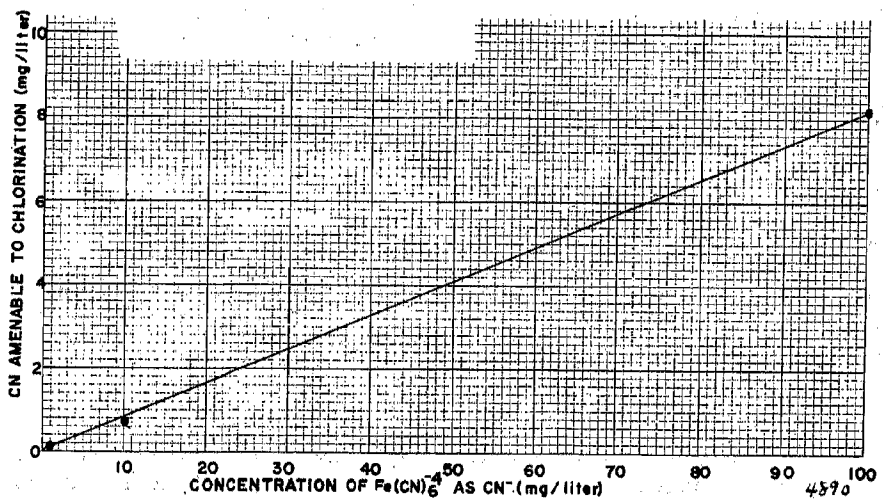

FIG. X1.1 Photodecomposition Rates for $Fe(CN)_6^{4-}$ in Direct Sunlight, 20°C, pH 7, in Buffered Distilled Water, 75 mm Solution Layer, 1 h Exposure

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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An American National Standard

Designation: 264/72(85)

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.

[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.

Current edition approved Oct. 15, 1991. Published December 1991. Originally published as D 2163 – 63. Last previous edition D 2163 – 87.

[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.

[4] Suitable reference standard mixtures of pure hydrocarbons are available from Scott Specialty Gases, Inc., Plumsteadville, PA.

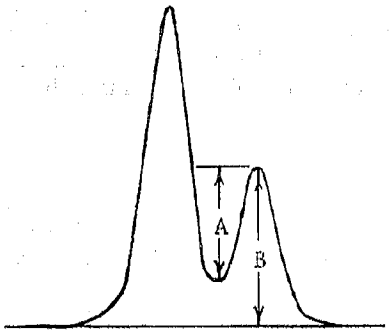

FIG. 1 Illustration of *A/B* Ratio

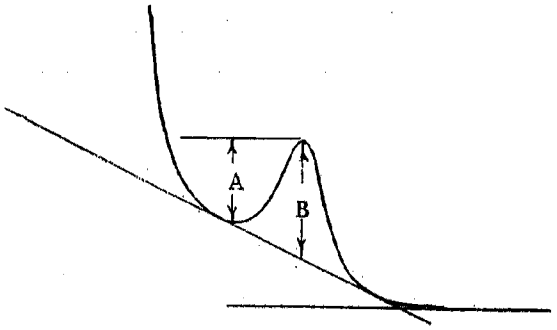

FIG. 2 Illustration of *A/B* Ratio for Small-Component Peak

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.

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

[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

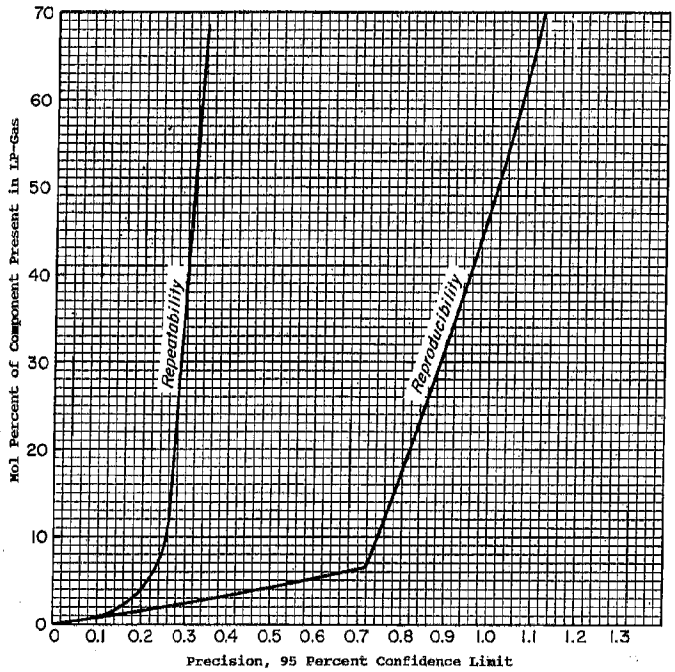

FIG. 3 Precision Curves

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)

[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

[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:

$$w = [(M_{cws} - M_{cs})/(M_{cs} - M_c)] \times 100 = \frac{M_w}{M_s} \times 100 \quad (1)$$

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/ft^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

[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.

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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.

[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:

Test Method	Section
Sampling of Coals Based on Size and Condition of Preparation	8.1
General-Purpose Sampling Procedure	8.1.1
Number and Weight of Increments	8.1.1.2
Number of Gross Samples	8.1.1.4
Special-Purpose Sampling	8.1.2
Number and Weight of Increments	8.1.2.2
Number of Gross Samples	8.1.2.3
Sampling of Coals Based on Known Sampling Characteristics	8.2
Principles of Sampling by Sampling Characteristics	8.2.1
General-Purpose Sampling	8.2.2
Number and Weight of Increments	8.2.2.1
Number of Gross Samples	8.2.2.2
Special-Purpose Sampling	8.2.3
Number and Weight of Increments and Number of Gross Samples	8.2.3.2
Division of the Gross Samples Before Crushing	8.3
Sampling of Coal for Total Moisture Determination	8.4
Types of Moisture Samples	8.4.1
Entire Gross Samples	8.4.1.1
Special Moisture Subsamples	8.4.1.2
Other Subsamples for Moisture Testing	8.4.1.3
Special Precautions	8.4.2
Weight of Increments	8.4.3
Number of Increments	8.4.4
Moisture Sampling Based on Known Sampling Characteristics	8.4.4.1
Moisture Sampling Based Only on Size	8.4.4.2

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		Type II Human Discretion Is Used	
	Spacing of Increments		Spacing of Increments	
	1. Systematic	2. Random	1. Systematic	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:

$$N_2 = N_1 \sqrt{\frac{\text{total lot size (tons or Mg)}}{\text{1000 tons or 908 mg}}} \quad (1)$$

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	¾ 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:

$$N_I = (s_s^2 + s_r^2/W)/(s_G^2 - s_{da}^2/P) \quad (2)$$

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

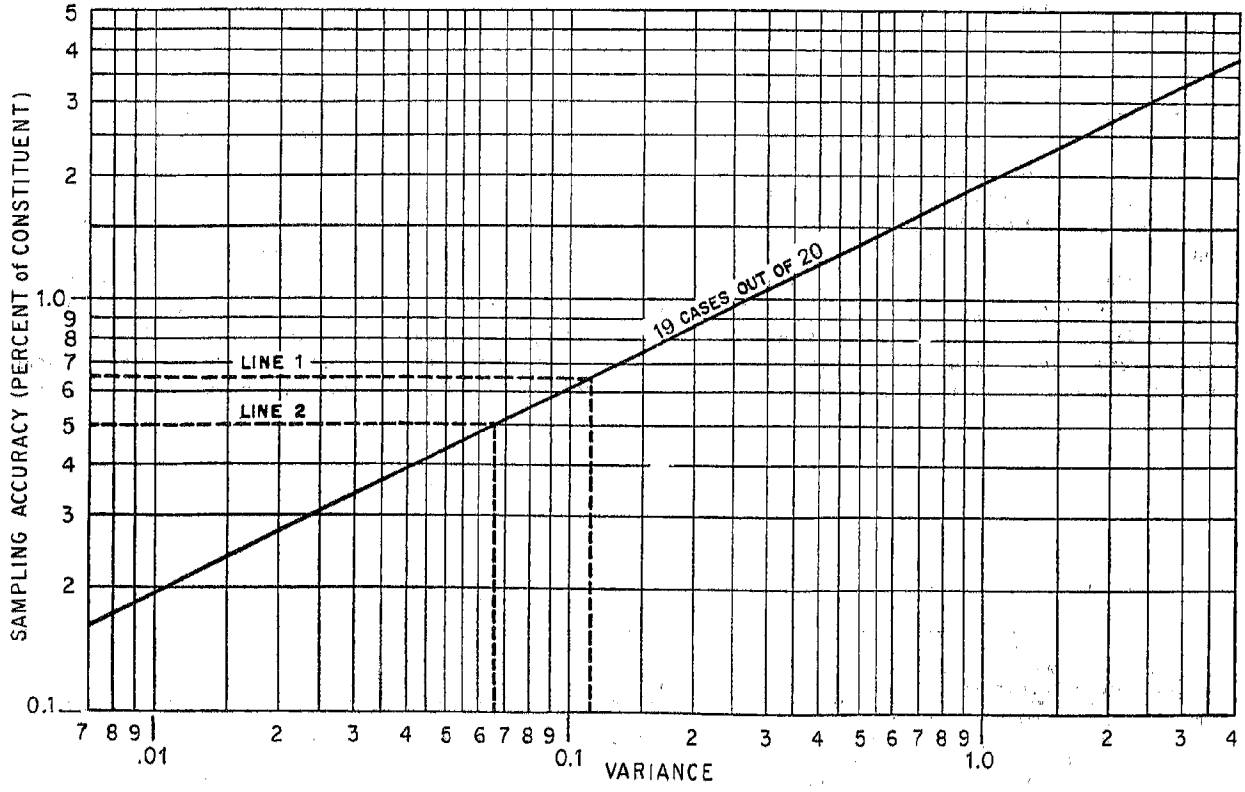


FIG. 1 Conversion of Sampling Accuracy to Variance

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:

$$s_T^2 = s_G^2/N_G \quad (3)$$

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:

$$s_T^2 = [(s_o^2 - s_{da}^2)/N_G N_I] + s_{da}^2/PN_G \quad (4)$$

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 ±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

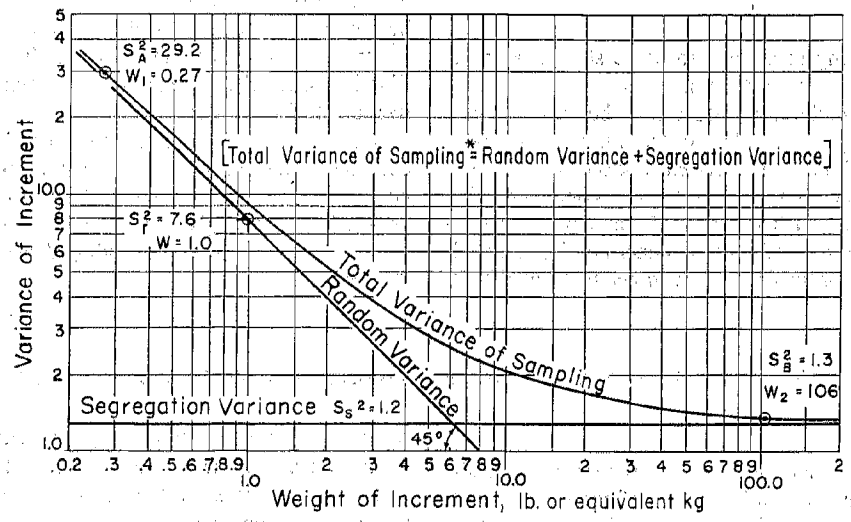


Fig. A1.1 Relation of Variance to Weight

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:

$$\text{Variance} = (\Sigma x^2 - (\Sigma x)^2/n)/(n - 1) \quad (5)$$

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:

$$s_r^2 = [W_1 W_2 (s_A^2 - s_B^2)]/(W_2 - W_1) \quad (6)$$

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:

$$s_s^2 = s_B^2 - s_r^2/W_2 \quad (7)$$

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).

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:

$$s^2 = (\Sigma x^2 - (\Sigma x)^2/n)/(n - 1) \quad (8)$$

where:

TABLE A2.1 Variance Ratio Limit Values

1	2	3
Increment per Set	Variance Ratio Limit	"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

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:

$$s_o^2 = C[(s_1^2 + s_2^2)/2] \quad (9)$$

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.

CERTIFICATE

By Authority Of
THE UNITED STATES OF AMERICA
Legally Binding Document

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

Document Name: ASTM 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

APPROVED

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

Designation: D 2460 – 97

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.

[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.

[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 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

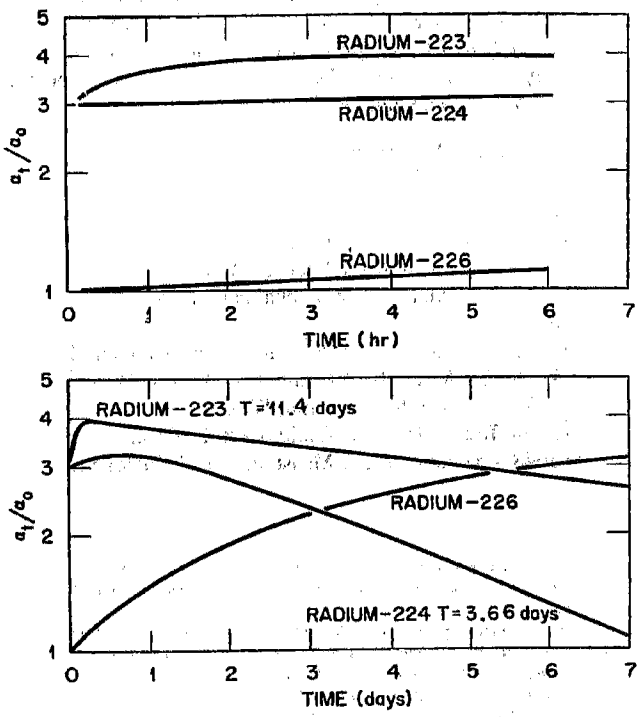
10.2 Sample 1 L, or a smaller volume, provided that it is estimated to contain from 3.7 to 370 Bq (100 to 10 00 pCi) of radium. Add 10 mL of HNO_3/L of sample.

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

TABLE 2 Important Alpha-Particle-Emitting Isotopes of Radium and their Descendents[A]

Nuclide		Radiation		
Parent	Descendents	Type[B]	Energy, MeV[C]	Half-Life
^{226}Ra		α	4.784 (94.5 %)	1.60×10^3 years
			4.601 (5.5 %)	
	^{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 %)	3.66 days
			5.449 (4.9 %)	
	^{220}Rn	α	6.288 (99.9 %)	55.6 s
	^{216}Po	α	6.779 (100.0 %)	0.15 s
	^{212}Pb	β (γ)		10.6 h
	^{212}Bi	β (64.1 %) (γ)		1.01 h
		α (35.9 %)	6.090 (9.6 %)	
			6.051 (25.2 %)	
			others	
	^{212}Po	α	8.784	0.30 μs
	^{208}Tl	β (γ)		3.05 min
^{223}Ra		α (γ)	5.716 (52.5 %)	11.4 days
			5.607 (24.2 %)	
			5.747 (9.5 %)	
			5.540 (9.2 %)	
			others	
	^{219}Rn	α (γ)	6.819 (81 %)	3.96 s
			6.553 (12 %)	
			6.425 (7.5 %)	
	^{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 %)	2.14 min
			6.279 (16.0 %)	
	^{207}Tl	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:

$$Y = (M_B - M_P) / 0.01699 \quad (1)$$

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:

$$D = C/EVYF \quad (2)$$

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:

$$\sigma_D\,(Bq)/L = D(Bq/L) * [(\sigma_N/N)^2 + (\sigma_E/E)^2 + (\sigma_V/V)^2 + (\sigma_Y/Y)^2]^{1/2} \quad (3)$$

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:

$$\sigma_N = (G/T_G^2 + B/t_B^2)^{1/2} \quad (4)$$

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:

$$MDC\,(Bq/L) = \frac{2.71 + 4.65 * (t_G * B)^{1/2}}{t_G * E * Y * V * I} \quad (5)$$

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

[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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CERTIFICATE

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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.

Document Name: ASTM D2502: Standard Test Method for Estimation of Molecular Weight (Relative Molecular Mass) of Petroleum Oils from Viscosity Measurements

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

Standards Body: American Society for Testing and Materials

APPROVED

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WASHINGTON, D.C.

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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,

[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

[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	105	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

Kinematic Viscosity, cSt, at 100°F (37.78°C)	*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

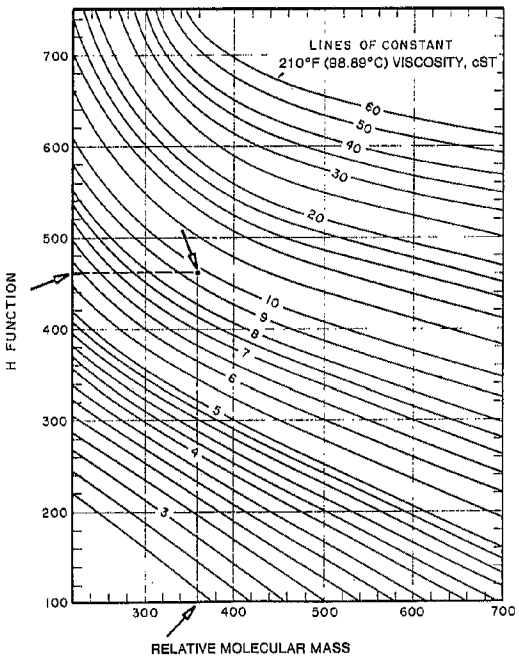

FIG. 1 Viscosity-Molecular Weight Chart