# EXHIBIT 150
# PART 8

# CERTIFICATE

## By Authority Of
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## Legally Binding Document

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

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**Document Name:**

**CFR Section(s):**

**Standards Body:**

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

**Designation: D 2503 – 92 (Reapproved 1997)**

An American National Standard

# Standard Test Method for Relative Molecular Mass (Molecular Weight) of Hydrocarbons by Thermoelectric Measurement of Vapor Pressure[1]

This standard is issued under the fixed designation D 2503; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

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

## 1. Scope

1.1 This test method covers the determination of the average relative molecular mass (molecular weight) of hydrocarbon oils. It can be applied to petroleum fractions with molecular weights (relative molecular mass) up to 3000; however, the precision of the method has not been established above 800 molecular weight (relative molecular mass). The method should not be applied to oils having initial boiling points lower than 220°C.

1.2 Values stated in SI units are to be regarded as the standard. The values given in parentheses are provided for information purposes only.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, 5.2.1, 5.2.3, and 5.2.3.

## 2. Summary of Test Method

2.1 A weighed portion of the sample is dissolved in a known quantity of appropriate solvent. A drop of this solution and a drop of solvent are suspended, side by side, on separate thermistors in a closed chamber saturated with solvent vapor. Since the vapor pressure of the solution is lower than that of the solvent, solvent condenses on the sample drop and causes a temperature difference between the two drops. The resultant change in temperature is measured and used to determine the relative molecular mass (molecular weight) of the sample by reference to a previously prepared calibration curve.

## 3. Significance and Use

3.1 Relative molecular mass (molecular weight) is a fundamental physical constant that can be used in conjunction with other physical properties to characterize pure hydrocarbons and their mixtures.

3.2 A knowledge of the relative molecular mass (molecular weight ) is required for the application of a number of correlative methods that are useful in determining the gross composition of the heavier fractions of petroleum.

## 4. Apparatus

4.1 *Vapor Pressure Osmometer*, with operating diagram.[2]

## 5. Reagents and Materials

5.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[3] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 *Solvents*—Solvents that do not react with the sample must be used. Since many organic materials exhibit a tendency to associate or dissociate in solution, it is desirable to use polar solvents for polar samples and nonpolar solvents for nonpolar samples. The solvents listed have been found suitable for hydrocarbons and petroleum fractions.

5.2.1 *Benzene*

NOTE 1—**Warning:** Poison. Carcinogen. Harmful if swallowed. Extremely flammable. Vapors may cause flash fire. Vapor harmful, may be absorbed through skin.

5.2.2 *Chloroform*

NOTE 2—**Warning:** May be fatal if swallowed. Harmful if inhaled. May produce toxic vapors if burned.

5.2.3 *1,1,1-Trichloroethane*

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[1] This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricantsand is the direct responsibility of Subcommittee D02.04on Hydrocarbon Analysis.

Current edition approved Aug. 15, 1992. Published October 1992. Originally published as D 2503 – 66T. Last previous edition D 2503 – 82 (1987)$^{\epsilon 1}$.

[2] A vapor pressure osmometer is available from H. Knauer and Co., Berlin, West Germany. The manufacture of the Mechrolab instrument previously referred to in this footnote has been discontinued. However, some models may be available from stocks on hand at laboratory supply houses, or as used equipment from laboratory instrument exchanges.

[3] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Analar Standards for Laboratory U.K. Chemicals," BDH Ltd., Poole, Dorset, and the "United States Pharmacopeia."

NOTE 3—**Warning:** Harmful if inhaled. High concentrations may cause unconsciousness or death. Contact may cause skin irritation and dermatitis.

NOTE 4—The precision data given in 10.1 and 10.2 will apply only when benzene is used as the solvent. There is also some evidence that determinations on the same oil sample carried out in different solvents will produce results that differ somewhat in absolute magnitude of apparent molecular weight (relative molecular mass).

5.3 *Reference Standards*—A calibration curve must be constructed for each new lot of solvent using a pure compound whose relative molecular mass (molecular weight) is accurately known. Compounds that have been used successfully include benzil (210.2), *n*-octadecane (254.5), and squalane (422.8).

## 6. Sampling

6.1 The sample must be completely soluble in the selected solvent at concentrations of at least 0.10 *M*, and it must not have an appreciable vapor pressure at the test temperature.

## 7. Preparation and Calibration of Apparatus

7.1 Prepare standard 0.01, 0.02, 0.04, 0.06, 0.08, and 0.1 *M* solutions of the calibrating compound in the solvent selected.

7.2 Remove the upper sample chamber assembly. Rinse the solvent cap with the solvent to be used. Install a vapor wick in the cup and fill with solvent to the bottom of the notches in the inner wick. Place the cup in the chamber base recess, align the vapor wick openings with the viewing tubes, and replace the upper assembly. Take care that the guide pins properly engage matching holes in the thermal block and that the matching surfaces of the base and block are clean. Be careful not to allow the thermistor beads to touch the cup or wicks as they may be bent out of alignment. Turn on the thermostat and allow the temperature of the sample chamber to reach equilibrium at 37°C.

NOTE 5—If the block is at room temperature, 2 to 3 h will be required. To avoid such delay, it is desirable to always leave the thermostat switch in the "on" position. If the chamber is at equilibrium and is opened briefly, 30 to 45 min will generally be required before temperature stabilization is regained. The exchange or refilling of syringes does not necessitate any waiting period.

7.3 Thoroughly rinse all syringes with the solvent being used and allow to dry.

7.4 Fill the syringes from guide tubes "5" and "6" with the solvent. Fill the syringes for guide tubes "1" through "4" with the standard solutions in order of increasing concentration.

7.5 Insert the syringes into the thermal block, keeping the guide pins pointed away from the probe. Turn on the "Null Detector" switch (Note 6). Set the sensitivity control to sufficient gain so that a 1.0-Ω shift in the "Dekastat" produces one major division shift of the meter needle.

NOTE 6—No measurements should be attempted until the "Null Detector" switch has been on for at least 30 min.

7.6 Turn on the "Bridge" switch and turn the "T-ΔT" switch to "T". Approximately zero the meter with the "T" potentiometer and observe the drift of the needle. If the solvent chamber is at equilibrium, the needle should not drift more than 1 to 2 mm during one complete heating cycle; a steady drift to the right indicates that the chamber is still warming up; if "T" is stable, switch the selector to the "ΔT" position.

7.7 While observing the thermistors in the viewing mirror, lower the syringe in position "5", by rotating the knurled collar of the holder fully clockwise. With the end of the needle directly above the reference thermistor, turn the feed screw and rinse the thermistor with about 4 drops of solvent. Finally, deposit a drop of solvent on the thermistor bead and raise the syringe by rotating the knurled collar in a counterclockwise direction. Rinse the sample thermistor with solvent from syringe "6" and apply a drop approximately the size of the drop on the reference thermistor. Depress the zero button, and zero the meter with the "Zero" control. Set the decade resistance to zero, and balance the bridge using the "Balance" control. Repeat the balancing of the bridge with fresh drops of solvent on each thermistor to assure a good reference zero.

7.8 Lower syringe "1" and rinse the sample thermistor with 3 to 4 drops of solution, finally applying one drop to the bead. Start the stop watch. Center the meter by means of the decade dials and take readings at 1-min intervals until two successive readings do not differ by more than 0.01 ohm. Record the Δ*R* value, estimating to the nearest 0.01 Ω from the meter. Record the time required to reach this steady state, and use this time for all subsequent readings for the solvent used.

7.9 Upon completing each series of sample readings, rinse the sample thermistor with solvent, deposit a drop, and recheck the zero point. The meter should reproduce the original indication within 0.5 mm. If the needle shows a negative deflection, the sample thermistor should be rinsed again. If it shows a positive deflection, the drop on the reference thermistor should be replaced.

7.10 Plot the Δ*R* values for each concentration of standard against the molarity of the standard for the solvent used.

NOTE 7—The calibration must be repeated for each of the solvents to be employed and separate working curves constructed. Recalibration is necessary each time a new batch of solvent is put into use.

## 8. Procedure

8.1 Select the solvent to be used and fill the solvent cup as described in 7.2. Weigh into a 25-mL volumetric flask the amount of sample suggested in the following table (Note 5):

| Estimated Relative Molecular Mass | Sample Size, g |
|---|---|
| Less than 200 | 0.3 |
| 200 to 500 | 0.3 to 0.6 |
| 500 to 700 | 0.6 to 0.9 |
| 700 to 1000 | 0.9 to 1.3 |

Record the weight to the nearest 0.1 mg and dilute to volume with solvent.

NOTE 8—If the amount of sample is limited, weigh the sample into a 5 or 1-mL volumetric flask, using one-fifth or one twenty-fifth respectively of the amount indicated in the table. Weigh to the nearest 0.001 mg using a microbalance.

8.2 Fill syringes "5" and "6" with solvent and fill one of the remaining syringes with the sample solution. With the sample chamber at thermal equilibrium, balance the bridge to establish the reference zero as described in 7.6 and 7.7.

8.3 Rinse the sample thermistor with 3 or 4 drops of the sample solution and deposit 1 drop on the thermistor. Start the stop watch. Center the meter with the decade dials and record

$\Delta R$ at the time interval determined during the standardization for the solvent being employed (7.8). When running a series of samples, check the zero point frequently as described in 7.9.

8.4 Using the appropriate calibration curve, obtain the molarity corresponding to the observed $\Delta R$ value.

## 9. Calculation

9.1 Calculate the relative molecular mass (molecular weight) of the sample as follows:

$$\text{Relative Molecular Mass (molecular weight)} = c/m \quad (1)$$

where:

$c$ = concentration of sample solution, g/L and

$m$ = molarity of solution, as determined in 8.4.

## 10. Report

10.1 Report the result to the nearest whole number.

## 11. Precision and Bias

11.1 **Precision**—The precision of this test method as obtained by statistical examination of interlaboratory test results is as follows:

11.1.1 Repeatability—The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the values shown in Table 1 only in one case in twenty.

11.1.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators, working in different laboratories on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the values shown in Table 1 only in one case in twenty.

11.1.3 The precision was not obtained in accordance with Committee D-2 Research Report RR-D-2-1007, "Manual on Determining Precision Data for ASTM Methods on Petroleum Products and Lubricants."[4]

11.2 *Bias*—Bias for this method has not been determined.

## 12. Keywords

12.1 hydrocarbons; molecular weight; osmometer; relative molecular mass; thermoelectric measurement; vapor pressure

TABLE 1 Precision Data (Benzene Solvent)

| Relative Molecular Mass (Molecular Weight) Range | Repeatability, g/mol | Reproducibility, g/mol |
|---|---|---|
| 245 to 399 | 5 | 14 |
| 400 to 599 | 12 | 32 |
| 600 to 800 | 30 | 94 |

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

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**Document Name:**

**CFR Section(s):**

**Standards Body:**

APPROVED

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

**Designation: D 2597 – 94 (Reapproved 1999)**

An American National Standard

# Standard Test Method for Analysis of Demethanized Hydrocarbon Liquid Mixtures Containing Nitrogen and Carbon Dioxide by Gas Chromatography[1]

This standard is issued under the fixed designation D 2597; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method covers the analysis of demethanized liquid hydrocarbon streams containing nitrogen/air and carbon dioxide, and purity products such as an ethane/propane mix that fall within the compositional ranges listed in Table 1. This test method is limited to mixtures containing less than 5 mol % of heptanes and heavier fractions.

1.2 The heptanes and heavier fraction, when present in the sample, is analyzed by either (*1*) reverse flow of carrier gas after *n*-hexane and peak grouping or (*2*) precut column to elute heptanes and heavier first as a single peak. For purity mixes without heptanes and heavier no reverse of carrier flow is required.

NOTE 1—**Caution:** In the case of unknown samples with a relatively large $C_5$ plus or $C_7$ plus fraction and where precise results are important, it is desirable to determine the molecular weight (or other pertinent physical properties) of these fractions. Since this test method makes no provision for determining physical properties, the physical properties needed can be determined by an extended analysis or agreed to by the contracting parties.

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

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements see Annex A3.

## 2. Referenced Documents

2.1 *ASTM Standards:*

D 3700 Practice for Containing Hydrocarbon Fluid Samples Using a Floating Piston Cylinder[2]

2.2 *Other Standard:*

GPA Standard 2177 Analysis of Demethanized Hydrocarbon Liquid Mixtures Containing Nitrogen and Carbon Dioxide by Gas Chromatography[3]

**TABLE 1 Components and Compositional Ranges Allowed**

| Components | Concentration Range, Mol % |
|---|---|
| Nitrogen | 0.01–5.0 |
| Carbon Dioxide | 0.01–5.0 |
| Methane | 0.01–5.0 |
| Ethane | 0.01–95.0 |
| Propane | 0.01–100.0 |
| Isobutane | 0.01–100.0 |
| *n*-Butane and 2,2-Dimethylpropane | 0.01–100.0 |
| Isopentane | 0.01–15.0 |
| *n*-Pentane | 0.01–15.0 |
| 2,2-Dimethylbutane | 0.01–0.5 |
| 2,3-Dimethylbutane and 2-Methylpentane | 0.01–15.0 |
| 3-Methylpentane and Cyclopentane | |
| *n*-Hexane | |
| Heptanes and Heavier | 0.01–5.0 |

## 3. Summary of Test Method

3.1 Components to be determined in a demethanized hydrocarbon liquid mixture are physically separated by gas chromatography and compared to calibration data obtained under identical operating conditions. A fixed volume of sample in the liquid phase is isolated in a suitable sample inlet system and entered onto the chromatographic column.

3.1.1 Components nitrogen/air through *n*-hexane are individually separated with the carrier flow in the forward direction. The numerous heavy end components are grouped into an irregular shape peak by reversing direction of carrier gas through the column by means of a switching valve immediately following the elution of normal hexane. (See Fig. 1.) Samples that contain no heptanes plus fraction are analyzed until the final component has eluted with no reverse of carrier flow.

3.1.2 An alternative to the single column backflush method is the use of a precut column which is backflushed to obtain the heptanes plus as a single peak at the beginning of the chromatogram. Two advantages of the alternate method are as follows: (*1*) better precision in measuring the $C_7$ plus portion of the sample and (*2*) reduction in analysis time over the single column approach by approximately 40 %.

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[1] This test method is under the jurisdiction of Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.H on Liquefied Petroleum Gas.

Current edition approved July 15, 1994. Published September 1994. Originally published as D 2597 – 67T. Last previous edition D 2597 – 88.

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

[3] Available from Gas Processors Assn., 6526 E. 60th St., Tulsa, OK 74145.

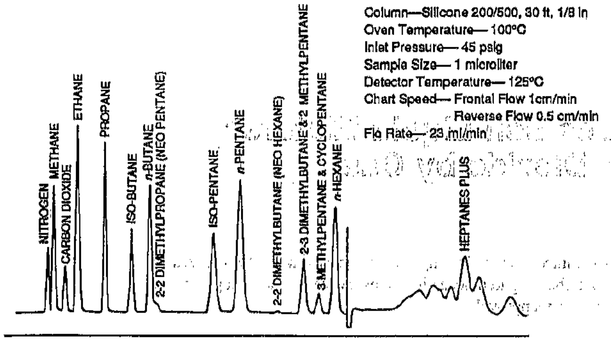

FIG. 1 Chromatogram of Demethanized Hydrocarbon Liquid Mixture (Frontal Carrier Gas Flow Through *N*-Hexane, Reverse Grouping Heptanes Plus)

3.2 The chromatogram is interpreted by comparing the areas of component peaks obtained from the unknown sample with corresponding areas obtained from a run of a selected reference standard. Any component in the unknown suspected to be outside the linearity range of the detector, with reference to the known amount of that component in the reference standard, must be determined by a response curve. Peak height method of integration can be used only if the chromatograph is operating in the linear range for all components analyzed. Linearity must be proved by peak height for all components when using peak height method. (See Section 6 for further explanation of instrument linearity check procedures.)

## 4. Significance and Use

4.1 The component distribution of hydrocarbon liquid mixtures is often required as a specification analysis for these materials. Wide use of these hydrocarbon mixtures as chemical feedstocks or as fuel require precise compositional data to ensure uniform quality of the reaction product. In addition, custody transfer of these products is often made on the basis of component analyses of liquid mixtures.

4.2 The component distribution data of hydrocarbon mixtures can be used to calculate physical properties such as specific gravity, vapor pressure, molecular weight, and other important properties. Precision and accuracy of compositional data are extremely important when these data are used to calculate physical properties of these products.

## 5. Apparatus

5.1 Any gas chromatograph can be used that meets the following specifications.

5.1.1 *Detector*—The detector shall be a thermal-conductivity type. It must be sufficiently sensitive to produce a deflection of at least 0.5 mv for 1 mol % of *n*-butane in a 1.0-μL sample.

5.1.2 *Sample Inlet System, Liquid*—A liquid sampling valve shall be provided, capable of entrapping a fixed volume of sample at a pressure at least 200 psi (1379 kPa) above the vapor pressure of the sample at valve temperature, and introducing this fixed volume into the carrier gas stream ahead of the analyzing column. The fixed sample volume should not exceed 1.0 μL and should be reproducible such that successive runs agree within ±2 % on each component peak area. The liquid sampling valve is mounted exterior of any type heated compartment and thus can operate at laboratory ambient conditions.

5.1.3 *Sample Inlet System, Gas (Instrument Linearity)*—Provision is to be made to introduce a gas phase sample into the carrier gas stream ahead of the chromatographic column so that linearity of the instrument can be estimated from response curves. The fixed volume loop in the gas sample valve shall be sized to deliver a total molar volume approximately equal to that delivered by the liquid sample valve in accordance with 5.1.2. (See Section 6 for further explanation of instrument linearity check procedures.)

5.1.4 *Chromatographic Columns*:

5.1.4.1 *Column No. 1*—A partition column shall be provided capable of separating nitrogen/air, carbon dioxide, and the hydrocarbons methane through normal hexane. (See Fig. 1 and Fig. 2.) Separation of carbon dioxide shall be sufficient so that a 1-μL sample containing 0.01 mol % carbon dioxide will produce a measurable peak on the chromatogram. (The silicone 200/500 column, containing a 27 to 30 weight % liquid phase load, has proven satisfactory for this type of analysis.)

5.1.4.2 *Column No. 2*—A partition column similar to Column No. 1. It shall be of the same diameter as Column No. 1. The column shall be of an appropriate length to clearly separate the heptanes plus fraction from the hexanes and lighter components.

5.1.5 *Attenuator*—A multistep device shall be included in the detector output circuitry to attenuate the signal from the detector to the recorder when using manual calculation methods. The attenuation between steps shall be accurate to ±0.5 %.

5.1.6 *Temperature Control*—The chromatographic column(s) and the detector shall be maintained at their respective temperatures, constant to ±0.3°C during the course of the sample and corresponding reference standard runs.

5.2 *Carrier Gas*—Pressure-reducing and control devices to

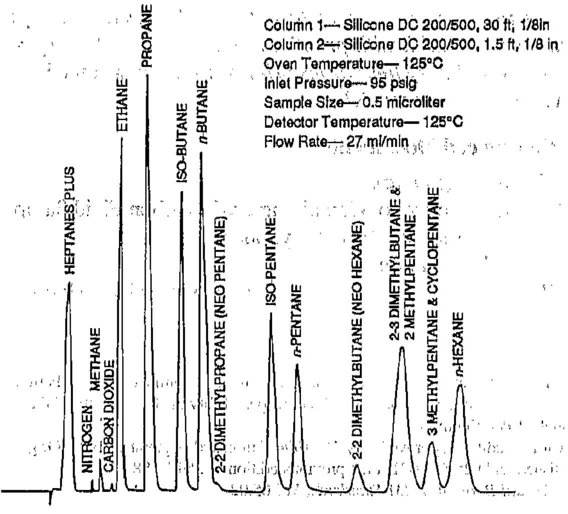

FIG. 2 Chromatogram of Demethanized Hydrocarbon Liquid Mixture (Precut Column Grouping Heptanes Plus, Frontal Carrier Gas Flow Remaining Components)

give repeatable flow rates.

5.3 *Recorder*—A strip chart recorder with a full-scale range of 1 mv shall be required when using manual calculation methods. A maximum pen response time of 1 s and a minimum chart speed of 1 cm/min (0.5 in./min accepted) shall be required. Faster speeds up to 10 cm/min (3 in./min accepted) are required if the chromatogram is to be interpreted using manual methods to obtain areas.

NOTE 2—A strip chart recorder is recommended for monitoring the progress of the analysis if an electronic digital integrator without plotting capability is in service.

5.4 *Electronic Digital Integrator*—A strongly preferred and recommended device for determining peak areas. This device offers the highest degree of precision and operator convenience.

NOTE 3—**Caution:** Electronic digital integrators are able to integrate peak areas by means of several different methods employing various correction adjustments. The operator should be well versed in integrator operation, preventing improper handling and manipulation of data—ultimately resulting in false information.

5.5 *Ball and Disk Integrator*—An alternative device in the absence of an electronic digital integrator for determining peak areas. This device gives more precise areas than manual methods and saves operator time in interpreting the chromatogram.

5.6 *Manometer*—Well type, equipped with an accurately graduated and easily readable scale covering the range from 0 to 900 mm of mercury. The manometer is required in order to charge partial pressure samples of pure hydrocarbons when determining response curves for linearity checks when using the gas sampling valve.

5.7 *Vacuum Pump*—Shall have the capability of producing a vacuum of 0.1 mm of mercury absolute or less. Required for linearity checks when using the gas sampling valve.

5.8 *Sample Filter*—An optional device to protect the liquid sampling valve from scoring due to the presence of foreign contaminates such as metal shavings, dirt, and so forth, in a natural gas liquid (NGL) sample. The filter can be of a small total volume, or an in-line type design and contain a replaceable/disposable element.

NOTE 4—**Caution:** A filter can introduce error if not handled properly. The filter should be clean and free of any residual product from previous samples so that a buildup of heavy end hydrocarbon components does not result. (Can be accomplished by a heating/cooling process or inert gas purge, etc.) The filter element should be 15-µm size or larger so that during the purging process NGL is not flashed, preventing fractionation and bubble formation.

5.9 *Sample Containers*:

5.9.1 *Floating Piston Cylinder*—A strongly preferred and recommended device suitable for securing, containing, and transferring samples into a liquid sample valve and which preserves the integrity of the sample. (See Fig. 3 and Test Method D 3700.)

5.9.2 *Double-Valve Displacement Cylinder*—An alternate device used in the absence of a floating piston cylinder suitable for securing, containing, and transferring samples into a liquid sample valve. (See Fig. 4 and Fig. 5.)

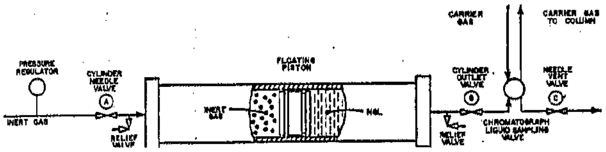

FIG. 3 Repressuring System and Chromatographic Valving with Floating Piston Cylinder

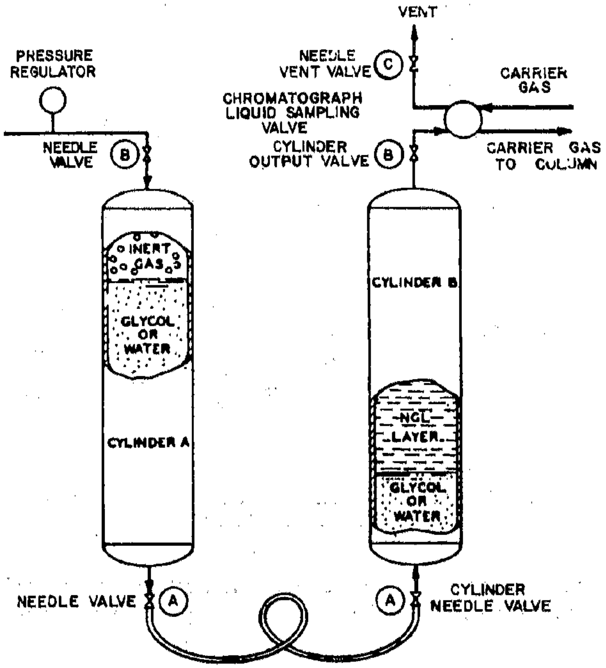

FIG. 4 Repressuring System and Chromatographic Valving with Double-Valve Displacement Cylinder

NOTE 5—**Caution:** This container is acceptable when the displacement liquid does not appreciably affect the composition of the sample of interest. Specifically, components such as $CO_2$ or aromatic hydrocarbons are partially soluble in many displacement liquids and thus can compromise the final analysis. This caution is of the utmost importance and should be investigated prior to utilizing this technique.

## 6. Calibration

6.1 In conjunction with a calibration on any specific chromatography, the linear range of the components of interest shall be determined. The linearity is established for any new chromatograph and reestablished whenever the instrument has undergone a major change (that is, replaced detectors, increased sample size, switched column size, or dramatically modified run parameters).

6.1.1 The preferred and more exacting procedure is to prepare response curves. The procedure for developing the data necessary to construct these response curves for all components nitrogen through *n*-pentane is set forth in Annex A2.

6.1.2 A second procedure utilizes gravimetrically constructed standards of a higher concentration than is contained in the unknown. A set of response factors are first determined for all components by means of a blend mix. (See 6.3.) A second (or third) gravimetrically determined standard (either purity or blend) can then be run, using the originally obtained

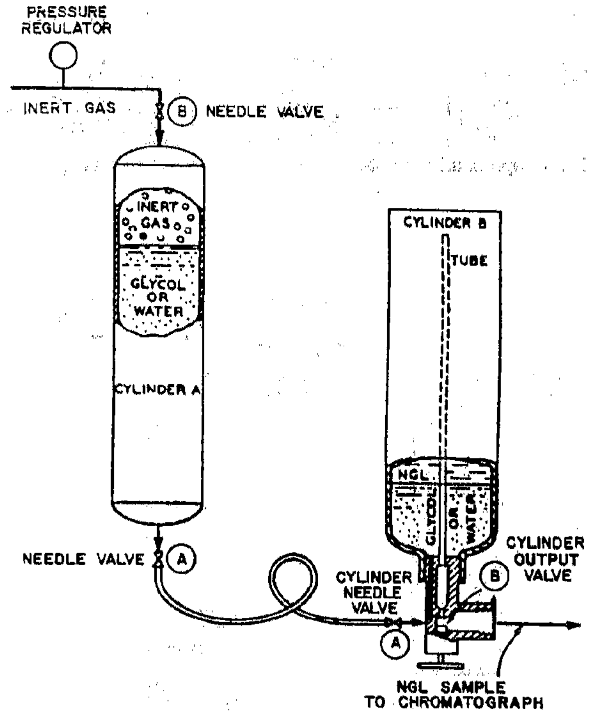

**FIG. 5 Alternate Repressuring System with Double-Valve Displacement Cylinder**

response factors, which contain a concentration of individual components exceeding the expected amounts in the unknowns. When both (or all three) runs match their respective standards within the precision guidelines allowed in Section 10, then the instrument can be considered linear within that range.

NOTE 6—This test method omits the need of a gas sample valve on the chromatographic instrument. However, several accurate primary NGL standards are required and the exact point at which nonlinearity occurs is not determined.

6.2 For routine analysis using this procedure it is intended that calibration be accomplished by use of a selected reference standard containing known amounts of all components of interest. It is recommended that the reference standard composition be similar to the one shown in Table 2, or closely resemble the composition of expected unknowns. This approach is valid for all components that lie within the proven linear range for a specific gas chromatograph.

NOTE 7—Check the reference standard for validity when received and periodically thereafter. Annex A1 details one procedure for making the validity check.

6.3 Using the selected liquid reference standard, obtain a chromatogram as outlined in Section 7.

6.3.1 Determine peak areas (or peak heights) from the chromatogram for all components. These data shall be used to calculate response factors in accordance with 9.1.

6.3.2 Repeat 6.3 through 6.3.1 until a satisfactory check is obtained. Usually two runs will suffice.

## 7. Procedure

7.1 *General*—In the routine analysis of samples described in the scope of this procedure, it is possible to obtain all components of interest from a single run. Response factors,

**TABLE 2 Example of Response Factors Determined from Reference Standard**

| Component | Mol % in Referenced Standard | Peak Area Referenced Standard Run | Mol % Response Factors (×10 000) | Relative Response Factor ($C_3$ Reference Peak) |
|---|---|---|---|---|
| Nitrogen/air | 0.10 | 311 | $\frac{0.10}{311} = 3.2154$ | $\frac{0.10}{311} \times \frac{122825}{28.05} = 1.4080$ |
| Methane | 1.49 | 3552 | $\frac{1.49}{3552} = 4.1948$ | $\frac{1.49}{3552} \times \frac{122825}{28.05} = 1.8368$ |
| Carbon dioxide | 0.50 | 1568 | $\frac{0.50}{1568} = 3.1888$ | $\frac{0.50}{1568} \times \frac{122825}{28.05} = 1.3963$ |
| Ethane | 53.90 | 182108 | $\frac{53.90}{182108} = 2.9598$ | $\frac{53.90}{182108} \times \frac{122825}{28.05} = 1.2960$ |
| Propane | 28.05 | 122825 | $\frac{28.05}{122825} = 2.2837$ | $\frac{28.05}{122825} \times \frac{122825}{28.05} = 1.0000$ |
| Isobutane | 3.05 | 15306 | $\frac{3.05}{15306} = 1.9927$ | $\frac{3.05}{15306} \times \frac{122825}{28.05} = 0.8726$ |
| *n*-Butane<br>2,2-Dimethylpropane | 6.01 | 30834 | $\frac{6.01}{30834} = 1.9491$ | $\frac{6.01}{30834} \times \frac{122825}{28.05} = 0.8535$ |
| Isopentane | 1.00 | 5856 | $\frac{1.00}{5856} = 1.7077$ | $\frac{1.00}{5856} \times \frac{122825}{28.05} = 0.7478$ |
| *n*-Pentane | 2.00 | 12280 | $\frac{2.00}{12280} = 1.6287$ | $\frac{2.00}{12280} \times \frac{122825}{28.05} = 0.7132$ |
| 2,2-Dimethylbutane | 0.02 | 132 | $\frac{0.02}{132} = 1.5152$ | $\frac{0.02}{132} \times \frac{122825}{28.05} = 0.6635$ |
| 2,3-Dimethylbutane<br>2-Methylbutane | 0.64 | 4513 | $\frac{0.64}{4513} = 1.4181$ | $\frac{0.64}{4513} \times \frac{122825}{28.05} = 0.6210$ |
| 3-Methylpentane<br>Cyclopentane | 0.41 | 2401 | $\frac{0.41}{2401} = 1.7076$ | $\frac{0.41}{2401} \times \frac{122825}{28.05} = 0.7477$ |
| *N*-Hexane | 0.74 | 5064 | $\frac{0.74}{5064} = 1.4613$ | $\frac{0.74}{5064} \times \frac{122825}{28.05} = 0.6399$ |
| Heptanes Plus | 2.09 | 14851 | $\frac{2.09}{14851} = 1.4073$ | $\frac{2.09}{14851} \times \frac{122825}{28.05} = 0.6162$ |

determined in duplicate runs on a selected reference standard, are used to convert peak areas (or peak heights) of the unknown sample to mol percent.

7.2 *Apparatus Preparation*—With the proper column(s) and liquid sample valve in place, adjust operating conditions to optimize the resultant chromatogram. Using the reference standard, introduce the sample in the following manner.

7.3 *Introduction of Sample*:

7.3.1 *Floating Piston Cylinders*—For floating piston cylinders, refer to Fig. 3 and proceed as follows: connect a source of inert gas to Valve *A* so that pressure can be applied to the sample by means of the floating piston. Apply a pressure not less than 200 psi (1379 kPa) above the vapor pressure of the sample at the temperature of the sample injection valve.

7.3.2 Thoroughly mix the sample.

7.3.3 Connect the sample end of the cylinder, Valve *B*, to the inlet of the chromatograph liquid sample valve. All connections and tubing are to be made of material impervious to the sample composition and of as small diameter and shortest length of plumbing as is practical, thereby minimizing dead space. All tubing between sample cylinder and liquid sampling valve shall be the same diameter.

7.3.4 With Valve *C* closed, open Valve *B* to fill the sample valve and associated lines.

7.3.5 Slowly crack Valve *C* to purge the sample valve. When the purge is complete, close Valve *C*. **Caution**—Use extreme care to ensure that no flashing of sample occurs in the inlet sampling line and valve system. Always meter at sample purge Valve *C*, never at sample Valve *B*. The sample line and valve system should remain at 1379 kPa (200 psi) above the vapor pressure of the product.

7.3.6 Operate the liquid sample valve either manually or automatically to inject the liquid sample into the carrier gas flow immediately ahead of the chromatographic column. Actuate the sample valve quickly and smoothly to place the sample on the column all at once and to ensure continuous carrier gas flow through the column.

7.3.7 *Double-Valve Displacement Cylinders*—For doublevalve displacement cylinders refer to Fig. 4 and Fig. 5 and proceed as follows: Connect the sample Cylinder *B* to Cylinder *A* so repressurizing fluid can be entered into the bottom of Cylinder *B*. With this configuration the hydrocarbon sample is taken from the upper portion of the cylinder. Pressurize Cylinder *A* with an inert gas and maintain a pressure at least 200 psi (1379 kPa) above the vapor pressure of the hydrocarbon sample at operating conditions. Open the necessary valves to admit pressurizing fluid into the sample Cylinder *B*.

7.3.8 Mix the sample thoroughly by gently inverting Cylinder *B* several times. Fix the cylinder in a vertical position by means of a ringstand, or similar device.

7.3.9 Connect the sample outlet Valve *B* on Cylinder *B* to the inlet of the chromatograph liquid sample valve. All connections and tubing are to be made of material impervious to the sample composition and of as small diameter and shortest length of plumbing as is practical, thereby minimizing "dead space." All tubing between sample cylinder and liquid valve should be the same diameter.

7.3.10 With Valve *C* closed, open Valve *B* to fill the sample valve and associated lines.

7.3.11 Slowly crack Valve *C* to purge the sample valve. When the purge is complete close Valve *C*. **Caution**—Use extreme care to ensure that no flashing of sample occurs in the inlet sampling line and valve system. Always meter at sample purge Valve *C*, never at sample Valve *B*. The sample line and valve system should remain at 1379 kPa (200 psi) above the vapor pressure or the product.

7.3.12 Operate the liquid sample valve either manually or automatically to inject the liquid sample into the carrier gas flow immediately ahead of the chromatographic column. The liquid sample valve should be actuated quickly and smoothly to place the sample on the column all at once and to ensure continuous carrier gas flow through the column.

7.4 *Valve Switching*:

7.4.1 After the elution of *n*-hexane the carrier gas flow is reversed by means of a backflush valve operated manually or automatically. (An acceptable backflush valve configuration is shown in Fig. 6.) Reversing carrier flow causes severe baseline deviations (see Fig. 1). When using electronic digital integrators, exercise care to ensure integration does not occur until baseline is adequately reestablished. The resulting irregular shaped $C_7$ plus peak is eluted over a period of time equivalent to time on forward flow minus the retention time for the air peak. Only after baseline is reestablished should the run be terminated and carrier flow returned to original direction.

7.4.2 An alternative to backflushing after normal hexane is the use of a precut column to group the $C_7$ plus fraction at the beginning of the chromatogram as a single peak. (An acceptable valve configuration for the precut method is illustrated in Fig. 7.) The valve position is switched when normal hexane and lighter components have traveled through Column 2 and are in Column 1. At this point, heptanes and heavier components are retained in Column 2. When the valve is reversed, the heptanes plus fraction will elute from Column 2 first. Baseline must be clearly and distinctly established before elution of the $C_7$ plus peak so an accurate measurement of this peak can be obtained. After the elution of *n*-hexane, terminate the run and return the valve to the initial position.

## 8. Unknown Sample Run

8.1 Obtain a chromatogram of the unknown sample in accordance with instructions outlined in Section 7.

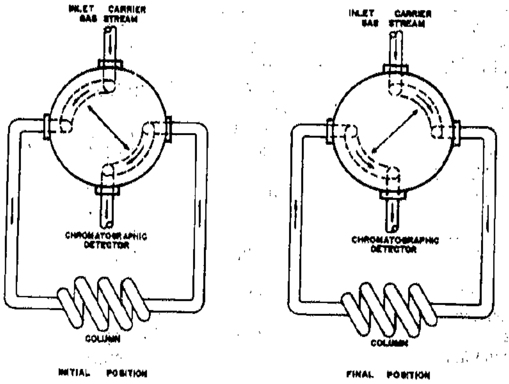

FIG. 6 Backflush Valve Configuration

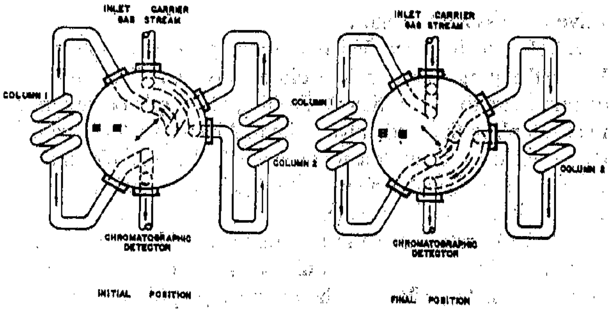

**FIG. 7 Precut Valve Configuration**

8.1.1 Determine peak areas (or peak heights) from the chromatogram for all components. These data shall be used to calculate composition of the unknown in accordance with instructions outlined in 9.2.

## 9. Calculation

9.1 *Calculation of Response Factors Using a Known Reference Standard*:

9.1.1 Determine the peak area (or peak height) of each component nitrogen/air through heptanes plus (if applicable) from the chromatogram of the known reference standard.

NOTE 8—The backflush peak (where applicable) for heptanes plus is considered to be a single component for the purpose of this calculation. In addition, the peak area method shall be used in calculating the heptanes plus fraction.

9.1.2 Calculate a response factor for each of the preceding components in accordance with the following equation (see Table 2):

$$K = \frac{M}{P} \tag{1}$$

where:

$K$ = response factor,
$M$ = mol percent of component in reference standard, and
$P$ = peak area or peak height in arbitrary units (millimetres, square inches, counts, and so forth) corrected to maximum sensitivity.

9.1.3 An alternative method of determining response factors is the use of a single reference component in the standard. Calculate a relative response factor for each component in accordance with the following equation (see Table 2):

$$KF_i = \frac{M_i}{P_i} \times \frac{P_{RP}}{M_{RP}} \tag{2}$$

where:

$KF_i$ = relative response factor for component $i$,
$M_i$ = mol percent of component $i$ in reference standard,
$P_i$ = peak area (or peak height) in arbitrary units corrected to maximum sensitivity for component $i$,
$P_{RP}$ = peak area (or peak height) of the component selected as the reference peak, and
$M_{RP}$ = mol percent of the component in reference standard as the reference peak.

From the equation defining the relative response factor, the component chosen as the reference peak always has a response factor of 1.000.

9.2 *Calculation of Mol Percent of Components in Unknown Sample*:

9.2.1 Determine peak area (or peak height) of each component nitrogen/air through heptanes plus from the chromatogram of the unknown sample using the same arbitrary units as in 9.1.

9.2.2 Calculate the concentration in mol percent of each of these components in accordance with the following equation (see Table 3):

$$M = P \times K \tag{3}$$

where:

$M$ = mol percent of component in unknown,
$P$ = peak area (or peak height) of each component in unknown sample, and

**TABLE 3 Calculation of Unknown Sample Using Response Factors from Table 2**

| Component | Peak Area | Mol % Response Factor (×10 000) | Unnormalized Mol % | Normalized Mol % | Relative Response Factor ($C_3$ Reference Peak) | Unnormalized Area × RRF | Normalized Mol % |
|---|---|---|---|---|---|---|---|
| Nitrogen/Air | 91 | 3.2154 | 0.02926 | 0.04 | 1.4080 | 128 | 0.04 |
| Methane | 4720 | 4.1948 | 1.97995 | 2.85 | 1.8368 | 8670 | 2.85 |
| Carbon Dioxide | 2615 | 3.1888 | 0.83387 | 1.20 | 1.3963 | 3651 | 1.20 |
| Ethane | 64090 | 2.9598 | 18.96936 | 27.27 | 1.2960 | 83061 | 27.27 |
| Propane | 113346 | 2.2837 | 25.88483 | 37.21 | 1.0000 | 113346 | 37.21 |
| Isobutane | 31590 | 1.9927 | 6.29494 | 9.05 | 0.8726 | 27565 | 9.05 |
| *n*-Butane | 33672 | 1.9491 | 6.56301 | 9.44 | 0.8535 | 28739 | 9.44 |
| 2,2-Dimethylpropane | | | | | | | |
| Isopentane | 16368 | 1.7077 | 2.79516 | 4.02 | 0.7478 | 12240 | 4.02 |
| N-Pentane | 17235 | 1.6287 | 2.80706 | 4.04 | 0.7132 | 12292 | 4.04 |
| 2,2-Dimethylbutane | 75 | 1.5152 | 0.01136 | 0.02 | 0.6635 | 50 | 0.02 |
| 2,3-Dimethylbutane | 4027 | 1.4181 | 0.57107 | 0.82 | 0.6210 | 2501 | 0.82 |
| 2-Methylpentane<br>3-Methylpentane<br>Cyclopentane | 1584 | 1.7076 | 0.27048 | 0.39 | 0.7477 | 1184 | 0.39 |
| *n*-Hexane | 4521 | 1.4613 | 0.66065 | 0.95 | 0.6399 | 2893 | 0.95 |
| Heptanes Plus | 13335 | 1.4073 | 1.87663 | 2.70 | 0.6162 | 8217 | 2.70 |
| | | | 69.54763 | 100.00 | | 304537 | 100.00 |

$K$ = response factor as determined in 9.1.

9.2.2.1 Total the mol percent values and normalize to 100 %.

9.2.3 Using the relative response factors calculate the concentration in mol percent of each of these components in accordance with the following equation (see Table 3):

$$M_i = \frac{KF_i \times P_i}{\sum_{i=1}^{n}(KF_i \times P_i)} \times 100 \quad (4)$$

where:

$M_i$ = mol percent of component $i$ in unknown,

$KF_i$ = relative response factor for component $i$,

$P_i$ = peak area (or peak height) of component $i$ in unknown, and

$\sum_{i=1}^{n}(KF_i \times P_i)$ = summation of all relative response areas in the chromatogram.

9.2.3.1 Total mol percent values and normalize to 100 %.

## 10. Precision and Bias

10.1 The precision of this test method as determined by statistical examination of interlaboratory results is as follows:

10.1.1 *Repeatability*—The difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

| Component | Mol % Range | Percent Relative Repeatability |
|---|---|---|
| Nitrogen | 0.01–.89 | 9 |
| Carbon Dioxide | 0.01–2.3 | 4 |
| Methane | 1.6–4.5 | 4 |
| Ethane | 27.–54. | .5 |
| Propane | 28.–34. | .5 |
| Isobutane | 3.0–8.8 | 1 |
| *n*-Butane | 6.0–9.3 | 1 |
| Isopentane | 1.0–3.9 | 2 |
| *n*-Pentane | 2.0–3.8 | 2 |
| $C_6^+$ | 3.6–5.7 | 2 |

10.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

| Component | Mol % Range | Percent Relative Reproducibility |
|---|---|---|
| Nitrogen | 0.01–89 | 60 |
| Carbon Dioxide | 0.01–2.3 | 30 |
| Methane | 1.6–4.5 | 10 |
| Ethane | 27.–54. | 2 |
| Propane | 38.–34. | 2 |
| Isobutane | 3.0–8.8 | 4 |
| *n*-Butane | 6.0–9.3 | 4 |
| Isopentane | 1.0–3.9 | 6 |
| *n*-Pentane | 2.0–3.8 | 6 |
| $C_6^+$ | 3.6–5.7 | 10 |

NOTE 9—The repeatability and reproducibility statements for this procedure are from the statistical data obtained in a GPA cooperative test program completed in 1986. The testing program included six samples analyzed in a round robin by eight laboratories.

10.2 *Bias*—The bias of the procedure in this test method has not been determined but is now under consideration.

## 11. Keywords

11.1 chromatography; demethanized hydrocarbons; liquefied petroleum gases; natural gas liquids

# ANNEXES

## (Mandatory Information)

## A1. FIDELITY OF SELECTED REFERENCE STANDARDS

A1.1 Referring to Section on Summary of Test Method, it is noted that the test method is based on response factors calculated from a selected reference standard using peak area measurements. Liquid reference standards are difficult to prepare and are subject to change in composition during use. Hence it is virtually mandatory that the reference standard be authenticated in some manner when received and periodically during use. One simple approach is described as follows:

A1.1.1 Determine mol percent response factors for normal hydrocarbons using area measurements of peaks recorded on chromatogram of reference standard run (see 9.1.2).

A1.1.2 Determine molecular weight corresponding to each component hydrocarbon in A1.1.1.

A1.1.3 Using log/log paper plot the response factor on the vertical scale versus molecular weights on the horizontal scale (see Fig. A1.1).

A1.1.4 If all is in order the resultant plot will be essentially a straight line with a negative slope. For a specific instrument, the slope of the plot should remain essentially constant. A change in the angle usually indicates a change in blend composition.

A1.1.5 An example follows using data from Table 2 in this test method (see Table A1.1).

A1.2 It should be noted the relationship described in A1.1.1-A1.1.5 is valid for reference blends in the vapor state as well as the liquid state, so long as the following conditions are met.

A1.2.1 Chromatogram is obtained using a thermal conductivity detector.

A1.2.2 Peak areas in arbitrary units are used for peak measurements.

A1.2.3 Known concentrations of hydrocarbon components

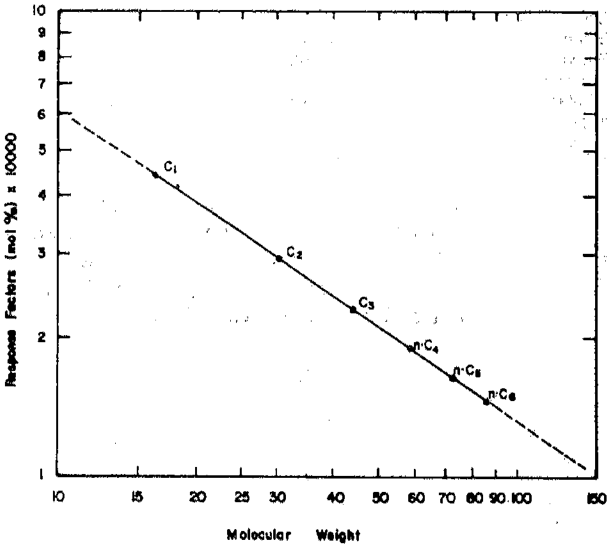

FIG. A1.1 Response Factors (mol %) Versus Molecular Weight

TABLE A1.1 Response Factors and Mol Weights Normal Hydrocarbon Components[A]

| Component | Response Factor × $10^{-4}$ | Mol Weight |
|---|---|---|
| Methane | 4.195 | 16.043 |
| Ethane | 2.960 | 30.070 |
| Propane | 2.284 | 44.097 |
| *n*-Butane | 1.949 | 58.123 |
| *n*-Pentane | 1.629 | 72.150 |
| *n*-Hexane | 1.461 | 86.177 |

[A] Initially with a new system and a new blend this check should be performed often, say once a day for the first week to satisfy the operator that the component analysis furnished with the blend is essentially correct. After this time the check should be performed each time a calibration run is made to verify the continued fidelity of the selected reference blend.

in the known reference blend are expressed in mol %.

A1.3 In addition to authentication of reported composition of a new blend and periodically verifying its validity, this plot can be used to:

A1.3.1 Reduce the frequency of calibrations required.

A1.3.2 Reveal calculation and interpretation errors in calibration runs.

A1.3.3 Pick off factors for components not in the standard by extrapolating the plot. A factor for the back flush peak can be picked off if the molecular weight can be satisfactorily estimated.

## A2. DETERMINATION OF RESPONSE FACTORS

### A2.1 Linearity Check

A2.1.1 In order to establish linearity of response for the thermal conductivity detector, it is necessary to carry out the procedure outlined as follows:

A2.1.2 The major component of interest (methane for natural gas) is charged to the chromatograph by means of the fixed-size sample loop at partial pressure of 100 to 700 mm of Hg in increments of 100 mm. The peak area of the methane is plotted versus partial pressure. Any deviation from linearity indicates the fixed volume sample loop is too large. The sample size should be reduced until the pure major component is linear over the concentration range expected in the samples.

A2.1.2.1 Connect the pure component source to the sample entry system. Evacuate the sample entry system and observe manometer for any leaks. (See Fig. A2.1 for a suggested manifold arrangement.) The sample entry system shall be vacuum tight.

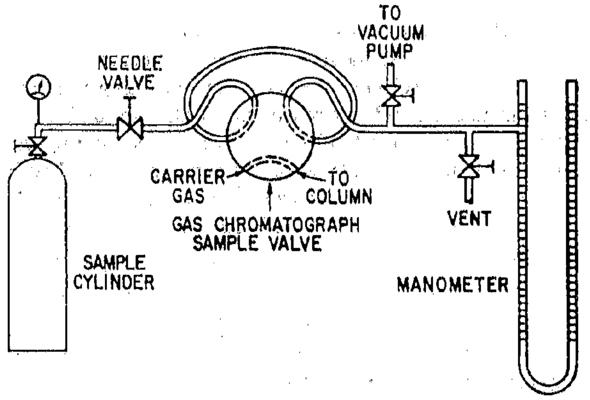

FIG. A2.1 Suggested Manifold Arrangement for Entering Vacuum Samples

A2.1.2.2 Carefully open the needle valve to admit the pure component up to 100 mm of partial pressure.

A2.1.2.3 Record exact partial pressure and actuate sample valve to place sample onto column. Record peak area of pure component.

A2.1.2.4 Repeat A2.2.3 for 200, 300, 400, 500, 600, and 700 mm of mercury. Record peak area obtained at each pressure.

A2.1.2.5 Plot the area data versus partial pressure on the *x* and *y* axes of linear graph paper as shown in Fig. A2.2.

NOTE A2.1—Experience has shown that if the major component is linear over the expected concentration range in the sample, the lesser components will also be linear. Methane and ethane exhibit less than 1 % compressibility at 760 mm Hg and are therefore the components of choice for linearity checks.

NOTE A2.2—**Caution:** *n*-Butane at atmospheric pressure exhibits 3.5 % compressibility, which, if the detector response is linear, will produce a nonlinear response opposite to detector non-linearity.

### A2.2 Calibration Procedure

A2.2.1 Response factors of the components of interest can be established in two ways. The routine method is to use a gas reference standard of known composition to determine response factors, provided all components in the reference standard and in the unknown samples lie within the proven linear range for a specific chromatography instrument. An acceptable non-routine method of determining response factors is to charge the pure components to the chromatograph. The latter method is described in Annex A1.

A2.2.1.1 Connect the reference standard gas to the sample entry system. Evacuate the sample entry system and observe the manometer for any leaks.

A2.2.1.2 Carefully open the needle valve to admit reference standard gas up to some predetermined partial pressure.

NOTE A2.3—The use of some constant partial pressure below atmospheric pressure avoids variations in sample size due to changes in barometric pressure.

A2.2.1.3 Record the partial pressure and operate the gas sampling valve to place the sample onto the column. Record the chromatogram, integrator/computer peak areas, and peak retention times.

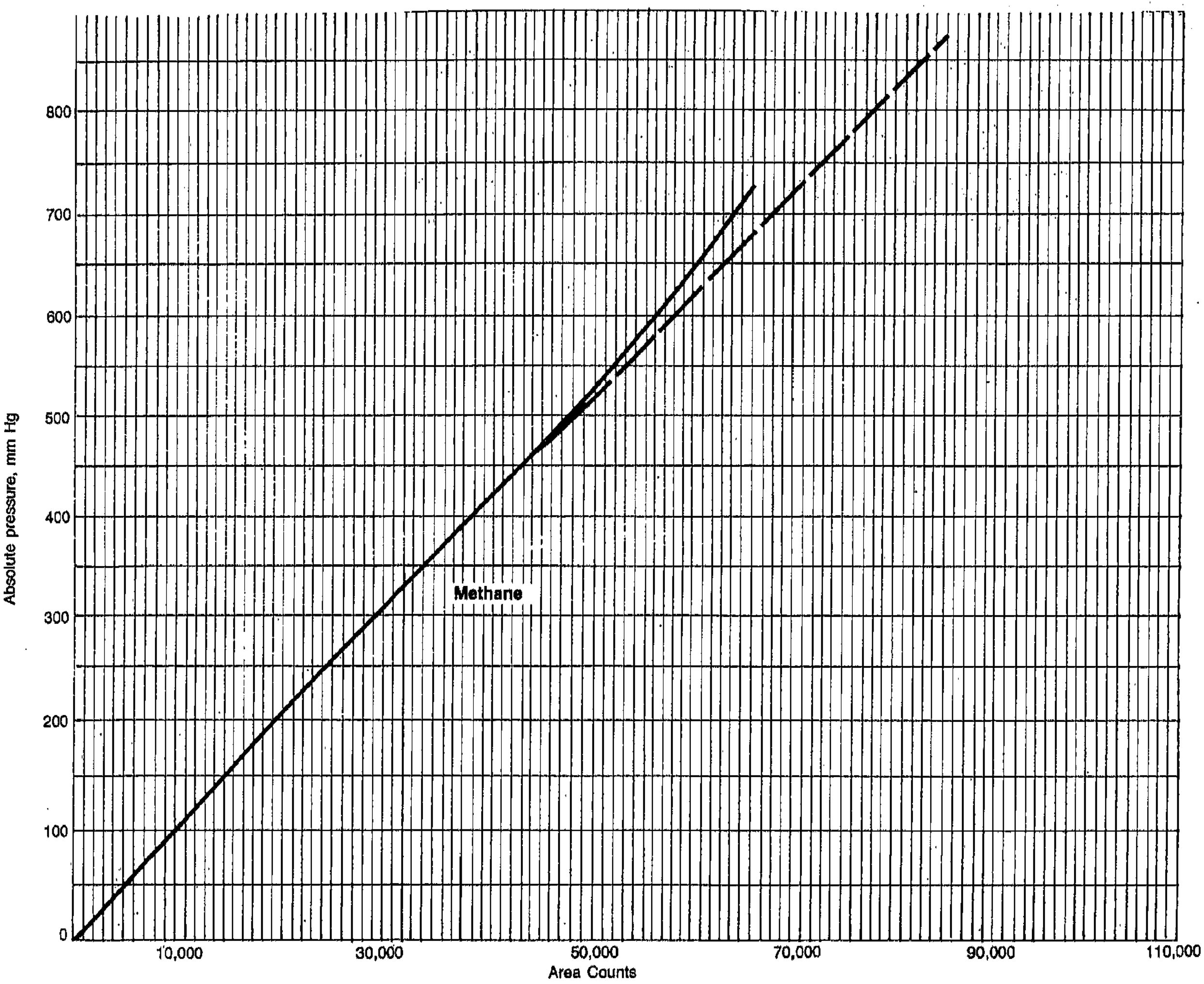

FIG. A2.2 Linearity of Detector Response

NOTE A2.4—It is recommended that the integrator/computer has the capability to print out retention times of peak maxima to aid in peak identification and to monitor instrument conditions for unknown changes.

## A3. PRECAUTIONARY STATEMENTS

### A3.1 Flammable Liquefied Gases

A3.1.1 Keep away from sparks and open flame.

A3.1.2 Keep container closed.

A3.1.3 Use with adequate ventilation.

A3.1.4 Avoid buildup of vapors and eliminate all sources of ignition, especially nonexplosive electrical devices and heaters.

A3.1.5 Avoid prolonged breathing of vapor or spray mist.

A3.1.6 Avoid prolonged or repeated skin contact.

### A3.2 Compressed Gases (Helium, Nitrogen)

A3.2.1 Keep container closed.

A3.2.2 Use adequate ventilation.

A3.2.3 Do not enter storage areas unless adequately ventilated.

A3.2.4 Always use a pressure regulator.

A3.2.5 Release regulator tension before opening cylinder.

A3.2.6 Do not transfer to cylinder other than one in which gas is received.

A3.2.7 Do not mix gases in cylinders.

A3.2.8 Do not drop cylinders.

A3.2.9 Make sure cylinder is supported at all times.

A3.2.10 Stand away from cylinder outlet when opening cylinder valve.

A3.2.11 Keep cylinder out of sun and away from heat.

A3.2.12 Keep cylinder from corrosive environment.

A3.2.13 Do not use cylinder without label.

A3.2.14 Do not use dented or damaged cylinder.

A3.2.15 For technical use only. Do not use for inhalation purposes.

# CERTIFICATE

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Designation: D 2622 – 98

# Standard Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry[1]

This standard is issued under the fixed designation D 2622; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

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

## 1. Scope

1.1 This test method covers the determination of total sulfur in petroleum and petroleum products that are single-phase and either liquid at ambient conditions, liquifiable with moderate heat, or soluble in hydrocarbon solvents. These materials can include diesel fuel, jet fuel, kerosine, other distillate oil, naphtha, residual oil, lubricating base oil, hydraulic oil, crude oil, unleaded gasoline, M-85 and M-100.

1.2 The interlaboratory study on precision covered a variety of materials with sulfur concentrations ranging from approximately 3 mg/kg to 5.3 mass %. For a subset of these samples, with sulfur concentrations below 60 mg/kg, the repeatability standard deviation ($S_r$) was 1.5 mg/kg. An estimate of the limit of detection is 3 × $S_r$, and an estimate of the limit of quantitation[2] is 10 × $S_r$. However, because instrumentation covered by this test method can vary in sensitivity, the applicability of the test method at sulfur concentrations below approximately 20 mg/kg must be determined on an individual basis.

1.3 Samples containing more than 5.0 mass % sulfur can be diluted to bring the sulfur concentration of the diluted material within the scope of this test method.

1.4 Volatile samples (such as high vapor pressure gasolines or light hydrocarbons) may not meet the stated precision because of selective loss of light materials during the analysis.

1.5 A fundamental assumption in this test method is that the standard and sample matrix are well matched. Matrix mismatch can be caused by C/H ratio differences between samples and standards (see Tables 1 and 2) or by the presence of other heteroatoms (see Table 3).

1.6 The values stated in either SI units or angstrom units are to be regarded separately as standard.

1.7 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard information, see Note 1.

## 2. Referenced Documents

2.1 *ASTM Standards:*

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

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products[3]

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

D 4927 Test Methods for Elemental Analysis of Lubricant and Additive Components—Barium, Calcium, Phosphorus, Sulfur, and Zinc by Wavelength-Dispersive X-Ray Fluorescence Spectroscopy[4]

E 29 Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications[5]

## 3. Summary of Test Method

3.1 The sample is placed in the X-ray beam, and the peak intensity of the sulfur Kα line at 5.373 Å is measured. The background intensity, measured at a recommended wavelength of 5.190 Å (5.437 Å for a Rh target tube) is subtracted from the peak intensity. The resultant net counting rate is then compared to a previously prepared calibration curve or equation to obtain the concentration of sulfur in mass %.

NOTE 1—**Warning:** Exposure to excessive quantities of X-radiation is injurious to health. The operator needs to take appropriate actions to avoid exposing any part of their body, not only to primary X-rays, but also to secondary or scattered radiation that might be present. The X-ray spectrometer should be operated in accordance with the regulations governing the use of ionizing radiation.

## 4. Significance and Use

4.1 This test method provides rapid and precise measurement of total sulfur in petroleum and petroleum products with a minimum of sample preparation. A typical analysis time is 1 to 2 min per sample.

4.2 The quality of many petroleum products is related to the amount of sulfur present. Knowledge of sulfur concentration is

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[1] This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.03.B on Spectrometric Methods.

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[2] *Analytical Chemistry*, Vol 55, 1983, pp. 2210–2218.

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

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

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

**TABLE 1 Comparison of NIST and ASTM Interlaboratory Study (RR) Results**

| NIST SRM | Sulfur, mass %, NIST | Sulfur, mass %, ASTM RR Average | C/H mass ratio | Apparent Bias, % Sulfur | Relative Bias, % | Signif icant |
|---|---|---|---|---|---|---|
| 1616a | 0.0146 | 0.0148 | 5.205 | 0.0002 | 1.37 | No |
| 1617a | 0.1731 | 0.1776 | 5.205 | 0.0045 | 2.60 | Yes |
| 2724a | 0.0430 | 0.0417 | 5.986 | -0.0013 | -3.02 | Yes |
| 1623c | 0.3806 | 0.3661 | 7.504 | -0.0145 | -3.81 | Yes |
| 2717 | 3.0220 | 2.948 | 8.229 | -0.0736 | -2.44 | Yes |
| 1621e | 0.948 | 0.8973 | 8.553 | -0.0507 | -5.35 | Yes |
| 1624c |  | 0.3918 | 6.511 |  |  |  |
| 2723 |  | 0.0299 | 5.937 |  |  |  |

**TABLE 2 Comparison of NIST and ASTM Interlaboratory Study (RR) Corrected Results, Mass % Sulfur**

NOTE—The correction factors were calculated from data determined with XRF-11. The correction formula, which is applicable when the base material used for the calibration standards is white oil, is:

$$S_{corrected} = S_{uncorrected} / (1.086 - 0.01511 \times C/H)$$

where

$C/H$ = mass ratio of carbon to hydrogen for the sample

Application of these correction factors requires separate determination of the C/H mass ratio. The significance was determined based on a $t$ test using a function of the NIST uncertainty at 1 sigma and the round robin reproducibility standard deviation.

| SRM | RR ID | NIST | RR Corrected | Apparent Bias | Relative Bias, % | Signif icant |
|---|---|---|---|---|---|---|
| 1616a | K2 | 0.0146 | 0.0147 | 0.0001 | 0.68 | No |
| 1617a | K1 | 0.1731 | 0.1763 | 0.0032 | 1.85 | No |
| 2724a | D2 | 0.0430 | 0.0419 | -0.0011 | -2.56 | No |
| 1623 c | R1 | 0.3806 | 0.3763 | -0.0043 | -1.13 | No |
| 2717 | R4 | 3.0220 | 3.065 | 0.0430 | 1.42 | No |
| 1621 e | R3 | 0.948 | 0.9382 | -0.0098 | -1.03 | No |
| 1624c | D3 |  | 0.397 |  |  |  |
| 2723 | D4 |  | 0.0300 |  |  |  |

**TABLE 3 Concentration of Interfering Elements**

| Element | Mass % Tolerated |
|---|---|
| Phosphorus | 0.3 |
| Zinc | 0.6 |
| Barium | 0.8 |
| Lead | 0.9 |
| Calcium | 1 |
| Chlorine | 3 |
| Ethanol (Note 12) | 8.6 |
| Methanol (Note 12) | 6 |

necessary for processing purposes. There are also regulations promulgated in federal, state, and local agencies that restrict the amount of sulfur present in some fuels.

4.3 This test method provides a means of determining whether the sulfur content of petroleum or a petroleum product meets specification or regulatory limits.

4.4 When this test method is applied to petroleum materials with matrices significantly different from the white oil calibration materials specified in this test method, the cautions and recommendations in Section 5 should be observed when interpreting results.

NOTE 2—Compared to other test methods for sulfur determination, Test Method D 2622 has high throughput, minimal sample preparation, and excellent precision, and is capable of determining sulfur over a wide range of concentrations. The equipment specified for Test Method D 2622 tends to be more expensive than that required for alternative test methods, such as Test Method D 4294. Consult the Index to ASTM Standards[6] for alternative test methods.

## 5. Interferences

5.1 When the elemental composition (excluding sulfur) of samples differs significantly from the standards, errors in the sulfur determination can result. For example, differences in the carbon-hydrogen ratio of sample and calibration standards introduce errors in the determination. Some other interferences and action levels are listed in Table 3.

5.2 M-85 and M-100 are fuels containing 85 and 100 % methanol, respectively. They have a high oxygen content leading to significant absorption of sulfur Kα radiation. Such fuels can, however, be analyzed using this test method provided either that correction factors are applied to the results (when calibrating with white oils) or that the calibration standards are prepared to match the matrix of the sample.

5.3 In general, petroleum materials with compositions that vary from white oils as specified in 9.1 can be analyzed with standards made from base materials that are of the same or similar composition. Thus a gasoline may be simulated by mixing *iso*octane and toluene in a ratio that approximates the expected aromatic content of the samples to be analyzed. Standards made from this simulated gasoline can produce results that are more accurate than results obtained using white oil standards.

5.4 Test Method D 4927 is the recommended test method for determination of sulfur in lubricating oils and lubricating oil additives because Test Methods D 4927 implements interelement correction factors.

## 6. Apparatus

6.1 *Wavelength Dispersive X-Ray Fluorescence Spectrometer (WDXRF)*, equipped for X-ray detection in the 5.37 Å range. For optimum sensitivity to sulfur, the instrument should be equipped with the following.

6.1.1 *Optical Path*, of helium.

6.1.2 *Pulse-Height Analyzer*, or other means of energy discrimination.

6.1.3 *Detector*, designed for the detection of long wavelength X-rays.

6.1.4 *Analyzing Crystal*, suitable for the dispersion of sulfur Kα X-rays within the angular range of the spectrometer employed. Pentaerythritol and germanium are popular although other materials, such as EDDT, ADP, graphite, and quartz can be used.

6.1.5 *X-ray Tube*, capable of exciting sulfur Kα radiation. Tubes with anodes of rhodium, chromium, and scandium are most popular although other anodes can be used.

## 7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that

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[6] *Annual Book of ASTM Standards*, Vol 00.01.

all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[7] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Di-n-butyl Sulfide*, a high-purity standard with a certified analysis for sulfur content. Use the certified sulfur content when calculating the exact concentrations of the calibration standards (see 9.1).

NOTE 3—It is essential to know the concentration of sulfur in the di-*n*-butyl sulfide, not the purity, since impurities may also be sulfur containing compounds.

7.3 *Drift Correction Monitor(s) (Optional)*—Several different materials have been found to be suitable for use as drift correction monitors. Examples of sulfur containing materials that have been found to be suitable include a renewable liquid petroleum material, a semipermanent solid, a pressed powder sample, a metal alloy, or a fused glass disk. The monitor's count rate, in combination with count time, shall be sufficient to give a relative counting error of less than 1 %. The count rate for the monitor sample is determined during calibration (see 9.4) and again at the time of analysis (see 10.1). These counting rates are used to calculate a drift correction factor (see 11.1)

7.3.1 Drift correction is usually implemented automatically in software, although the calculation can readily be done manually. For X-ray instruments that are highly stable, the magnitude of the drift correction factor may not differ significantly from unity.

NOTE 4—Calibration standards may be used for this purpose. Because it is desirable to discard standards after each determination, a lower cost material is suggested for daily use.

7.4 *White Oil*, containing less than 2 mg/kg sulfur or other suitable base material containing less than 2 mg/kg sulfur. When low level (<200 mg/kg) measurements are anticipated, then the sulfur content, if any, of the base material needs to be included in the calculation of calibration standard concentration (see 9.1).

7.5 *X-ray transparent film*—Any film that resists attack by the sample, is free of sulfur, and is sufficiently X-ray transparent can be used. Films can include polyester, polypropylene, polycarbonate, and polyimide. However, samples of high aromatic content can dissolve polyester and polycarbonate films.

7.6 *Helium Gas*, minimum purity 99.9 %.

7.7 *Counting Gas*, for instruments equipped with flow proportional counters.

7.8 *Sample Cells*, compatible with the sample and the geometry requirements of the spectrometer. Disposable cells are preferred.

7.9 *Calibration Check Samples*, portions of one or more liquid petroleum or product standards of known sulfur content and not used in the generation of the calibration curve. The check samples shall be used to determine the accuracy of the initial calibration. (see 9.5)

7.10 *Quality Control Samples*, stable petroleum or product samples representative of the samples of interest that are run on a regular basis to verify that the system is in statistical control (Section 13).

NOTE 5—Verification of system control through the use of QC samples and control charting is highly recommended. It is recognized that QC procedures are the province of the individual laboratory.

NOTE 6—Suitable QC samples can often be prepared by combining retains of typical samples.

## 8. Sampling and Specimen Preparation

8.1 Samples shall be taken in accordance with the instructions in Practices D 4057 or D 4177 when applicable.

8.2 When reusable sample cells are used, clean and dry cells before each use. Disposable sample cells shall not be reused. For each sample, an unused piece of X-ray film is required for the sample cell. Avoid touching the inside of the sample cell, the portion of the window film in the cell, or the instrument window that is exposed to X-rays. Oil from fingerprints can affect the reading when analyzing for low levels of sulfur. Wrinkles in the film will affect the intensity of the sulfur X-rays transmitted. Therefore, it is essential that the film be taut and clean to ensure reliable results. The analyzer may need recalibration if the type or thickness of the window film is changed. After the sample cell is filled, a small vent hole is provided.

8.3 Impurities or thickness variations, which may affect the measurement of low levels of sulfur, have been found in polyester films and may vary from lot to lot. Therefore, the calibration shall be checked after starting each new roll or batch of film.

## 9. Calibration

9.1 Prepare calibration standards by careful mass dilution of the certified di-*n*-butyl sulfide with white oil or other suitable base material (see 5.3). The standards, with accurately known sulfur concentrations, shall approximate the nominal sulfur concentrations listed in Table 4 for the sulfur concentration ranges of interest. Take into account any sulfur in the base material when calculating the concentration of standards below 0.02 mass %.

NOTE 7—If desired, additional standards can be analyzed with concentrations between those listed in Table 4.

NOTE 8—Commercially available standards can be used provided their sulfur concentrations are accurately known and they approximate the

TABLE 4 Sulfur Standards

| Sulfur Concentration, mass % | Sulfur Concentration, mass % | Sulfur Concentration, mass % |
|---|---|---|
| 0.0000[A] | 0.100 | 1.0 |
| 0.001 | 0.250 | 2.0 |
| 0.010 | 0.500 | 3.0 |
| 0.025 | | 4.0 |
| 0.050 | | 5.0 |
| 0.075 | | |

[A]Base material

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

nominal concentrations listed in Table 4.

9.2 Establish calibration curve data by carefully measuring the net intensity of the emitted sulfur radiation from each of the standards by the procedure described in Section 10 and Section 11.

9.3 Construct a calibration model by either:

9.3.1 Using the software and algorithms supplied by instrument manufacturer,

9.3.2 Fitting the data to one of the following equations:

$$S\,\% = (D + ER)(1+\alpha S) \text{ or} \qquad (1)$$

$$S\,\% = aR + bR^2 + c \qquad (2)$$

where:

$S$ = sulfur concentration in mass %,
$D$ = intercept of the calibration curve,
$E$ = slope of the calibration curve,
$R$ = net intensity for the sulfur radiation, and
$\alpha$ = correction factor for the effect of sulfur on the sulfur result and $a$, $b$, and $c$ are fitted constants.

NOTE 9—The factor $\alpha$ in Eq 1 can be determined empirically or theoretically. Equipment vendors can often supply theoretical alphas.

9.3.3 Plotting corrected net intensity in counts per second versus sulfur concentration. Plot the data in several small ranges to minimize non-linear effects.

NOTE 10—Calibration plots are linear to a minimum concentration of 0.10 mass % sulfur. The analyst should choose the other plotting ranges to match the testing requirements. Deviation from linearity can increase as sulfur concentration increases.

9.4 When using drift correction monitors, determine the intensity of the drift correction monitor sample(s) during the calibration procedure. The value determined corresponds to the factor $A$ in Eq 4 in 11.1.

9.5 Immediately after completing the calibration, determine the sulfur concentration of one or more of the calibration check samples (7.9). The measured value shall be in the range defined by the certified concentration ± the repeatability of this test method. When this is not the case, the calibration or calibration standards are suspect and corrective measures should be taken and the calibration rerun. The degree of matrix mismatch between samples and standards should also be considered when evaluating a calibration.

## 10. Procedure

10.1 When using drift correction monitors, prior to analyzing samples on a given day, analyze the drift correction monitor(s) and determine the counting rate, using the same material as used at the time of calibration. The value determined corresponds to the factor $B$ in Eq 4 in 11.1.

10.1.1 When the factor $F'$ is used in Eq 5 (Section 11), regularly analyze a blank sample to determine the factor $F'$ in Eq 5. On a sulfur free sample, such as the base material, determine the count rate at the appropriate sulfur peak and background angles.

10.2 Place the sample in an appropriate cell using techniques consistent with good practice for the particular instrument being used. Although sulfur radiation will penetrate only a small distance into the sample, scatter from the sample cell and the sample can vary. Laboratory personnel shall ensure that the sample cell is filled above a minimum depth, beyond which additional sample does not significantly affect the count rate. Generally, fill the sample cell to a minimum of three-fourths of the cell's capacity. Provide a small vent hole in the sample cell.

10.3 Place the sample in the X-ray beam and allow the X-ray optical path to come to equilibrium.

10.4 Determine the intensity of the sulfur K$\alpha$ radiation at 5.373 Å by making counting rate measurements at the precise angular settings for this wavelength.

NOTE 11—It is suggested that a sufficient number of counts be taken to satisfy at least a 1.0 % expected coefficient of variation (% rsd) when practical. When sensitivity or concentration, or both, make it impractical to collect a sufficient number of counts to achieve a 1.0 % coefficient of variation, accepted techniques, which will allow the greatest statistical precision in the time allotted for each analysis, should be used. The coefficient of variation is calculated as follows:

$$\text{coefficient of variation, \%} = (100\sqrt{Ns + Nb})/(Ns - Nb) \qquad (3)$$

where

$N_s$ = number of counts collected at sulfur line, and
$N_b$ = number of counts collected at background wavelength in the same time interval taken to collect $N_s$ counts.

10.5 Measure background count-rate at a previously-selected, fixed, angular setting, adjacent to the sulfur K$\alpha$ peak.

NOTE 12—Suitability of any background setting will depend on the X-ray tube anode employed. A wavelength of 5.190 Å is recommended where chromium or scandium is used whereas 5.437 Å has been found suitable for rhodium, 2θ, peak and background, angles for various crystals are listed in Table 5.

10.6 Determine the corrected counting rate and calculate the concentration of the sample as described in Section 11.

10.7 When, from the measurements made in accordance with 10.2-10.6, the counting rate is higher than that of the highest point of the calibration curve, dilute the sample with the base material used to prepare the calibration standards until the sulfur counting rate is within the limits of the calibration curve and repeat the procedure described in 10.3-10.6.

10.8 When the sample is known or believed to contain concentrations of interfering substances higher than those listed in Table 3, dilute the sample by mass with base material to concentrations below those listed.

NOTE 13—The concentrations of substances in Table 3 were determined by the calculation of the sum of the mass absorption coefficients times

TABLE 5 2θ Angles for Various Crystals

| Crystal | 2d (Å) | S Kα (5.373 Å) | Background (5.190 Å) | Background (5.437 Å) |
|---|---|---|---|---|
| NaCl (200) | 5.6406 | 144.56 | 133.89 | 149.12 |
| EDDT (020) | 8.806 | 75.18 | 72.21 | 76.24 |
| ADP (101) | 10.640 | 60.65 | 58.39 | 61.46 |
| Pentaerythritol (002) | 8.742 | 75.85 | 72.84 | 76.92 |
| Quartz (101) | 6.5872 | 106.93 | 101.81 | 106.97 |
| Ge (111) | 6.532 | 110.68 | 105.23 | 112.68 |
| Graphite (002) | 6.706 | 106.45 | 101.38 | 106.29 |
| Graphite (002) (PG) | 6.74 | 105.72 | 100.71 | 107.55 |

mass fraction of each element present. This calculation was made for dilutions of representative samples containing approximately 3 % of interfering substances and 0.5 % sulfur.

10.8.1 The data collected showed reasonable X-ray results when the calculated sum of mass absorption coefficients times mass fractions for samples was not greater than 4 to 5 % above the sum of mass absorption coefficients times mass fractions for the calibration standards. Absorption interferences are additive, and they are only minimized by dilution, not completely eliminated. Table 3 is therefore to be used as a guide to concentrations that can be tolerated without significant error, not as an absolute quantity.

NOTE 14—The effect of matrix interferences can also be corrected on an empirical or theoretical basis. Except for gasohol, these corrections are not within the scope of this test method.

NOTE 15—The concentrations of ethanol and methanol were calculated using a theoretical mixture of hydrocarbons and di-butyl sulfide to which ethanol (or methanol) was added until the sum of the mass coefficients times mass fractions increased by 5 %. In other words, the amount of ethanol (or methanol) that caused a negative 5 % error in the sulfur measurement was calculated. This information is included in Table 3 to inform those who wish to use Test Method D 2622 for determining sulfur in gasohol (or M-85 and M-100) of the nature of the error involved.

10.8.2 Thoroughly mix the blend to ensure homogeneity, and transfer it to the instrument for measurement.

10.8.3 Determine the sulfur content of the blend in the normal manner as described in 10.2-10.6, and calculate the sulfur content of the original sample as described in Section 11.

## 11. Calculation

11.1 When using the drift correction monitor described in 7.3, calculate a correction factor for changes in daily instrument sensitivity as follows:

$$F = A/B \tag{4}$$

where:

$A$ = counting rate of the drift correction monitor as determined at the time of calibration (see 9.4), and

$B$ = counting rate of the drift correction monitor as determined at the time of analysis (see 10.1).

NOTE 16—The inclusion of this factor in Eq 5 may not be necessary or desirable with some instrumentation. In this case $F$ is set to unity. It is recommended that the user chart the $F$ factor and develop criteria for its application based on the stability of the instrumentation and standard SQC principles.

11.2 Determine the corrected net counting rate as follows:

$$R = [(C_K/S_1) - (C_B F'/S_2)]F \tag{5}$$

where:

$C_K$ = total counts collected at 5.373 Å,

$C_B$ = total counts collected at the background location chosen in 10.5,

S1 and S2 = seconds required to collect $C$ counts,

$R$ = corrected net counting rate, and

$F'$ = (counts/s at 5.373 Å)/(counts/s) at background chosen in 10.5 on a sample containing no sulfur.

11.2.1 The use of the factor $F$ in Eq 5 is optional. (Note 14)

11.2.2 The inclusion of the factor $F'$ in Eq 5 is optional. In general it is needed for multichannel spectrometers, which use different spectrometer channels to measure peak and background intensities.

NOTE 17—Charting the $F'$ factor, even if it is not used in Eq 5, will alert the user to changes in instrument operation due to contamination of system elements, such as crystals, collimators, and fixed windows.

11.3 Calculate the sulfur content of the sample by inserting the corrected net counting rate from Eq 5 in the chosen calibration model from Section 9. In many cases the instrument vendor will provide software or the required calculations.

11.4 Calculate the concentration of sulfur in samples, which have been diluted, as follows:

$$S, \text{mass \%} = S_b \times [(W_s + W_o)/W_s] \tag{6}$$

where:

$S_b$ = mass % sulfur in diluted blend,

$W_s$ = mass of original sample, g, and

$W_o$ = mass of diluent, g.

The instrument vendor may have provided software to perform this calculation when required masses are input.

## 12. Reporting

12.1 For samples analyzed without dilution, report the result calculated in 11.3. For samples that have been diluted, report the result calculated in 11.4. Report the result as the total sulfur content, mass %, to three significant figures for concentrations greater than 0.0100 %, to two significant figures between 0.0010 % and 0.0099 % and to one significant figure below 0.0010 %. For guidance in properly rounding significant figures, refer to the rounding method in Practice E 29. State that the results were obtained according to Test Method D 2622.

12.2 When analyzing M-85 or M-100 fuels with a calibration determined with white oil based standards, divide the result obtained in 11.3 as follows (Note 13):

$$S\,(\text{in M}-85), \text{mass \%} = S, \text{mass \%} / 0.59 \tag{7}$$

$$S\,(\text{in M}-100), \text{mass \%} = S, \text{mass \%} / 0.55 \tag{8}$$

This correction is not required if the standards are prepared in the same matrix as the samples, as described in 5.2.

NOTE 18—One laboratory compared the sulfur sensitivity for M-85 and M-100 fuels to the sulfur sensitivity for paraffin oils (Test Method D 2622) by theoretical calculation.[8] This laboratory and one other found excellent agreement between the theoretical and measured factors, therefore creating these correction factors.

## 13. Quality Control

13.1 It is recommended that each laboratory establish a program to ensure that the measurement system described in this test method is in statistical control. One part of such a program might be the regular use and charting[9] of quality control samples (see7.10). It is recommended that at least one type of quality control sample be analyzed that is representative of typical laboratory samples.

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[8] XRF-11, Criss Software, Largo, MD.

[9] ASTM MNL 7, Manual on Presentation of Data and Control Chart Analysis, Section 3, Control Chart for Individuals.

## 14. Precision and Bias [10]

14.1 The precision of the test method was determined by statistical analysis of results obtained in two separate interlaboratory studies. The first interlaboratory study (Case I) covered distillates, kerosines, residual oils, and crude oils. The second interlaboratory study (Case II) covered a set of 21 gasolines. Neither M-85 nor M-100 was included. The ranges of sulfur concentrations represented by the sample sets, together with the precisions, are listed in 14.1.1 and 14.1.2.

14.1.1 *Repeatability*—The difference between successive test results obtained by the same operator with the same apparatus under constant operation conditions on identical test material would, in the long run, in the normal and correct operation of the test method exceed the following values only in one case in twenty:

| Case | Range, Mass % | Repeatability |
|---|---|---|
| I | 0.006 - 5.3 | $0.02651\ X^{0.9}$ |
| II | 0.0003 - 0.093 | $0.00736\ (X+0.0002)^{0.4}$ |

where $X$ is the sulfur concentration, mass %.

14.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method exceed the following values only in one case in twenty:

| Case | Range, Mass % | Reproducibility |
|---|---|---|
| I | 0.006 - 5.3 | $0.0913\ X^{0.9}$ |
| II | 0.0003 - 0.093 | $0.0105\ (X+0.0002)^{0.4}$ |

where $X$ is the sulfur concentration, mass %.

14.2 *Bias*—One interlaboratory study (Case I) included eight NIST reference materials. The certified sulfur value, interlaboratory round robin (RR) value, measured C/H, apparent bias, and relative bias are given in Table 1. Table 2 compares NIST value with sulfur concentrations corrected for C/H ratio. The white oil was assumed to have a C/H mass ratio of 5.698 ($C_{22}H_{46}$).

14.2.1 The variation in relative sulfur sensitivity as a function of C/H mass ratio is shown graphically in Fig. 1.

## 15. Keywords

15.1 analysis; diesel; gasoline; jet fuel; kerosine; petroleum; spectrometry; sulfur; X-ray

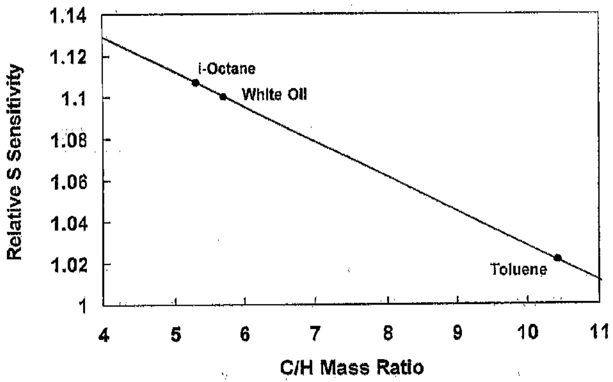

FIG. 1 Relative Sulfur Sensitivity

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[10] Support data are available from ASTM Headquarters. Request RR:D02-1428.

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Designation: D 2724 – 87(Reapproved 1995)

# Standard Test Methods for Bonded, Fused, and Laminated Apparel Fabrics[1]

This standard is issued under the fixed designation D 2724; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 These test methods cover procedures for characterizing the delamination, strength of bond, appearance, and shrinkage propensity of bonded, fused, and laminated apparel fabrics after drycleaning and laundering.

1.2 The values stated in SI units are to be regarded as standard; the values in parentheses are provided as information only.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

## 2. Referenced Documents

2.1 *ASTM Standards:*

D 76 Specification for Tensile Testing Machines for Textiles[2]

D 123 Terminology Relating to Textiles[2]

E 337 Test Method for Measuring Humidity with a Psychrometer (the Measurement of Wet- and Dry-Bulb Temperatures)[3]

2.2 *AATCC Standard:*

124 Appearance of Durable Press Fabrics After Repeated Home Launderings[4]

2.3 *Federal Trade Commission Trade Regulation Rule:*

16 CFR 423 Care Labeling of Textile Wearing Apparel and Certain Piece Goods[5]

## 3. Terminology

3.1 *blister, n—in bonded, fused, or laminated fabrics,* a bulge, swelling, or similar surface condition on either the face fabric or the backing fabric characterized by the fabric being raised from the plane of the underlying component over a limited area to give a puffy appearance.

3.2 *bonded fabric, n*—a layered fabric structure wherein a face or shell fabric is joined to a backing fabric, such as tricot, with an adhesive that does not significantly add to the thickness of the combined fabrics.

3.2.1 *Discussion*—In this context a thin layer of foam is considered an adhesive when the cell structure is completely collapsed by a flame.

3.3 *bond strength, n— of bonded, fused, or laminated fabrics,* the tensile force expressed in ounces per 25 mm (1 in.) of width, required to separate the component layers under specified conditions.

3.4 *bubble*—See preferred term *blister.*

3.5 *crack mark, n—in bonded, fused, or laminated fabrics,* a sharp break or crease in the surface contour of either the face fabric or the backing fabric that becomes evident when the bonded, fused, or laminated composite is rolled, bent, draped, or folded.

3.5.1 *Discussion*—Crack marks are usually the result of combining tight fabric constructions at least one of which does not have sufficient residual stretch to allow the combined fabrics to be bent in an arc without producing crack marks on the concave side of the arc. Crack marks also occur when bonded fabrics are allowed to remain in a creased or wrinkled state before full adhesive cure has taken place. Other causes include the use of excessive adhesive in bonding, or excessive foam thicknesses and excessive foam collapse in flame lamination.

3.6 *foam tear, n*—a condition wherein the foam portion of a laminated fabric ruptures prior to the failure of the bond.

3.7 *fused fabric, n*—a type of bonded fabric made by adhering a fusible fabric to another fabric, such as for use as an interlining.

3.8 *fusible fabric, n*—a utilitarian fabric which has a thermoplastic adhesive applied to one side, sometimes in a pattern of dots, so that the surface can be bonded to another fabric surface by the use of heat and pressure.

3.9 *interlining, n*—any textile which is intended for incorporation into an article of wearing apparel as a layer between an outer shell and an inner lining.

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[1] These test methods are under the jurisdiction of ASTM Committee D13 on Textiles, and are the direct responsibility of Subcommittee D13.59 on Fabric Test Methods, General.

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[2] *Annual Book of ASTM Standards*, Vol 07.01.

[3] *Annual Book of ASTM Standards*, Vol 11.03.

[4] Available from American Association of Textile Chemists and Colorists, P.O. Box 12215, Research Triangle Park, NC 27709.

[5] As amended effective January 2, 1984, Section A236, available from U.S. Government Printing Office, North Capital and H Streets NW, Washington DC, 20401.

3.10 *laminated fabric, n*—a layered fabric structure wherein a face or outer fabric is joined to a continuous sheet material, such as polyurethane foam, in such a way that the identity of the continuous sheet material is retained, either by the flame method or by an adhesive, and this in turn normally but not always, is joined on the back with a backing fabric such as tricot.

3.11 *lot, n—in bonded, fused, or laminated fabric,* a single run on the bonding or laminating machine in which the processing is carried out without stopping or changing processing conditions, and consisting of either a single dye lot or a single gray goods lot.

3.12 *puckering, n— in bonded, fused, or laminated fabrics,* a wavy, three-dimensional effect typified by closely spaced wrinkles, on either the face fabric or the backing fabric or both.

3.12.1 *Discussion*—Puckering may be due to (*1*) differential shrinkage of the component layers, (*2*) differences in tension when the component layers are combined, or (*3*) selective lineal delamination.

3.13 *solvent relative humidity, n*—the humidity of air over a drycleaning bath and in equilibrium with the solvent and its small amount of water.

3.13.1 *Discussion*—Every drycleaning solvent bath containing detergent can require a different absolute water content to reach the Federal Trade Commission (FTC) specified level of solvent relative humidity for a normal drycleaning. The actual solvent relative humidity in the air over a solvent must be measured by an hygrometer after equilibrium has been reached between the water content of air and the solvent.

3.14 For definitions of other textile terms used in this test method, refer to Terminology D 123.

## 4. Summary of Test Methods

4.1 Bench marks are placed at specified distances on the fabrics, which are then measured, and subsequently drycleaned, or laundered and dried, or both, through a prescribed cycle that is repeated a specified number of times. The drycleaned or washed specimens are examined for appearance and delamination and measured to determine any accompanying shrinkage and, if desired, tested to determine the strength of the bond.

## 5. Uses and Significance

5.1 These test methods for the determination of properties of bonded, fused, or laminated apparel fabrics, are considered satisfactory for acceptance testing of commercial shipments of bonded and laminated apparel fabrics since the methods have been used extensively in the trade for acceptance testing.

5.1.1 In case of a dispute arising from differences in reported test results when using Test Methods D 2724 for acceptance testing of commercial shipments, the purchaser and the supplier should conduct comparative tests to determine if there is a statistical bias between their laboratories. Competent statistical assistance is recommended for the investigation of bias. As a minimum, the two parties should take a group of test specimens that are as homogeneous as possible and that are from a lot of material of the type in question. The test specimens should then be randomly assigned in equal numbers to each laboratory for testing. The average results from the two laboratories should be compared using Student's *t*-test for unpaired data and an acceptable probability level chosen by the two parties before the testing is begun. If a bias is found, either its cause must be found and corrected or the purchaser and the supplier must agree to interpret future test results in the light of the known bias.

## 6. Apparatus and Materials

6.1 *Drycleaning Machine,*[6] single-unit, coin-operated type, capable of providing a complete automatic dry-to-dry cycle using perchlorethylene. It shall consist of a commercial rotating cage type, totally enclosed machine. The diameter of the rotating cage shall be not less than 600 mm (24 in.) and not more than 1080 mm (42 in.). Its depth shall be not less than 300 mm (12 in.). It shall be fitted with two to four lifters. The speed shall be such as to give a *g*-factor between 0.5 and 0.9 for cleaning and between 35 and 120 for extraction. The machine shall be equipped with thermometers for the measurement of the solvent temperature and the air drying temperature.

NOTE 1—The $g$-factor is calculated using Eq 1 or Eq 2:

$$g = 1.42n^2D/100\ 000 \qquad (1)$$

$$g = 5.59n^2d/10\ 000\ 000 \qquad (2)$$

where:

$n$ = revolutions per minute,
$D$ = cage diameter, in., and
$d$ = cage diameter, mm.

6.2 *Domestic Automatic Washer,*[7] top-loading, spin-extracting type.

6.3 *Domestic Automatic Tumble Dryer,*[7] front-loading type.

6.4 *Aspirated Psychrometer,* which meets the requirements of Test Method E 337.

6.5 *Marking Device*[8]—A thin sheet of stainless steel or other rigid flat material in which a square opening 254 by 254 mm (10 by 10 in.) has been cut.

6.6 *Rule,* 305-mm (12-in.) or longer, preferably divided into tenths of an inch. A premarked device calibrated to give the percentage of shrinkage or growth may also be used.

6.7 *Sewing Machine,* suitable for sewing a single row of stitching, preferably with No. 00 mercerized cotton thread, 25 mm (1 in.) from the edge of the fabric specimen.

6.8 *Steam Iron,* hand type.

6.9 *Steam Press,*[9] a press, 600 by 1250 mm (24 by 50 in.), or larger, provided with 60 to 70 psig steam pressure at the press. Any steam press large enough for pressing a specimen 380 mm (15 in.) square may be used.

6.10 *Tensile Testing Machine,* conforming to Specification

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[6] Sources of suitable equipment are: McGraw-Edison Co., Speed Queen Div., Ripon, Wis.; Philco-Bendix Corp., Fairfield, IO; American Permac, Inc., 175 Express St., Plainview, L. I.; Valley Industries Productions, Inc., 133 E. Jericho Turnpike, Mineola, NY; and Atlas Electric Devices, Chicago, IL.

[7] Kenmore Model 600 washer and dryer, available from Sears Roebuck and Co., are satisfactory for this purpose.

[8] Other suitable devices are available from Better Fabrics Testing Bureau, Inc., 101 W. 31 St., New York, NY, and from Cluett, Peabody and Co., Inc., Sanforized Div., Troy, NY.

[9] Sources of suitable equipment are: Hoffman Machine Co., Syracuse, NY; Pentax Co., Pawtucket, R. I.; Prosperity Co., Syracuse, NY; U. S. Testing Co., Hoboken, NJ.

D 76, either a constant rate of traverse type[10] or a constant rate of extension type, equipped with clamps having a width of 76.2 mm (3.00 in.) and preferably calibrated in kilograms with a range from 0 to 4.5 kg (0 to 160 oz). The constant rate of extension type machine is preferred because of the inherently lower machine-induced errors in this type of machine.

6.11 *Detergent*, home laundry type.

6.12 *Perchlorethylene*, commercial grade.

NOTE 2—**Warning:** Perchlorethylene is toxic, and the usual precautions for handling chlorinated solvents should be taken. It should be used only under well-ventilated conditions. The solvent is nonflammable.

6.13 *Drycleaning Detergent,*[11] anionic drycleaning detergent.

## 7. Sampling

7.1 *Lot Sample*—As a lot sample for acceptance testing, take at random the number of rolls of fabric directed in an applicable material specification or other agreement between the purchaser and the supplier. Consider rolls of fabric to be the primary sampling units.

NOTE 3—An adequate specification or other agreement between the purchaser and the supplier requires taking into account the variability between rolls of fabric and between specimens from a swatch from a roll of fabric so as to provide a sampling plan with a meaningful producer's risk, consumer's risk, acceptable quality level, and limiting quality level.

7.2 *Laboratory Sample*—As a laboratory sample for acceptance testing, take a full width swatch 1 m (1 yd) long from the end of each roll of fabric in the lot sample, after first discarding a minimum of 1 m (1 yd) of fabric from the very outside of the roll.

7.3 *Test Specimens*—Proceed as follows:

7.3.1 *Drycleaning and Laundering*—Cut four specimens from each swatch in the laboratory sample with each specimen being 380 by 380 mm (15 by 15 in.) in size, with the one side of the specimens from a single swatch parallel to the selvage. Locate two of the specimens from each swatch about ⅓ of the distance from one selvage and locate the other two specimens from each swatch about ⅓ of the distance from the other selvage. Locate each of the two specimens from one side of the swatch along a diagonal line on the swatch so that they will contain different warp ends and filling picks. Sew a straight line of stitching around each specimen 25 mm (1 in.) from each edge. Reserve the rest of the swatch for comparison with the drycleaned and laundered test specimens.

7.3.2 *Strength of Bond*—Prepare three test specimens, each measuring 76 mm (3 in.) wide, and 152 mm (6 in.) long, the length of the specimens corresponding to the length direction of the fabric. Do not take the test specimens closer to the selvage than a distance equal to 20 % of the fabric width.

NOTE 4—Samples that are 51 mm (2 in.) wide may be used as the minimum width.

## 8. Conditioning

8.1 Bring the samples from the prevailing atmosphere and condition them for at least 4 h in the standard atmosphere for testing textiles if shrinkage is to be determined. Preconditioning is not necessary.

## 9. Specimen Preparation

9.1 Using an indelible fineline marker, mark a 254 by 254 mm (10 by 10 in.) reference square centrally located on the face of each test specimen. Apply three sets of reference markings 254 ± 2 mm (10 ± 0.1 in.) apart, as measured with a rule, in the direction of the fabric length. Locate the markings within 25 mm (1 in.) of each end and at the midpoint of each side of the square. Similarly, apply three sets of markings in the direction of the fabric width. Any other method of accurately locating the 254-mm reference marks is satisfactory as long as the three marks on each side of the square are at least 105 mm (4 in.) apart.

## 10. Drycleaning Procedure

NOTE 5—Launderable fabrics are expected normally to be drycleanable, except where the face fabric is not drycleanable and is so labeled. For example, the fabric could contain a functional finish soluble in the solvent, or the fiber could be degraded by the solvent, which would be the case with poly(vinyl chloride) fiber.

10.1 *Solvent Preparation*—Prepare a standard detergent/drycleaning solvent mixture by adding sufficient detergent to the solvent to make a 1 % volume/volume solution. Add sufficient water to the solution to give a solvent relative humidity level of 75 % for the particular drycleaning detergent used. Put this solvent in the machine storage tank. The same solution can be used for repeated cleanings until it becomes dirty and needs replacing as long as the necessary water additions to maintain the solvent relative humidity constant are made prior to each test run. This is so because the specimens being run could conceivably alter the solvent relative humidity for succeeding test runs while the detergent level would remain constant.

10.2 *Sample and Dummy Load Preparation*— Prepare a load consisting of all specimens to be tested and made up to 3.6 kg (8 lb) total with dummy load of approximately 380 by 380-mm (15 by 15-in.) fabric pieces of similar material. Condition this load at least 4 h in the standard atmosphere for testing textiles. After the drycleaning operation, condition the load again before running through each additional drycleaning cycle. Conditioning before each drycleaning cycle is intended to minimize depletion of water from the drycleaning solution specified in 10.1.1 which may affect shrinkage results.

10.3 *Drycleaning Procedure*—Run through the complete dry-to-dry cycle in the machine. Run the solvent phase of the drycleaning cycle with the solvent no higher than 32°C (90°F). During the drying phase of the drycleaning cycle, either the air outlet temperature should not exceed 60°C (140°F) or the inlet air temperature should not exceed 80°C (175°F). If heat-sensitive fibers, for example, modacrylic fibers, are involved, the outlet air temperature should not exceed 40°C (105°F) or the inlet air temperature should not exceed 60°C (140°F). After the complete drycleaning cycle, remove the sample from machine for examination and reconditioning.

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[10] Model X-5, available from Edward H. Benz Co., 283 Whiteford Ave., Providence, RI 02908, has been found satisfactory.

[11] Formula 886, petroleum sulfonate type or staticol, amine sulforate type, available from R. R. Street, Inc., 561 W. Monroe St., Chicago, IL; or Perksheen 324, amine sulfonate type, available from Adco, Inc., 900 W. Main St., Sedalia, MO, have been found suitable for this purpose.

10.4 Repeat the drycleaning operation through two additional cycles. At the end of the third cycle remove the test specimens from the machine, lay on a flat surface, smooth the test specimens by hand, and examine. Press the test specimens using the steam press according to the following cycle:

10.4.1 Five seconds steam with head up.

10.4.2 Five seconds dry hot press with head down, 145 to 151°C (293 to 303°F) of steam pressure at the press.

10.4.3 Five seconds vacuum, steam off, head down.

10.4.4 Five seconds vacuum, steam off, head up.

10.4.5 Allow the pressed specimens to condition in the standard atmosphere for testing textiles for at least 4 h.

10.5 Measure the distance between each of the six sets of reference marks on each test specimen.

10.6 Lay the fabric flat on a table or board with a surface rough enough so that the fabric side touching the table will not readily slide. Examine each test specimen for any evidence of delamination. Place the fingers on the specimen and attempt to slide the upper fabric layer over the bottom or intermediary substrate. If in doubt, make a small cut through the specimen with scissors to determine if any separation of substrates has occurred. Turn the fabric over and make the same type of examination on the other side.

10.7 Examine the face fabric for any alteration in appearance as compared with the original sample. This may be done with conventional room lighting, or with "Lighting Equipment for Viewing Test Specimens," as described in Fig. 1 of AATCC Method 124 – 1984. Examine only the area of the test specimen bounded by the stitching.

## 11. Laundering Procedure

11.1 *Machine Laundering*—Wash the test specimens in the automatic home laundry machine, using 50 g of laundry detergent, or a sufficient amount to give a safe suds level, at the applicable domestic automatic temperature and procedure under which the fabric is to be marketed. In the absence of this information use the "normal" cycle and high water level settings and determine the washing temperature according to the fabric type and construction as follows:

11.1.1 Face fabrics containing 20 % or more of wool, acetate, modacrylic, or acrylic fibers, 41 ± 3°C (105 ± 5°F).

11.1.2 Face fabrics of tricots, circular knits, woven nylon, and print fabrics other than those described under 11.1.1, 49 ± 3°C (120 ± 5°F).

11.1.3 All other woven face fabrics, 60 ± 3°C (140 ± 5°F).

11.2 *Load for Machine Laundering*—Use a total load of 1.8 kg (4 lb) including test specimens plus a dummy load of approximately 380 by 380 mm (15 by 15 in.) fabrics of similar fabric construction. Load all fabrics in the flat position.

11.3 *Hand Laundering*—If the fabrics are to be designated "Hand Washable," dissolve 20 g of laundry detergent in 7.6 L (2 gal) of water at 41 ± 3°C (105 ± 5°F) in a 9.5-L (10-qt) pail and then add two test specimens. Wash by lifting each specimen out of the bath followed by immediate reimmersion at least ten times. Just before the final reimmersion, lightly rub by hand the center of each specimen separately for a period of 1 min. Rinse by transferring the specimens to 7.6 L of water at 41 ± 3°C (105 ± 5°F) and gently agitating the specimens by hand for a period of 2 min with no twisting or wringing. Remove the specimens and dry as directed in 11.6.

11.4 *Tumble Drying*—Immediately after the first wash cycle, as directed in 11.1, remove the test specimens and dummy load from the laundry machine and transfer to the tumble dryer. Run the dryer at the "moderate" setting and dry for the minimum time required for adequately drying the fabrics being tested. Remove the test specimens and dummy load immediately following the shut-off and examine.

11.5 Repeat the washing and drying cycles as directed in 11.1 and 11.4 four more times. After the fifth cycle, remove the test specimens, lay on a flat surface, smooth by hand, and examine. Press the face fabric side lightly with a sliding action using the hand steam iron, with no pressure other than the weight of the iron. If no ironing temperature is specified for the face fabric, use the safe ironing temperature guide appearing in Table 1. Allow the specimens to condition on a flat surface in the standard atmosphere for testing textiles for a minimum of 4 h before rating and measuring as directed in 10.5-10.7.

11.6 *Drip Drying*—Remove the specimens from the pail or from the automatic washer just before the water begins to drain for the final spin-dry cycle, squeeze by hand without wringing or twisting, and hang each specimen by two adjacent corners, with the fabric length in the vertical direction, in still air at room temperature until dry and examine.

11.7 Repeat the washing and drying cycles as directed in 11.2 or 11.3, and 11.6, four more times. After the fifth cycle, lay on a flat surface, smooth the test specimens by hand, and examine. Press the face fabric side lightly with a sliding action using a hand steam iron with no pressure other than the weight

TABLE 1 Safe Ironing Temperature Guide

| Class 0 | Class I | Class II | Class III | Class IV |
|---|---|---|---|---|
| Below 121°C (250°F) | 121 to 135°C (250 to 275°F) | 149 to 163°C (300 to 325°F) | 177 to 191°C (350 to 375°F) | 204°C (400°F) and Above |
| Modacrylic 93 to 121°C (200 to 250°F) | Acetate | Triacetate (unheat set) | Nylon 66 | Cotton |
| | Olefin (polypropylene) | Acrylic | Polyester | Fluorocarbon<br>Glass |
| Olefin (polyethylene) 79 to 121°C (175 to 250°F) | Silk | Azlon<br>Nylon 6 | | Hemp, Jute<br>Ramie |
| Rubber 82 to 93°C (180 to 200°F) | | Spandex<br>Wool | | Linen<br>Rayon, Viscose |
| Saran 66 to 93°C (150 to 200°F) | | | | Triacetate (heat set) |
| Vinyon 54°C (130°F) | | | | |

TABLE 2 Components of Variance Shrinkage

| | | Single-Operator Component Percentage Points | DF | Between-Laboratory Component Percentage Points | DF |
|---|---|---|---|---|---|
| Drycleaning | length shrinkage | 0.68 | 45 | 0.97 | 4 |
| | width shrinkage | 0.59 | 45 | 0.77 | 4 |
| Hand wash-line dry | length shrinkage | 1.00 | 20 | 1.48 | 4 |
| | width shrinkage | 0.33 | 20 | 1.11 | 4 |
| Machine wash-tumble dry | length shrinkage | 0.56 | 25 | 0.79 | 4 |
| | width shrinkage | 1.00 | 25 | 1.18 | 4 |

TABLE 3 Critical Differences, Percentage Points, Between Average Percentages for the Conditions Noted

| | Number of Observations in Each Average | Length Shrinkage | | Width Shrinkage | |
|---|---|---|---|---|---|
| | | Single-Operator Precision | Between-Laboratory Precision | Single-Operator Precision | Between-Laboratory Precision |
| Drycleaning | 2 | 1.4 | 4.2 | 1.2 | 3.6 |
| | 4 | 1.1 | 4.1 | 1.0 | 3.3 |
| | 6 | 0.8 | 4.0 | 0.7 | 3.2 |
| Hand wash-line dry | 2 | 2.1 | 6.3 | 0.6 | 4.4 |
| | 4 | 1.5 | 6.1 | 0.5 | 4.4 |
| | 6 | 1.2 | 6.0 | 0.4 | 4.3 |
| Machine wash-tumble dry | 2 | 1.2 | 3.4 | 2.1 | 5.2 |
| | 4 | 0.9 | 3.3 | 1.5 | 5.0 |
| | 6 | 0.7 | 3.2 | 1.2 | 4.9 |

of the iron. If no ironing temperature is specified for the face fabric, the safe ironing temperature guide appearing in Table 1 may be used. Allow the specimens to condition on a flat surface in the standard atmosphere for testing textiles for a minimum of 4 h before rating and measuring as directed in 10.5-10.7.

NOTE 6—All specimens hand washed as directed in 11.3 should be drip dried. Specimens machine washed as directed in 11.1.1 should be drip dried only when the fabrics are to be marketed as "Machine Wash, Drip Dry."

## 12. Calculation

12.1 Calculate the shrinkage or gain in each direction by averaging the three measurements in each direction on each test specimen and using these average measurements in accordance with Eq 3:

$$\text{Shrinkage, \%} = (A - B)100/A \quad (3)$$

where:

$A$ = average original distance between bench marks, and

$B$ = average final distance between bench marks.

12.2 Calculate the average length shrinkage and the average width shrinkage of both test specimens separately fordrycleaning and for each laundering and drying procedure used.

## 13. Precision and Bias

13.1 *Interlaboratory Test Data*[12]—An interlaboratory test, in which nine different bonded and laminated fabrics were used, was run during 1969. Five laboratories participated and calculated the percent shrinkage in length and width as a result of drycleaning, hand washing followed by line drying, and machine washing followed by tumble drying. The calculated components of variance expressed as standard deviations and the degrees of freedom on which they are based are shown in Table 2.

NOTE 7—The within-laboratory (multioperator) component was not determined separately and is included in the between-laboratory component.

13.2 *Precision*—Based upon the components of variance stated in Table 2, the average test results should be considered significantly different at the 95 % probability level if the difference equals or exceeds the differences listed in Table 3.

NOTE 8—The critical differences listed in Table 3 were calculated using the values of $t$ that correspond to the degrees of freedom listed in Table 2.

13.3 *Bias*—The procedure in Test Methods D 2724 for measuring dimensional stability during drycleaning or laundering has no bias because the value of this property can be defined only in terms of a test method.

## STRENGTH OF BOND (OPTIONAL)

## 14. Test Conditions

14.1 Bond strength tests may be made on the fabric as bonded or laminated, or after the three specified drycleaning cycles or after the five specified laundering cycles. These tests also may be made on dry specimens (conditioned in the standard atmosphere for testing textiles for a minimum of 4 h), or on wet specimens (saturated with perchlorethylene at room temperature following the drycleaning tests or saturated with water at room temperature following the laundering tests).

14.2 Alternatively, following the drycleaning tests, wet strength-of-bond tests may be made on flame-laminated fabrics with the specimens saturated in water instead of perchlorethylene. An interlaboratory test run in 1975[9] showed no significant differences between perchlorethylene and water in wet tests on flamelaminated fabrics. However, there were significant differences on adhesive-bonded fabrics. Therefore, water is not a suitable substitute for perchlorethylene in wet tests on these fabrics.

## 15. Procedure for Bonded and Fused Fabrics

15.1 Manually separate the two layers of fabric along the

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[12] ASTM Research Report RR: D13-1003 is available on loan from ASTM Headquarters, 100 Barr Harbor Drive, West Conshohocken, PA 19428.

76.2 mm (3 in.) width of each test specimen for a distance of approximately 25 mm (1 in.) in the direction of the specimen length.

15.2 Set the lower clamp at a distance of 25 mm (1 in.) from the upper clamp. Secure the separated face fabric of a test specimen in the upper clamp of the tensile testing machine in such a way that the longitudinal axis of the specimen forms a right angle with the closed clamping surface. Secure the separated backing fabric in the lower clamp of the machine in such a way that the longitudinal axis of the specimen forms a right angle with the closed jaws of the lower clamp.

15.3 If the indicating scale on the machine is provided with a pawl and ratchet mechanism, disengage the mechanism to permit readings of variable force when the machine is placed in operation.

15.4 Operate the machine at a pulling speed of 5.1 ± 0.2 mm/s (12 ± 0.5 in./min).

15.5 Estimate the bond strength to the nearest 140 mN (0.5 ozf) as the average of at least the five highest and the five lowest peak loads of resistance per inch of width, registered for 100 mm (4 in.) of delamination.

15.6 Repeat the operations described in 15.2-15.5 for each of the remaining two test specimens.

15.7 Report the bond strength in ounces per inch of width as the average strength of the three test specimens.

## 16. Procedure for Laminated Fabrics

16.1 Manually separate the face fabric from the foam along the 76.2-mm (3-in.) width of each test specimen for a distance of approximately 25 mm (1 in.) in the direction of the specimen length.

16.2 Set the lower clamp at a distance of 25 mm (1 in.) from the upper clamp. Secure the separated face fabric of a test specimen in the upper clamp of the tensile testing machine in such a way that the longitudinal axis of the specimen forms a right angle with the closed clamping surface. Secure the separated foam or foam and backing fabric in the lower clamp of the machine in such a way that the longitudinal axis of the specimen forms a right angle with the closed jaws of the lower clamp.

16.3 Proceed as instructed in 15.3-15.7.

16.4 If foam is laminated to a backing fabric, retain each test specimen from 16.3 after the bond strength has been determined for face to foam. Manually separate the backing fabric from the foam as instructed in 16.1 except that the manual separation should be made at the opposite end of the test specimen separated for the face fabric-to-foam test.

16.5 Set the lower clamps at a distance of 25 mm (1 in.) from the upper clamp. Secure the separated foam or foam and face fabric of a test specimen in the upper clamp of the tensile testing machine in such a way that the longitudinal axis of the specimen forms a right angle with the closed clamping surface. Secure the separated backing fabric in the lower clamp of the machine in such a way that the longitudinal axis of the specimen forms a right angle with the closed jaws of the lower clamp.

16.6 Proceed as instructed in 15.3-15.7.

16.7 Examine both sides of the foam on the test specimens after testing for bond strength. Determine whether the foam portion ruptured during delamination allowing some foam to adhere to either fabric surface. If this has occurred, make the notation "foam tear" for that test specimen for the side or sides where "foam tear" occurred. If "foam tear" occurs on only one side of one test specimen, disregard this result and report the average bond strength for that side of the remaining two specimens. If "foam tear" occurs on the same side of two or three specimens, report the bond strength for that side as "foam tear."

16.8 In the event it is impossible to separate manually the foam from either the face or the backing fabric as instructed in 16.1 and 16.4 without rupturing the foam, report the bond strength for the side or sides where this occurs as "foam tear."

## 17. Report

17.1 State that the tests were made as directed in ASTM Test Methods D 2724. Describe the material or product sampled and the method of sampling used.

17.2 Report the following information:

17.2.1 The individual length and width dimensional changes to the nearest 0.5 % for each test specimen as well as the average length and width shrinkage for both test specimens and identify these results with the procedures used.

17.2.2 The absence or presence of any delamination in the drycleaned or laundered and dried specimens before pressing or ironing. Use the term "acceptable bond" for fabrics that have not delaminated and "unacceptable bond" for fabrics that have delaminated. In the case of three-layer laminated fabrics, report whether the delamination has occurred on the face or backing fabric or both. Rate the lot as "unacceptable" if either fabric has delaminated.

17.2.3 Any alteration in appearance or esthetic properties of the drycleaned or laundered and dried specimens when compared with the residual portion of the original sample. For example, report whether the specimens, identified by the drycleaning or laundering and drying procedures used, show:

17.2.3.1 Puckering,

17.2.3.2 Crack marks,

17.2.3.3 Bubbling or blisters,

17.2.3.4 Face fabric pilling,

17.2.3.5 Loss or gain of stiffness,

17.2.3.6 Color change, and

17.2.3.7 Wrinkles.

17.2.4 If strength of bond tests were run, report the following information along with the solvent used for wet specimens:

17.2.4.1 Whether the tests were run on the fabric as bonded or laminated, or after the three drycleaning cycles, or after the five laundering cycles.

17.2.4.2 Whether the tests were run on dry or wet specimens as described in Section 14.

17.2.4.3 Whether constant rate of transverse or constant rate of extension type tensile testing machine was used.

NOTE 9—While this method provides for three drycleaning cycles, five laundering and drying cycles, or both, the number of cycles can be decreased or increased for special purposes but in this case the report should state what cycles were used.

## 18. Precision and Bias

18.1 *Interlaboratory Test Data*[11]—An interlaboratory test, in which nine different bonded and laminated fabrics were used, was run during 1969. Five laboratories participated and recorded the average wet bond strength (sometimes called wet peel bond strength) for 76-mm (3-in.) wide specimens after drycleaning, hand washing, and machine washing the specified number of times. No data is reported for machine wash-tumble dry wet-bond strength because some of the fabrics delaminated before the five wash cycles were completed and some exhibited "foam tear." Of the participating laboratories, four used the constant rate of extension type tensile testing machine, and one used the constant rate of traverse type machine. The calculated components of variance expressed as standard deviations and the degrees of freedom on which they are based, are listed in Table 4.

18.2 *Precision*—Based upon the components of variance stated in 18.1, the average test results should be considered significantly different at the 95 % level if the difference equals or exceeds the differences listed in Table 5.

NOTE 10—The critical differences listed in Table 5 were calculated using the values of *t* that correspond to the degrees of freedom listed in Table 4.

18.3 *Bias*—The procedure in Test Methods D 2724 for measuring strength of bond has no bias because the value of this property can be defined only in terms of a test method.

NOTE 11—The nature of the bonding and laminating processes which involve the adhesion of two or three components with adhesive systems that apply the adhesive in discrete quantities in a discontinuous form on the textile surface, produces bonded and laminated fabrics that are nonuniform in their bond strength characteristics. Considerable variations in bond strength are commonly found at various points across the width of the fabric and from one end to the other in a single piece. Because of this, it is often desirable to report the bond strength value of the test specimen with the lowest bond strength in addition to reporting the average as specified in 15.7.

**TABLE 4 Components of Variance, Wet Bond Strength**

| | Single-Operator Component, oz/in. | DF | Between-Laboratory Component, oz/in. | DF |
|---|---|---|---|---|
| Drycleaning | 0.54 | 30 | 0.00 | 4 |
| Hand wash-line dry | 0.23 | 15 | 0.48 | 4 |

**TABLE 5 Critical Differences, Wet Bond Strength**

| | Number of Observations in Each Average | Critical Differences oz/1 in. Wide Test Specimen | |
|---|---|---|---|
| | | Single-Operator Precision | Between-Laboratory Precision |
| Drycleaning | 2 | 1.1 | 1.1 |
| | 3 | 0.9 | 0.9 |
| | 4 | 0.8 | 0.8 |
| Hand wash-line dry | 2 | 0.6 | 2.0 |
| | 3 | 0.5 | 1.9 |
| | 4 | 0.4 | 1.9 |

## 19. Indexing Terms

19.1 This standard is indexed under the following terms: apparel, bonded fabric, and delamination strength.

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# Standard Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D-19 on Water[1]

This standard is issued under the fixed designation D 2777; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This practice establishes uniform standards for estimating and expressing the precision and bias of applicable test methods for Committee D-19 on Water.

1.2 Except as specified in 1.3, 1.4, and 1.5, this practice requires the task group proposing a new test method to carry out a collaborative study from which statements for precision (overall and single-operator standard deviation estimates) and bias can be developed. This practice provides general guidance to task groups in planning and conducting such determinations of precision and bias.

1.3 If a full-scale collaborative study is not technically feasible, due to the nature of the test method or instability of samples, the largest feasible scaled-down collaborative study shall be conducted to provide the best possible limited basis for estimating the overall and single-operator standard deviations.

1.3.1 Examples of acceptable scaled-down studies are the local-area studies conducted by Subcommittee D19.24 on microbiological methods because of inherent sample instability. These studies involve six or more completely independent local-area analysts who can begin analysis of uniform samples at an agreed upon time.

1.3.2 If uniform samples are not feasible under any circumstances, a statement of single-operator precision will meet the requirements of this practice. Whenever possible, this statement should be developed from data generated by independent multiple operators, each doing replicate analyses on independent samples of a specific matrix type, which generally fall within specified concentration ranges (see 7.2.5.2(*3*)).

1.3.3 This practice is not applicable to methodology involving continuous sampling or measurement, or both, of specific constituents and properties.

1.3.4 This practice is also not applicable to open-channel flow measurements.

1.4 A collaborative study that satisfied the requirements of the version of this practice in force when the study was conducted will continue to be considered an adequate basis for the precision and bias statement required in each test method. If the study does not satisfy the current minimum requirements for a collaborative study, a statement listing the study's deficiencies and a reference to this paragraph shall be included in the precision and bias statement as the basis for an exemption from the current requirements.

1.5 This paragraph relates to special exemptions not clearly acceptable under 1.3 or 1.4. With the approval of Committee D-19 on the recommendation of the Results Advisor and the Technical Operations Section of the Executive Subcommittee of Committee D-19, a statement giving a compelling reason why compliance with all or specific points of this practice cannot be achieved will meet both ASTM requirements **(1)**[2] and the related requirements of this practice. Precision and bias statements authorized by this paragraph shall include the date of approval by Committee D-19.

1.6 In principle, all test methods are covered by this practice.

1.7 In Section 11 this practice shows exemplary precision and bias statement formats for: (*1*) test methods yielding a numerical measure, (*2*) test methods yielding a non-numerical report of success or failure based on criteria specified in the procedure, and (*3*) test methods specifying that procedures in another ASTM test method are to be used with only insignificant modifications.

1.8 All studies, even those exempt from some requirements under 1.3 or 1.5, shall receive approval from the Results Advisor before being conducted (see Section 8) and after completion (see Section 12).

## 2. Referenced Documents

2.1 *ASTM Standards:*

D 1129 Terminology Relating to Water[3]
D 1141 Specification for Substitute Ocean Water[3]
D 1193 Specification for Reagent Water[3]
D 4375 Terminology for Basic Statistics in Committee D-19 on Water[3]
D 5790 Test Method for Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry[4]
D 5905 Specification for Substitute Wastewater[3]

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[1] This practice is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.02 on General Specifications, Technical Resources, and Statistical Methods.

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[2] The boldface numbers in parentheses refer to the list of standards at the end of this practice.

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

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

E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods[5]
E 178 Practice for Dealing with Outlying Observations[5]
E 456 Terminology Relating to Quality and Statistics[5]
E 1169 Guide for Conducting Ruggedness Tests[5]

## 3. Terminology

3.1 *Definitions*—For definitions of terms used in this practice, refer to Terminologies D 1129, D 4375 and E 456, and Practice E 177.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *accuracy*—a measure of the degree of conformity of a single test result generated by a specific procedure to the assumed or accepted true value and includes both precision and bias.

3.2.2 *bias*—the persistent positive or negative deviation of the average value of a test method from the assumed or accepted true value.

3.2.3 *laboratory*—a single and completely independent analytical system with its own specific apparatus, source of reagents, set of internal standard operating procedures, etc. Different laboratories will differ from each other in all of these aspects, regardless of how physically or organizationally close they may be to each other.

3.2.4 *operator*—usually the individual analyst within each laboratory who performs the test method throughout the collaborative study. However, for complicated test methods, the operator may be a team of individuals, each performing a specific function throughout the study.

3.2.5 *precision*—the degree of agreement of repeated measurements of the same property, expressed in terms of dispersion of test results about the arithmetical mean result obtained by repetitive testing of a homogeneous sample under specified conditions. The precision of a test method is expressed quantitatively as the standard deviation computed from the results of a series of controlled determinations.

## 4. Summary of Practice

4.1 After the task group has assured itself that the test method has had all preliminary evaluation work completed, it should prepare the test method write-up in final form. The plan for collaborative study is developed in accordance with this practice and submitted along with the test method write-up to the Results Advisor for concurrence except as specified in 1.3, 1.4, and 1.5. Upon receipt of concurrence, the collaborative test is conducted, data analyzed, and precision and bias statements formulated by the task group. The final precision and bias statistics must be based on retained data from at least six independent laboratories. The statements, with backup data including the reported results summary, the calculations leading up to the statements, and the test method write-up with precision and bias statements included are submitted to the subcommittee vice-chairman who in turn sends a copy of it to the Results Advisor for concurrence before balloting. This assures having an acceptable copy of the collaborative study results to send to ASTM for items on the main committee ballot. In most instances, the collaborative study shall be complete before a subcommittee ballot. If the collaborative study is not complete, the test method may go on the ballot as a provisional test method rather than a standard test method. Copies of the test data, approved calculations, and statistical results shall be filed at ASTM Headquarters when the test method is submitted by the subcommittee chairman as an item for the main committee ballot.

4.1.1 The appendix shows an example of "Form A—Approval of Plans for Interlaboratory Testing," as Fig. X1.1.

4.1.2 For an example of a data reporting form, see Fig. X2.1.

4.1.3 In addition, the appendix shows a sample calculation of precision and bias from real collaborative test data, the related table of statistics, and the related precision and bias statement.

## 5. Significance and Use

5.1 Following this practice should result in precision and bias statements which can be achieved by any laboratory properly using the test method studied. These precision and bias statements provide the basis for generic limits for use in the Quality Control section of the test method.

5.2 The method specifies the media for which the test method is appropriate. The collaborative test corroborates the write-up within the limitations of the test design. An extensive test can only use representative media so that universal applicability cannot be implied from the results.

5.3 The fundamental assumption of the collaborative study is that the media tested, the concentrations tested, and the participating laboratories are a representative and fair evaluation of the scope and applicability of the test method as written.

## 6. Preliminary Studies

6.1 Considerable pilot work on a test method must precede the determination of its precision and bias **(2,3)**. This pilot work should explore such variables as preservation requirements, reaction time, concentration of reagents, interferences, calibration, and sample size. Potentially significant factors must be investigated and controlled in the written test method in advance of the collaborative test. Also, disregard of such factors may introduce so much variation among operators that results are misleading or inconclusive **(4)** (see 9.3 and 9.4). A ruggedness study conducted in a single laboratory is particularly useful for such investigations and should be conducted to prove a test method is ready for interlaboratory testing (see Guide E 1169 for details).

6.2 Only after a proposed test method has been tried, proved, and reduced to unequivocal written form should a determination of its precision and bias be attempted.

## 7. Planning the Collaborative Test

7.1 Based upon the task group's knowledge of a test method and having the unequivocal write-up, several factors must be considered in planning the collaborative test to properly assess the precision of the test method. The testing variables that must be considered in planning are discussed below. It is generally not acceptable to control significant sources of variability in the

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

collaborative study which cannot be controlled in routine use of the test method, because this leads to false estimates of the test method precision and bias. In addition, the task group must determine within the resources available how to best estimate the bias of the test method.

7.2 *Testing Variables*:

7.2.1 It is desirable to develop a statement of precision of a test method that indicates the contribution to overall variation of selected causes such as laboratory, operator, sample matrix, analyte concentration, and other factors that may or have been shown to have strong effects on the results. Since any test method can be tried in only a limited number of applications, the standard deviation calculated from the results of a study can be only an estimate of the universe standard deviation. For this reason, the symbol $s$ (sample standard deviation) is used herein. The precision estimates generated from the study data will usually be the overall standard deviation ($s_T$) and the pooled single-operator standard deviation ($s_o$) for each sample matrix and concentration studied.

7.2.2 Laboratories, operators, sample matrices, and analyte concentrations are the only sources of variability represented in the precision and bias statements resulting from the usual collaborative study. They may not represent the additional influence that can arise from differences in sample splitting, field preservation, transportation, etc., all of which may influence routine analytical results as shown in the general precision definitions in Terminology D 1129.

7.2.3 *Laboratories*—The final precision and bias statistics for each analyte, matrix, and concentration must be based on data from at least six laboratories that passed all of the outlier tests (see 10.3 and 10.4), that is, retained data. To be assured of meeting this requirement, it is recommended that usable data be obtained from a minimum of eight independent laboratories. To guarantee eight providing usable data, it will often be necessary to get ten or more laboratories to agree to participate, because some may not provide data and others may not provide usable data. Maximizing the number of participating laboratories is often the most important thing that can be done to guarantee a successful study.

7.2.4 Even if the single-operator standard deviation is the only statistic to be estimated in the study (see 1.3.2), there should be a minimum of eight operators providing usable data, so you are assured of data from six operators after all outlier removal.

7.2.5 *Sample Matrices*—The collaborative study shall be conducted with at least one representative sample matrix, which should be reproducible by subsequent user-laboratories so that they can compare their results with the results of the collaborative study.

7.2.5.1 Typically, a reagent water prepared according to Specification D 1193 or a synthetic medium, such as the substitute wastewater described in Specification D 5905 or the substitute ocean water described in Specification D 1141, is used as the reference matrix. Analytes may be supplied separately as concentrates for addition to this matrix by each laboratory or the reference matrix containing the analyte(s) may be supplied to each participant. Information on how the reference matrix was prepared in the study shall be clear in the precision and bias statement of the test method so users can reproduce it properly.

7.2.5.2 Additional collaborative testing should also be conducted using other matrices specified in the scope of the test method. Since these matrices must be the same for each study participant, they may have to be prepared (or obtained from a single source), preserved, and distributed to all laboratories. As with the reference matrix, analytes may be supplied in a separate spiking solution or already added to the matrix. A particularly attractive matrix might be a standard material available from an organization such as the National Institute of Standards and Technology (NIST). Use of uniform sample matrices is necessary in these studies since they enable a more certain comparison with the reference matrix than is possibly with matrices supplied separately by each participant.

*(1)* Use of matrices with naturally occurring, non-zero background levels of the analyte(s) being studied will result in precision and bias estimates that will be much more difficult to properly compare with estimates from the reference matrix.

*(2)* Any matrix spiking that may be necessary shall not significantly change the natural characteristics of the matrix.

*(3)* With the exception of the kind of limited study described in 1.3.2, the matrix-of-choice approach, in which each participant is expected to acquire their own sample of a designated type, should not be used. Such studies are basically incompatible with the statistical approaches employed in this practice; both the ranking test and the individual outlier test are incapable of distinguishing laboratory effects from matrix effects. In addition, the presence of variable background concentrations prevents the assignment of a proper mean concentration level to each precision estimate produced in the study.

7.2.5.3 The same study design should be used for all sample matrices. A separate precision and bias statement should be generated for each sample matrix with a brief description of the matrix tested.

7.2.5.4 When studies are available indicating the applicability of the test method for matrices untested in 7.2.5.1 and 7.2.5.2 and not meeting the other requirements of this practice, at the discretion of the task group responsible for the test method and the Results Advisor, and providing the data are analyzed in accordance with Section 10 of this practice, this supporting data may be included in a separate section of the precision and bias statement. A clear but brief description of the matrices shall be included and the study protocol employed. It is the intent of this practice that ultimately, data concerning the precision and bias of the test method in the full range of matrices covered in the scope and analyzed in accordance with this practice, will be made available to the users of the test method.

7.2.6 *Analyte Concentrations*—If pilot work has shown that precision is linear with increasing analyte concentrations, at least three Youden pairs **(5)**, that is, six concentrations, covering the range of the test method should be included for each matrix. If the pilot work suggests that precision is other than constant or linear, more concentration levels should be analyzed. The study concentrations should generally be rather uniformly distributed over the range of the test method.

7.2.6.1 Study samples with concentrations at or near the detection limit of a test method are likely to produce non-quantitative results from many of the participating laboratories if participants are permitted to use their detection limit to censor their results. Zeroes or less thans that result from this censoring process are non-quantitative results and cannot be included in the statistical analysis of study results specified later in this practice. Conducting the specified statistical analysis on whatever quantitative data are available under such circumstances can produce misleading precision and bias estimates. If it is considered necessary to include samples at or near the detection limit, such samples shall be in addition to the minimum required three Youden pairs at concentrations that can be readily measured by qualified laboratories. Data from analyses of the basic three or more Youden pairs that can be quantified can then be statistically analyzed as specified to produce a proper traditional precision and bias statement for the test method. Results from analyses of Youden pairs at or near the detection limit can be included in this traditional statistical analysis if it turns out that most laboratories report quantified results. Otherwise, results for low-level samples must be statistically analyzed using specialized procedures, for example, procedures similar to those under development in Subcommittee D19.02, which are beyond the scope of this practice.

7.2.7 Since the order of analyses should not be a source of systematic variability in the study, each participant should either be told to randomize the order of study sample analyses or be given a specific random order for their analyses.

7.2.7.1 Whenever the time of analyses has been shown to influence the analytical results, close control over the time of analyses will be essential.

7.2.8 If pilot work has shown that the sample container must be of a specific material prepared in a specific manner prior to use, the variation in containers obtained and prepared by the participants will be a random variable and should be treated as such in the planning of the study and in the statistical analysis of the data.

7.2.9 The manner of preservation or other treatment of the sample prior to typical use of the test method, if known to affect the precision or bias, or both, of results, shall be incorporated into the collaborative study design.

7.3 *Measurement of Precision:*

7.3.1 Every interlaboratory study done to provide precision and bias estimates for a D-19 test method must use a Youden-pair design rather than a replicate sample design. Justifiable exceptions to this requirement shall be approved through the process provided in 1.5. In a Youden-pair design, each participant receives (or prepares from a concentrate) a separate sample *for each analysis required in the study*. There are no replicate analyses; each participant analyzes each study sample once and only once, per analyte if appropriate. Among the set of samples each laboratory analyzes for a specific matrix, there are pairs of samples containing similar but usually different analyte concentrations that differ from each other by up to 20 %. As a matter of convenience to whomever is preparing the samples or spiking concentrates, up to half the Youden pairs may have the same concentration, that is, be blind duplicates, but the participants must have no basis for comparing their single test results from analyses of different study samples.

7.3.2 The only difference in treatment of data from a Youden-pair study is the calculation used to estimate the means and standard deviations; these calculations may be found in Youden and Steiner **(6)**. Once developed, these mean and standard deviation estimates are treated the same as statistics from a study with the usual replicate design. A detailed example with and without raw experimental data is given in Refs. **(7)** and **(8)**, respectively.

7.3.3 The value of the nonreplicate design is that the single-operator standard deviation estimates are free of any conscious or unconscious analyst bias. The procedures for calculating overall and single-operator standard deviations are given in 10.4 and 10.5 and illustrated in Appendix X3.

7.4 *Measurement of Bias:*

7.4.1 The concept of accuracy comprises both precision and bias (see Terminology D 1129 and Practice E 177). As discussed in Practice E 177, there is not a single form for statements of accuracy that can be universally recommended. Since the accuracy of a measurement process is affected by both random and systematic sources of error, measures of both kinds of error are needed. The standard deviation is a universal measure of random sources of error (or precision). Bias is a measure of the systematic errors of a test method.

7.4.2 A collaborative study evaluation of bias for a specific matrix produces a set of analyte/sample means. The difference between a true value (however defined) and the related mean is an estimate of the average systematic error, that is, bias of the test method.

7.4.3 There are three major approaches commonly used to test a measurement procedure: (*1*) measurement of known materials, (*2*) comparison with other measurement procedures, and (*3*) comparison with modifications of the procedure itself **(9)**. The third approach may involve the standard addition technique or the simultaneous analysis of several aliquots of different sizes (for example, 0.5, 1, 1.5, 2, 2.5 units). The task group will select the approach that best suits its needs within the resources available to it.

7.4.4 The most likely task group approach will be the use of known materials. Since reference standards are unlikely to be available, the task group will prepare its samples with added (therefore known to them) quantities of the constituent(s) being tested. The best available chemical and analytical techniques for preparing, stabilizing, if necessary, storing and shipping the prepared samples should be known within the task group and will not be addressed in this practice. However, if the sample preparation and handling techniques used for the study are different from those expected to be used for samples during routine application of the test method, those differences shall be pointed out in the precision and bias statement. Future users of the test method may decide that these differences had an effect on the precision or bias results, or both, from the study.

7.5 *Quality Control During the Study:*

7.5.1 The Quality Control section to appear in the test method must be drafted before the collaborative study design is finalized and the study design must assure that the collaborative study will produce any background data not otherwise available to properly complete the final Quality Control section. Each part of the draft Quality Control section must be used during the collaborative study unless insufficient background data exist to establish credible interim required performance criteria for that part.

7.5.2 All quality control data/information produced to meet the requirements of 7.5.1 shall be reported to the task group chair along with results from analyses on the study samples.

## 8. Collaborative Study Design Approval

8.1 After approval by the task group, the task group chair (or designee) will summarize the proposed design of the collaborative study. This summary will include: (*1*) the test method to be tested in ASTM format and as approved by the task group; (*2*) the analytes to be included in the study; (*3*) the number of samples in accordance with the paired-sample plan of 7.3.1; (*4*) the approach for determining the bias of the test method as exemplified in the collaborative study; (*5*) the range of concentration covered, and approximate concentration of material in each sample or set; (*6*) the approximate number of laboratories and analysts; (*7*) the matrices and QC samples being tested; (*8*) plans for developing study samples; and (*9*) a copy of the instruction and data reporting package to be given to each study participant. This summary should be presented to the Results Advisor in the form of a letter.

8.1.1 As an aid, the task group chairman may use, "Approval of Plans for Interlaboratory Testing," Form A, and in Appendix X1 (a completed example is shown in Fig. X1.1).

8.2 Upon review of the plan, the Results Advisor will advise the task group chairman whether the plan meets the requirements of this practice or what changes are necessary to meet the requirements of this practice.

8.3 Upon receipt of approval of the collaborative test plan by the Results Advisor, the task group chairman (or designee) will conduct the collaborative test.

## 9. Conducting the Collaborative Study

9.1 A single entity, acting for the task group, will prepare the samples for the collaborative study and ship them to the participants with instructions for the study, a copy of the exact test method (if not already supplied), and the participant reporting form (or reporting instructions).

9.1.1 The instructions for the collaborative study shall require sufficient preliminary work by potential collaborators to adequately familiarize them with the test method prior to study measurements. This is necessary to ensure that each collaborative study is made by a peer group and that a learning experience is not included in the statistics of the collaborative study. The task group may also develop procedures to qualify prospective collaborators, and this approach is strongly recommended.

9.1.2 Each laboratory should usually supply its own calibration materials, as independent calibration materials are a significant source of interlaboratory variability. However, if the cost of availability of calibration materials is judged to be a significant deterrent to participation or if currently available materials are inadequate and not considered typical for subsequent routine use of the test method, these materials may be distributed with the study samples. If calibration standards are provided, the Precision and Bias section of the test method should so note, including the concentrations and matrix of the standards and any specific instructions for their use.

9.1.3 As an aid, the task group chairman may use Form B, "Data Report from Individual Laboratories," as in Appendix X2 (a completed example is shown in Fig. X2.1).

9.2 The batch of samples containing a specific member of a Youden pair should be clearly marked with a common unique code, informative to the distributors but not informative to the study participants. Samples should be sized to supply more than the minimum amount necessary to participate in the study (with reasonable allowance for pipetting, rinsing, etc.) to allow for trial runs and analytical restarts that may be necessary. A separate set of samples shall be provided for each operator. Sample concentrations should not be easily surmised values (1, 5, etc.). The assignment of samples to the participating laboratories should be randomized within each concentration level. The above recommendations should help assure statistical independence of results.

9.3 A copy of the test method under investigation, the written instructions for carrying out his/her part of the program, and the necessary study samples should be supplied to each operator. No supplementary instructions or explanations such as by telephone or from a task group member within a cooperating laboratory should be supplied to one participant if not to all. Study materials should be distributed from one location, and the operator's reports should be returned to one location.

9.4 The written instructions should cover such items as: (*1*) directives for storing and subdividing the sample; (*2*) preparation of sample prior to using the test method; (*3*) order of analyses of samples (random order within each laboratory is often best); (*4*) details regarding the reporting of study results on the reporting form; and (*5*) the time limit for return of the reporting form.

9.4.1 Laboratories shall be required to report all figures obtained in making measurements, instead of rounding results before recording them. This may result in recording one or more significant figures beyond what may be usual in the Report section of the test method. A decision about rounding all data can be made by the task group when the final statistical analyses are performed.

9.4.2 The laboratories shall report results from analyses of study samples without background subtraction and shall also report background levels for every matrix that they use in the study. The task group will make any background corrections that may be necessary.

9.4.3 Zeros and negative numbers should be reported whenever they represent the actual test results produced. Test results should never be censored by a participant. The reporting of less than or greater than results negates the objectivity of subsequent statistical calculations and should be avoided. Never report zero in place of a less-than or other nonquantitative test result.

9.5 The task group chair (or designee) should monitor the collaborative study to assure that results are reported back within the agreed upon time limit and are free of obvious procedural, transcription, clerical, or calculation errors. Careful design of the reporting form (or reporting instructions) will facilitate this task.

## 10. Collaborative Study Data Analysis

10.1 For each matrix/analyte, the steps involved by the task group chair in the data analysis consist of: (*1*) tabulating the data; (*2*) eliminating any laboratories that did not follow significant study instructions, were not in control during the study, or were so consistently high or low that their results are unreasonable (see 10.3); (*3*) eliminating any individual outlier data points (10.4); (*4*) for each matrix and analyte concentration studied, calculating the overall and single-operator standard deviations and means from the retained data and calculating the bias from each mean spike recovery (must subtract the mean reported background value whenever necessary); (*5*) tabulating the statistics; (*6*) assembling information required for the research report; and, if desired, (*7*) summarizing these results in a graph or regression equation for the test method statement.

10.1.1 As an aid to following the steps, the task group chair may find it helpful to review the sample calculations of precision and bias given in Appendix X3.

10.2 *Tabulation of Data*—The data reported by the laboratories shall be made consistent in reporting units and, if possible, in the number of reported values per operator or laboratory **(10)**. Before beginning, remove any unusable data sets generated by laboratories that did not follow significant study instructions or used an unacceptable variation of the test method being studied. Unless each laboratory used its own matrix with a unique background concentration, all outlier testing and precision estimates are to be based on the concentration reported rather than on background-corrected results.

10.2.1 Sometimes looking at the histogram of a set of data will help one recognize or understand, or both, the cause of unusual data.

10.3 *Rejection of Outlier Laboratories*— If one or more laboratory's data for an analyte in a specific matrix are so consistently high or low that there must be a large systematic error specific to that laboratory, all the data from the laboratory for that analyte/matrix should be rejected. Identify outlier laboratories by applying the Youden laboratory ranking test **(11)** at the 5 % significance level.

10.3.1 For example, say *n* laboratories reported results for a specific matrix and analyte. Within the data set reported for each concentration, assign a rank score from 1 for the highest result to *n* for the lowest result.

10.3.1.1 For this test, all *n* rank scores for each concentration shall be assigned, even if one or more of the laboratories did not report a result for this particular concentration. The rank of any missing results should be the mean rank of the actual data reported by that laboratory for the other concentrations of the same analyte and matrix. Also, assign an appropriate rank to nonquantitative results.

10.3.1.2 Identical results would each be given the average of the ranks the group is entitled to receive.

10.3.2 For the matrix/analyte, total the rank scores for each laboratory over all of the *q* concentrations. If the total rank sum for any particular laboratory is designated as *R*, then if either:

$R <$ the lower value in Table 1, or
$R >$ the upper value in Table 1,

that laboratory is a candidate to be marked as an outlier and ignored in subsequent calculations with a 5 % risk of this judgement being incorrect.

10.3.2.1 If more than 20 % of the laboratories reporting usable data for the matrix/analyte are outlier candidates, order the candidate laboratories according to the difference between their total rank sum and the nearest critical value given above, and reject individual or tied groups of laboratories until rejection of the next laboratory would exceed the 20 % limit. If rejection of a group of laboratories with equal distances would cause the 20 % limit to be exceeded, randomly reject laboratories from the group until rejection of the next laboratory would exceed the 20 % limit. Data from laboratories ultimately marked as outliers should be ignored for subsequent calculations.

10.3.3 Repeat 10.3 for every matrix and analyte studied.

10.4 *Rejection of Unusable Data and Individual Outlier Results, and Calculation of Final Mean and Overall Standard Deviation Estimates*:

10.4.1 Reject nonquantitative responses since they are useless for subsequent calculations. These rejections do not count against the 10 % limit in 10.4.4 because such responses are unusable. It is the task group's responsibility to judge whether reported zeros are truly quantitative analytical results, and this should usually be done after consulting with each laboratory that reported a zero, whenever that is possible.

10.4.2 Let the remaining data reported for a specific matrix/analyte/concentration be designated $x_i$, $i = 1$ to $n$. Then calculate the mean ($\bar{x}$) and overall standard deviation ($s_T$) as follows:

$$\bar{x} = \frac{\left(\sum_{i=1}^{n} x_i\right)}{n} \tag{1}$$

and

$$s_T = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}} \tag{2}$$

10.4.3 Calculate the *T* value for the most extreme remaining value ($x_e$) as follows:

$$T = (x_e - \bar{x}) / s_T \tag{3}$$

If the absolute value of *T* is greater than the critical value for *n* measurements from Table 2, $x_e$ is considered an outlier value and ignored for subsequent calculations **(12,13,14)**.

10.4.4 If an outlier was just removed in 10.4.3, return to 10.4.2 unless the removal of one more individual outlier would exceed 10 % of the usable data originally reported for this matrix, analyte, and concentration. If 10.4.2 cannot be repeated for this matrix/analyte/concentration, proceed to the next step.

10.4.5 Return to 10.4.2 for the next matrix, analyte and concentration, until final retained data sets and the related mean and overall standard deviation estimates are available for every combination studied.

**TABLE 1 Upper and Lower Limits of the Acceptable Ranges for Total Rank Sums (5 % Level of Significance)**

NOTE 1—This table was prepared by James Longbottom, USEPA, NERL, Cincinnati, OH, and is an adaptation and extension of Youden's Table 7 (**3**). According to Thompson and Willke (**15**), lower values in this table = $g + n\ (0.05(g!)/2\ n)^{1/g} - (g + 1)/2$, and upper values = $ng - n\ (0.05(\ g!)/2n)^{1/g} + (g + 1)/2$, where $n$ = the number of laboratories and $g$ = the number of concentrations.

| Number of Laboratories | Number of Concentrations | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 6 | | 8 | | 10 | | 12 | | 14 | |
| | Lower | Upper | Lower | Upper | Lower | Upper | Lower | Upper | Lower | Upper |
| 7 | 11 | 37 | 17 | 47 | 23 | 57 | 29 | 67 | 35 | 77 |
| 8 | 12 | 42 | 18.5 | 53.5 | 25 | 65 | 32 | 76 | 39 | 87 |
| 9 | 13 | 47 | 20 | 60 | 27.5 | 72.5 | 35 | 85 | 42.5 | 97.5 |
| 10 | 14 | 52 | 21.5 | 66.5 | 29.5 | 80.5 | 38 | 94 | 46 | 108 |
| 11 | 14.5 | 57.5 | 23 | 73 | 32 | 88 | 41 | 103 | 50 | 118 |
| 12 | 15.5 | 62.5 | 24.5 | 79.5 | 34 | 96 | 43.5 | 112.5 | 53.5 | 128.5 |
| 13 | 16.5 | 67.5 | 26 | 86 | 36.5 | 103.5 | 46.5 | 121.5 | 57 | 139 |
| 14 | 17.5 | 72.5 | 27.5 | 92.5 | 38.5 | 111.5 | 49.5 | 130.5 | 60.5 | 149.5 |
| 15 | 18 | 78 | 29 | 99 | 40.5 | 119.5 | 52.5 | 139.5 | 64 | 160 |
| 16 | 19 | 83 | 30.5 | 105.5 | 42.5 | 127.5 | 55 | 149 | 67.5 | 170.5 |
| 17 | 20 | 88 | 32 | 112 | 45 | 135 | 58 | 158 | 71.5 | 180.5 |
| 18 | 21 | 93.5 | 33.5 | 118.5 | 47 | 143 | 61 | 167 | 75 | 191 |
| 19 | 21.5 | 98.5 | 35 | 125 | 49 | 151 | 63.5 | 176.5 | 78.5 | 201.5 |
| 20 | 22.5 | 103.5 | 36.5 | 131.5 | 51 | 159 | 66.5 | 185.5 | 82 | 212 |
| 21 | 23 | 109 | 38 | 138 | 53.5 | 166.5 | 69 | 195 | 85 | 223 |
| 22 | 24 | 114 | 39 | 145 | 55.5 | 174.5 | 72 | 204 | 88.5 | 233.5 |
| 23 | 25 | 119 | 40.5 | 151.5 | 57.5 | 182.5 | 74.5 | 213.5 | 92 | 244 |
| 24 | 25.5 | 124.5 | 42 | 158 | 59.5 | 190.5 | 77.5 | 222.5 | 95.5 | 254.5 |
| 25 | 26.5 | 129.5 | 43.5 | 164.5 | 61.5 | 198.5 | 80 | 232 | 99 | 265 |
| 26 | 27 | 135 | 45 | 171 | 63.5 | 206.5 | 83 | 241 | 102.5 | 275.5 |
| 27 | 28 | 140 | 46 | 178 | 65.5 | 214.5 | 85.5 | 250.5 | 106 | 286 |
| 28 | 29 | 145 | 47.5 | 184.5 | 67.5 | 222.5 | 88 | 260 | 109.5 | 296.5 |
| 29 | 29.5 | 150.5 | 49 | 191 | 69.5 | 230.5 | 91 | 269 | 112.5 | 307.5 |
| 30 | 30.5 | 155.5 | 50.5 | 197.5 | 71.5 | 238.5 | 93.5 | 278.5 | 116 | 318 |
| 31 | 31 | 161 | 51.5 | 204.5 | 73.5 | 246.5 | 96.5 | 287.5 | 119.5 | 328.5 |
| 32 | 32 | 166 | 53 | 211 | 75.5 | 254.5 | 99 | 297 | 123 | 339 |
| 33 | 32.5 | 171.5 | 54.5 | 217.5 | 77.5 | 262.5 | 101.5 | 306.5 | 126 | 350 |
| 34 | 33.5 | 176.5 | 55.5 | 224.5 | 79.5 | 270.5 | 104.5 | 315.5 | 129.5 | 360.5 |
| 35 | 34 | 182 | 57 | 231 | 81.5 | 278.5 | 107 | 325 | 133 | 371 |
| 36 | 35 | 187 | 58.5 | 237.5 | 83.5 | 286.5 | 109.5 | 334.5 | 136 | 382 |
| 37 | 35.5 | 192.5 | 59.5 | 244.5 | 85.5 | 294.5 | 112.5 | 343.5 | 139.5 | 392.5 |
| 38 | 36.5 | 197.5 | 61 | 251 | 87.5 | 302.5 | 115 | 353 | 143 | 403 |
| 39 | 37 | 203 | 62.5 | 257.5 | 89.5 | 310.5 | 117.5 | 362.5 | 146 | 414 |
| 40 | 38 | 208 | 63.5 | 264.5 | 91.5 | 318.5 | 120 | 372 | 149.5 | 424.5 |
| 41 | 38.5 | 213.5 | 65 | 271 | 93.5 | 326.5 | 123 | 381 | 153 | 435 |
| 42 | 39 | 219 | 66 | 278 | 95.5 | 334.5 | 125.5 | 390.5 | 156 | 446 |
| 43 | 40 | 224 | 67.5 | 284.5 | 97 | 343 | 128 | 400 | 159.5 | 456.5 |
| 44 | 40.5 | 229.5 | 69 | 291 | 99 | 351 | 130.5 | 409.5 | 162.5 | 467.5 |
| 45 | 41.5 | 234.5 | 70 | 298 | 101 | 359 | 133 | 419 | 166 | 478 |
| 46 | 42 | 240 | 71.5 | 304.5 | 103 | 367 | 136 | 428 | 169.5 | 488.5 |
| 47 | 43 | 245 | 72.5 | 311.5 | 105 | 375 | 138.5 | 437.5 | 172.5 | 499.5 |
| 48 | 43.5 | 250.5 | 74 | 318 | 107 | 383 | 141 | 447 | 176 | 510 |
| 49 | 44 | 256 | 75.5 | 324.5 | 108.5 | 391.5 | 143.5 | 456.5 | 179 | 521 |
| 50 | 45 | 261 | 76.5 | 331.5 | 110.5 | 399.5 | 146 | 466 | 182.5 | 531.5 |

10.5 *Calculation of Single-Operator Standard Deviation Estimates:*

10.5.1 To complete the required statistical calculations, estimate the single-operator standard deviation ($s_o$) from the retained data pairs available for each Youden pair, analyte, and matrix in the study as follows:

$$s_O = \sqrt{\frac{\sum_{i=1}^{m} (D_i - \bar{D})^2}{2\,(m - 1)}} \quad (4)$$

where:

$m$ = the number of retained pairs of results available for that Youden pair, analyte, and matrix,

$D_i$ = the difference between the retained value from laboratory $i$ for the Youden sample with the higher true value of the pair minus the retained value from laboratory $i$ for the other sample of the pair, and

$\bar{D}$ = the mean of the $m$ usable $D_i$ values.

10.5.2 The calculation of $s_o$ for a blind duplicate is the same

**TABLE 2 Critical Values for $T$ (Two-Sided Test at a 5 % Significance Level) When Standard Deviation is Calculated from the Same Samples (for Single-Value Outlier Testing) (see 10.4)[A]**

| Number of Useable Values, $n$ | Critical Value for $T$ |
|---|---|
| 7 | 2.02 |
| 8 | 2.13 |
| 9 | 2.21 |
| 10 | 2.29 |
| 11 | 2.36 |
| 12 | 2.41 |
| 13 | 2.46 |
| 14 | 2.51 |
| 15 | 2.55 |
| 16 | 2.58 |
| 17 | 2.62 |
| 18 | 2.65 |
| 19 | 2.68 |
| 20 | 2.71 |
| 21 | 2.73 |
| 22 | 2.76 |
| 23 | 2.78 |
| 24 | 2.80 |
| 25 | 2.82 |
| 30 | 2.91 |
| 35 | 2.98 |
| 40 | 3.04 |
| 45 | 3.08 |
| 50 | 3.13 |
| 60 | 3.20 |
| 70 | 3.26 |
| 80 | 3.30 |
| 90 | 3.35 |
| 100 | 3.38 |

[A] Values of $T$ for $n \leq 25$ are based on Grubbs (**12**). For $n > 25$, the values of $T$ are approximate. All values have been adjusted for division by $n - 1$ instead of $n$ in calculating $s$. Tabulated values come from Practice E 178 and may also be found in Grubbs (**14**), although the level of significance shown in Practice E 178 has been doubled because our use here is a two-sided test, rather than a one-sided test.

as for a Youden pair. One of the duplicate samples is arbitrarily selected as the higher sample for this calculation.

10.6 *Calculation of Bias*:

10.6.1 The calculation of the bias of a test method will logically follow the collaborative study design (7.4). The usual collaborative study technique will involve reporting the recovery of added (therefore known) amounts of the analytes being measured.

10.6.2 The calculation of bias for a specific matrix, analyte, and concentration is as follows:

$$Bias\ (\%) = 100(\bar{x} - b - c) / c \tag{5}$$

where:

$\bar{x}$ = the mean of retained data for that matrix, analyte and concentration,
$c$ = the true concentration added, and
$b$ = the mean background concentration reported, if necessary.

10.6.3 Where other types of studies are used to develop a true concentration for use in estimation of the test method bias, special care shall be taken to assure that the other study provides a logical reference value. Consultation with the Results Advisor and other recognized experts may be appropriate in such cases.

## 11. Format of the Precision and Bias Statement Required in Each Test Method

11.1 For most test methods, a collaborative study will be conducted and the following requirements apply.

11.1.1 A brief note shall provide the reader of the test method with a complete understanding of the collaborative study conducted. At a minimum, this note shall include the number of laboratories that contributed data, the matrices studied, the version of Practice D 2777 followed in designing and analyzing the study data, and any other significant aspects of the study not presented elsewhere in the test method.

11.1.1.1 Regarding significant study aspects that *must* be described, if the analytical conditions used during the collaborative study were more restrictive than those allowed in the test method, it is particularly important that these restrictive conditions be fully described in the Precision and Bias statement of the test method. Results from the collaborative study may not apply to other analytical conditions allowed in the test method.

11.1.2 The following caution shall also be included, "Results of this collaborative study may not be typical of results for matrices other than those studied."

11.1.3 The study results shall always be available in the form of a table, which, for each matrix, analyte, and concentration studied, will usually include the true concentration ($c$) added to the matrix, and must include the number of values reported, the number of values retained (that is, left after outlier testing), and (from the retained data): (*1*) the mean response ($\bar{X}$), (*2*) bias as a percent of $c$, and (*3*) the overall standard deviation ($s_T$). For each matrix, analyte, and Youden pair of sample concentrations, the table shall include the number of retained data *pairs* and the single-operator standard deviation ($s_o$) estimated from these pairs of retained values. This table shall be included in the test method unless equivalent mathematical or graphical relationships of the mean (or bias), $s_T$ and $s_o$, to concentration are provided instead. If a matrix had a naturally occurring, non-zero background level for this analyte, the mean background level reported by laboratories passing the outlier testing for the Youden pair with the lowest study concentration shall also be reported in this table, and the bias estimates shall be calculated from the recovery of the true spikes, that is, $x$—average background. This table shall always be included in the research report provided to the Results Advisor and filed at ASTM Headquarters. If the full table is not included in the test method, at least a listing of the true concentrations studied for each matrix and analyte, and the number of values retained for each, shall be included in the precision and bias statement.

11.1.4 Mathematical or graphical relationships developed from the study results shall represent the general way precision and bias vary with concentration. These relationships can be very helpful to a user of a test method who must estimate the precision and bias at a specific concentration within the range studied. Graphs that simply connect the estimates from the collaborative study (connect the dots) are not acceptable. Mathematical relationships shall be accompanied by some indication of the goodness of their fit to the study statistics, unless those statistics are given in the test method.

11.2 If there is some reason why a full collaborative study could not be done, the precision and bias statement shall present a complete justification with reference to 1.3, 1.4, or 1.5, whenever appropriate. If a special exemption was approved by Committee D-19 on the recommendation of the Results Advisor and the Technical Operations Section of the Executive Subcommittee of Committee D-19, the date of that exemption shall also be provided.

11.3 *Test Methods with Non-Numerical Reports*:

11.3.1 When a method specifies that a test result is a non-numerical report of success or failure based on criteria in the procedure, the statement on precision and bias should read as follows:

11.3.1.1 *Precision and Bias*—No statement is made about either the precision or the bias of Method D XXXX for measuring (insert here the name of property) since the result merely states whether there is conformance to the criteria for success specified in the procedure.

11.4 *Test Methods Specifying Other Procedures*:

11.4.1 When a method specifies that the procedures in another ASTM method are to be used, a statement such as the following should be used to assure the user that precision and bias statements apply.

11.4.1.1 *Precision and Bias*—The precision and bias of this test method of measuring (insert here the name of the property) are as specified in Method (insert here the designation of the other method).

## 12. Approval of Data Analysis and Statements

12.1 Approval of the precision and bias statement shall be obtained from the Results Advisor before the test method is submitted for committee ballot, providing him/her with a copy of:

12.1.1 All test data resulting from the collaborative test.

12.1.2 All statistical calculations.

12.1.3 A summary of the final statistical estimates in tabular form.

12.1.4 A copy of the final test method, including the precision and bias statement based on the study results.

12.1.5 A copy of every document given to the participants during the collaborative study.

12.1.6 A complete list of the laboratories (names, addresses, principal contact, etc.) that participated in the study. Do not identify the source of specific study data using anything other than randomly assigned laboratory numbers or codes. The relationship between these numbers/codes and the contributing laboratories must be held strictly confidential.

12.1.7 A description of how the study samples were prepared, etc.

12.1.8 Any background information that may have influenced the results and any other information required for the research report, along with a copy of correspondence documenting approval by the Results Advisor.

12.1.9 Once satisfied with this study file, the Results Advisor shall see that it is sent to ASTM for filing as the official research report.

12.2 *Experimental Data*—The precision and bias statement in the test method shall include a footnote indicating where the supporting data can be found. The footnote shall read as in the following example:

Supporting data for the precision and bias statements have been filed at ASTM Headquarters. Request RR:D_____.

## 13. Keywords

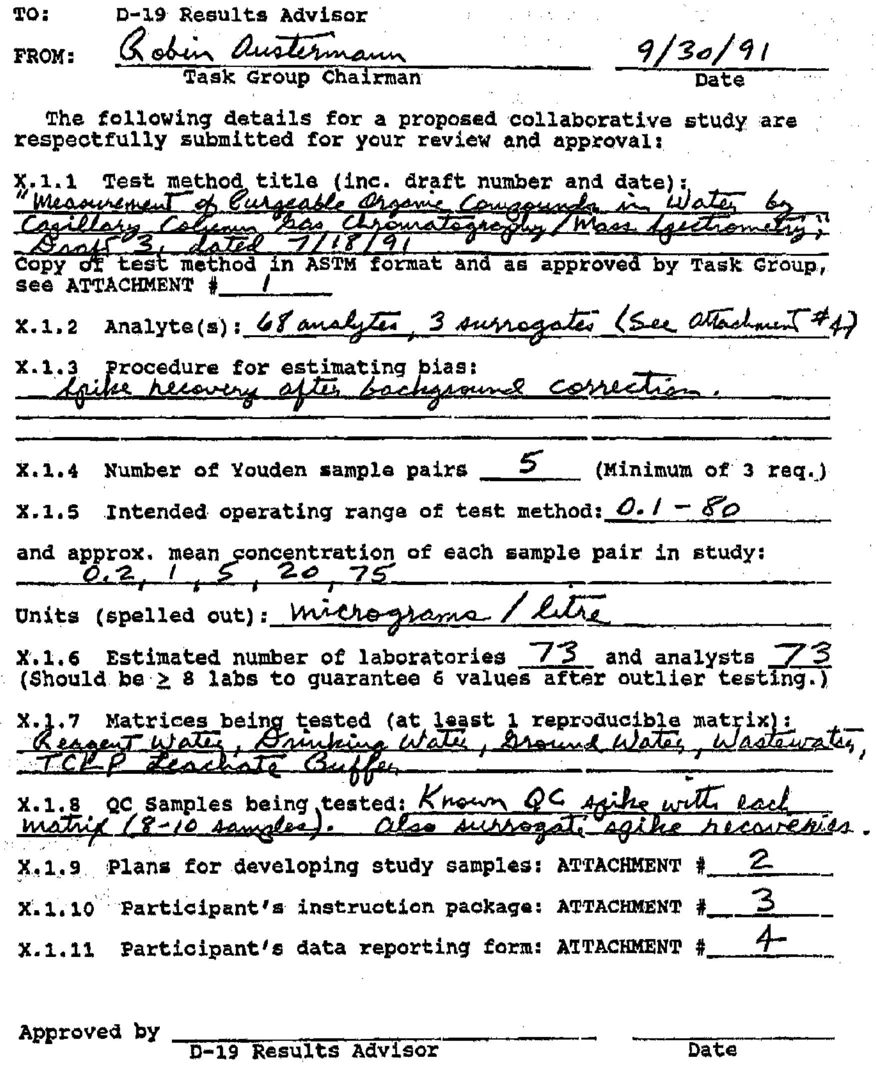
13.1 collaborative study; interlaboratory study; method bias; method precision; method recovery; round-robin study; statistical analysis; Youden study design

# APPENDIXES

## (Nonmandatory Information)

## X1. APPROVAL OF STUDY DESIGN

X1.1 Using Test Method D 5790 also known as USEPA Method 524.2, as an example, Fig. X1.1 was sent by the Task Group Chair to the Results Advisor for his approval before preparation of the samples for the interlaboratory study actually began.



TO: D-19 Results Advisor

FROM: Robin Austermann — 9/30/91

Task Group Chairman — Date

The following details for a proposed collaborative study are respectfully submitted for your review and approval:

X.1.1 Test method title (inc. draft number and date): "Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry"; Draft 3, dated 7/18/91

Copy of test method in ASTM format and as approved by Task Group, see ATTACHMENT # 1

X.1.2 Analyte(s): 68 analytes, 3 surrogates (See Attachment #4)

X.1.3 Procedure for estimating bias: Spike recovery after background correction.

X.1.4 Number of Youden sample pairs 5 (Minimum of 3 req.)

X.1.5 Intended operating range of test method: 0.1 - 80

and approx. mean concentration of each sample pair in study: 0.2, 1, 5, 20, 75

Units (spelled out): micrograms / litre

X.1.6 Estimated number of laboratories 73 and analysts 73
(Should be ≥ 8 labs to guarantee 6 values after outlier testing.)

X.1.7 Matrices being tested (at least 1 reproducible matrix): Reagent Water, Drinking Water, Ground Water, Wastewater, TCLP Leachate Buffer

X.1.8 QC Samples being tested: Known QC spike with each matrix (8-10 samples). Also surrogate spike recoveries.

X.1.9 Plans for developing study samples: ATTACHMENT # 2

X.1.10 Participant's instruction package: ATTACHMENT # 3

X.1.11 Participant's data reporting form: ATTACHMENT # 4

Approved by ______________________ ____________

D-19 Results Advisor — Date

FIG. X1.1 Approval of Study Design: Form A—Approval of Plans for Interlaboratory Testing

## X2. REPORTING OF STUDY DATA

X2.1 An example of the data reporting forms that could have been submitted by each participating laboratory for each analyte is provided as Fig. X2.1.

X2.2 Each participant was also required to provide specific information defining their analytical system and the analytical conditions they used from among options allowed in the test method. On this questionnaire, they were also encouraged to provide any comments they considered appropriate.

Complete Title of Test Method, Draft Number, and Date: Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography, Draft 3, July 18, 1991.

Laboratory Code: 1

Analyte: Chlorobenzene

| Reagent Water | | Drinking Water | | Wastewater | | Ground Water | | TCLP Buffer | |
|---|---|---|---|---|---|---|---|---|---|
| Sple No. | Result μg/L | Sple No. | Result μg/L | Sple No. | Result μg/L | Sple No. | Result μg/L | Sple No. | Result μg/L |
| QC1 | 9.06 | QC2 | | QC3 | | QC4 | 9.98 | QC5 | |
| Bkg | nd | Bkg | | Bkg | | Bkg | nd | Bkg | |
| 1 | 0.23 | 11 | | 21 | | 31 | nd | 41 | |
| 2 | 0.21 | 12 | | 22 | | 32 | 0.20 | 42 | |
| 3 | 1.24 | 13 | | 23 | | 33 | 1.14 | 43 | |
| 4 | 23.82 | 14 | | 24 | | 34 | 21.95 | 44 | |
| 5 | 1.08 | 15 | | 25 | | 35 | 0.97 | 45 | |
| 6 | 5.71 | 16 | | 26 | | 36 | 5.25 | 46 | |
| 7 | 19.21 | 17 | | 27 | | 37 | 18.04 | 47 | |
| 8 | 4.45 | 18 | | 28 | | 38 | 4.61 | 48 | |
| 9 | 82.99 | 19 | | 29 | | 39 | 77.89 | 49 | |
| 10 | 67.65 | 20 | | 30 | | 40 | 65.23 | 50 | |

**FIG. X2.1 Reporting of Study Data: Sample of Form B—Data Report from Individual Laboratories**

## X3. SAMPLE CALCULATION OF PRECISION AND BIAS

X3.1 The following is a sample of the precision and bias calculations from the data reported in the Test Method D 5790 study for one analyte in one matrix. These procedures shall be followed for each analyte and matrix combination in the study.

X3.2 Example data are presented in Table X3.1, as suggested in 10.2. Note that values shown represent analytical results after correction for background concentration by the task group or its representative, the study coordinator.

X3.3 Test for lab-ranking outliers (see 10.3). Table X3.2 shows the results of the lab-ranking calculations on the data in

**TABLE X3.1 ASTM Test Method D 5790: Reagent Water, 5 mL Purge—Raw Data for Chlorobenzene Analysis** [A]

| Laboratory or Analyst | Concentration in μg/L | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Sample 5 [B] 0.88 | Sample 3 1.10 | Sample 8 4.41 | Sample 6 5.29 | Sample 7 17.64 | Sample 4 22.05 | Sample 10 61.73 | Sample 9 74.96 |
| 1 | 1.08 | 1.24 | 4.45 | 5.71 | 19.21 | 23.82 | 67.65 | 82.99 |
| 6 | 2.35 | 0.96 | 4.53 | 5.24 | 17.14 | 21.43 | 64.30 | 70.40 |
| 8 | 1.30 | 1.30 | 4.90 | 6.80 | 21.70 | 25.60 | 61.40 | 85.40 |
| 15 | 1.20 | 1.40 | 3.90 | 4.80 | 15.70 | 18.70 | 54.10 | 66.10 |
| 21 | 2.20 | 0.93 | 4.90 | 4.00 | 16.90 | 18.10 | 53.80 | 81.80 |
| 25 | 1.21 | 1.10 | 4.50 | 5.37 | 17.90 | 22.22 | 62.10 | 75.10 |
| 26 | 1.20 | 1.20 | 4.40 | 4.90 | 16.70 | 21.50 | 62.40 | 71.80 |
| 27 | 1.10 | 1.00 | 4.30 | 5.80 | 22.10 | 26.60 | 75.00 | 89.10 |
| 31 | 0.80 | 0.00 | 5.30 | 5.50 | 19.10 | 24.03 | 74.80 | 88.90 |
| 38 | 1.30 | 1.70 | 4.70 | 6.60 | 23.50 | 24.10 | 74.40 | 89.50 |
| 47 | 1.10 | 1.20 | 4.10 | 5.30 | 17.90 | 22.40 | 77.90 | 63.50 |
| 49 | 1.00 | 1.30 | 4.90 | 5.40 | 12.80 | 18.70 | 26.10 | 37.60 |
| 52 | 1.20 | 1.10 | 4.80 | 5.60 | 19.80 | 23.50 | 69.80 | 83.10 |
| 54 | 0.55 | 0.79 | 3.33 | 3.65 | 14.31 | 17.86 | 50.41 | 60.89 |
| 56 | 1.00 | 1.30 | 4.70 | 5.80 | 19.30 | 24.10 | 66.50 | 82.90 |

[A] Values represent analytical results after correction for background concentration by the study coordinator.

[B] Change to match sample identification used during study.

**TABLE X3.2 ASTM Test Method D 5790: Reagent Water, 5 mL Purge—Ranking Test for Chlorobenzene Analyses**

| Laboratory or Analyst | Sample 5 [A] | Sample 3 | Sample 8 | Sample 6 | Sample 7 | Sample 4 | Sample 10 | Sample 9 | Rank Sum by Laboratory or Analyst |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 11 | 6 | 10 | 5 | 6 | 6 | 6 | 6 | 56 |
| 6 | 1 | 12 | 8 | 11 | 10 | 11 | 8 | 11 | 72 |
| 8 | 3.5 | 4 | 3 | 1 | 3 | 2 | 11 | 4 | 31.5 |
| 15 | 7 | 2 | 14 | 13 | 13 | 12.5 | 12 | 12 | 85.5 |
| 21 | 2 | 13 | 3 | 14 | 11 | 14 | 13 | 8 | 78 |
| 25 | 5 | 9.5 | 9 | 9 | 8.5 | 9 | 10 | 9 | 69 |
| 26 | 7 | 7.5 | 11 | 12 | 12 | 10 | 9 | 10 | 78.5 |
| 27 | 9.5 | 11 | 12 | 3.5 | 2 | 1 | 2 | 2 | 43 |
| 31 | 14 | 15 | 1 | 7 | 7 | 5 | 3 | 3 | 55 |
| 38 | 3.5 | 1 | 6.5 | 2 | 1 | 3.5 | 4 | 1 | 22.5 [B] |
| 47 | 9.5 | 7.5 | 13 | 10 | 8.5 | 8 | 1 | 13 | 70.5 |
| 49 | 12.5 | 4 | 3 | 8 | 15 | 12.5 | 15 | 15 | 85 |
| 52 | 7 | 9.5 | 5 | 6 | 4 | 7 | 5 | 5 | 48.5 |
| 54 | 15 | 14 | 15 | 15 | 14 | 15 | 14 | 14 | 116 [C] |
| 56 | 12.5 | 4 | 6.5 | 3.5 | 5 | 3.5 | 7 | 7 | 49 |

[A] Change to match sample identification used during study.

[B] This rank sum is below the lower limit given in Table 1; reject all data from this laboratory for this analyte.

[C] This rank sum is above the upper limit given in Table 1; reject all data from this laboratory for this analyte.

Table X3.1. Since 20 % of the 15 laboratories reporting usable data is exactly three, up to three laboratories can be removed with this test. Laboratory 38 fails for providing consistently high responses and Laboratory 54 fails for providing consistently low responses, relative to the other laboratories that reported.

X3.4 There are no less-than values to reject as unusable; however, the zero reported by Laboratory 31 for Sample 3 is not considered to be a legitimate quantitative response and is therefore rejected as unusable. Under normal study conditions, Laboratory 31 would be contacted to resolve questions regarding their zero response, but this was not possible for preparation of this example.

X3.5 Calculate the initial mean (*XBAR*) and standard deviation ($s_T$) of the remaining data for each concentration and calculate the initial single-outlier test values, *T* (see 10.4). Since at least one value, but not more than 10 % of the usable data, can be removed for each concentration, and 10 % of 13 is less than two, at most, one value can be removed using single-outlier testing, for each concentration. Only the *T* values for the most extreme values for Samples 10 and 9 exceed the 2.46 critical value for sets of 13 values, and so are removed as outliers. Table X3.3 gives the results of these calculations.

X3.6 Table X3.4 shows the data with all outliers indicated and Table X3.5 contains the final statistics.

X3.7 From the final statistics, the responsible task group chose to develop the following regressions to relate *XBAR*, $s_T$, and $s_o$ to the true concentration (*C*) for *C* values between 0.88 and 75 micrograms per litre:

$$XBAR = 1.035\,(C) + 0.03,\ (R^2 = 1.00)$$
$$s_T = 0.119\,(C) + 0.01,\ (R^2 = 0.97)$$
$$s_o = 0.074\,(C) + 0.08,\ (R^2 = 0.75)$$

$R^2$ indicates the proportion of the total variability in the dependent variable which can be explained by the regression.

NOTE X3.1—This X3.7 step is optional and need not be followed by other task groups.

**TABLE X3.3 ASTM Test Method D 5790: Reagent Water, 5 mL Purge—Single-Outlier Tests for Chlorobenzene Analyses**

| Sample Number | 5 | 3 | 8 | 6 | 7 | 4 | 10 | 9 |
|---|---|---|---|---|---|---|---|---|
| True concentration (*C*) µg/L | 0.88 | 1.10 | 4.41 | 5.29 | 17.64 | 22.05 | 61.73 | 74.96 |
| Number of retained values | 13 | 12 | 13 | 13 | 13 | 13 | 13 | 13 |
| Mean recovery (*XBAR*) | 1.29 | 1.17 | 4.59 | 5.40 | 18.17 | 22.36 | 62.76 | 75.28 |
| Overall standard deviation ($s_T$) | 0.46 | 0.15 | 0.38 | 0.65 | 2.48 | 2.65 | 13.28 | 14.08 |
| Most extreme value | 2.35 | 0.93 | 5.30 | 4.00 | 12.80 | 18.10 | 26.10 | 37.60 |
| Single-outlier test value (*T*) | 2.30 | 1.60 | 1.87 | 2.15 | 2.17 | 1.61 | 2.76 [A] | 2.68 [A] |

[A] This *T* value exceeds the critical value of 2.46 in Table 2 for sets of 13 reported values.

### TABLE X3.4 ASTM Test Method D 5790: Reagent Water, 5 mL Purge—Retained Data for Chlorobenzene Analyses

NOTE 1—Current significance levels:

1. Lab ranking data rejection tests, alpha = 0.05.
2. Individual outlier tests using Thompson(s) role, alpha = 0.05.

| Laboratory or Analyst | Lab Rejected | Concentration in μg/L<br>Sample 5<br>0.88 | Sample 3<br>1.10 | Sample 8<br>4.41 | Sample 6<br>5.29 | Sample 7<br>17.64 | Sample 4<br>22.05 | Sample 10<br>61.73 | Sample 9<br>74.96 |
|---|---|---|---|---|---|---|---|---|---|
| 1 | | 1.08 | 1.24 | 4.45 | 5.71 | 19.21 | 23.82 | 67.65 | 82.99 |
| 6 | | 2.35 | 0.96 | 4.53 | 5.24 | 17.14 | 21.43 | 64.30 | 70.40 |
| 8 | | 1.30 | 1.30 | 4.90 | 6.80 | 21.70 | 25.60 | 61.40 | 85.40 |
| 15 | | 1.20 | 1.40 | 3.90 | 4.80 | 15.70 | 18.70 | 54.10 | 66.10 |
| 21 | | 2.20 | 0.93 | 4.90 | 4.00 | 16.90 | 18.10 | 53.80 | 81.80 |
| 25 | | 1.21 | 1.10 | 4.50 | 5.37 | 17.90 | 22.22 | 62.10 | 75.10 |
| 26 | | 1.20 | 1.20 | 4.40 | 4.90 | 16.70 | 21.50 | 62.40 | 71.80 |
| 27 | | 1.10 | 1.00 | 4.30 | 5.80 | 22.10 | 26.60 | 75.00 | 89.10 |
| 31 | | 0.80 | 0.00 [A] | 5.30 | 5.50 | 19.10 | 24.03 | 74.80 | 88.90 |
| 38 | [B] | 1.30 [B] | 1.70 [B] | 4.70 [B] | 6.60 [B] | 23.50 [B] | 24.10 [B] | 74.40 [B] | 89.50 [B] |
| 47 | | 1.10 | 1.20 | 4.10 | 5.30 | 17.90 | 22.40 | 77.90 | 63.50 |
| 49 | | 1.00 | 1.30 | 4.90 | 5.40 | 12.80 | 18.70 | 26.10 [B] | 37.60 [B] |
| 52 | | 1.20 | 1.10 | 4.80 | 5.60 | 19.80 | 23.50 | 69.80 | 83.10 |
| 54 | [B] | 0.55 [B] | 0.79 [B] | 3.33 [B] | 3.65 [B] | 14.31 [B] | 17.86 [B] | 50.41 [B] | 60.89 [B] |
| 56 | | 1.00 | 1.30 | 4.70 | 5.80 | 19.30 | 24.10 | 66.50 | 82.90 |

[A] = Rejected as a nonquantitative response.
[B] = Rejected.

### TABLE X3.5 ASTM Test Method D 5790: Reagent Water, 5 mL Purge—Final Statistical Summary for Chlorobenzene Analyses

| Sample Number | 5 | 3 | 8 | 6 | 7 | 4 | 10 | 9 |
|---|---|---|---|---|---|---|---|---|
| Number of retained values | 13 | 12 | 13 | 13 | 13 | 13 | 12 | 12 |
| True concentration ($C$) μg/L | 0.88 | 1.10 | 4.41 | 5.29 | 17.64 | 22.05 | 61.73 | 74.96 |
| Mean recovery (*XBAR*) | 1.29 | 1.17 | 4.59 | 5.40 | 18.17 | 22.36 | 65.81 | 78.42 |
| Percent recovery | 146.33 | 106.29 | 104.10 | 102.11 | 103.02 | 101.41 | 106.61 | 104.62 |
| Overall standard deviation ($s_T$) | 0.46 | 0.15 | 0.38 | 0.65 | 2.48 | 2.65 | 7.74 | 8.74 |
| Overall relative standard deviation,% | 35.50 | 12.91 | 8.24 | 11.99 | 13.64 | 11.85 | 11.77 | 11.15 |
| Number of retained pairs | 12 | | 13 | | 13 | | 12 | |
| Single standard deviation, ($s_o$) | 0.40 | | 0.48 | | 0.80 | | 7.31 | |
| Analyst relative deviation,% | 32.60 | | 9.68 | | 3.94 | | 10.14 | |

## REFERENCES

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(15) Thompson, W. A., and Willke, T. A., "On an Extreme Rank Sum Test for Outliers," *Biometrika* (1963), 50, 3 and 4, pp. 375–383.

# CERTIFICATE

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**Designation: D 2879 – 97**

An American National Standard

# Standard Test Method for Vapor Pressure-Temperature Relationship and Initial Decomposition Temperature of Liquids by Isoteniscope[1]

This standard is issued under the fixed designation D 2879; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method covers the determination of the vapor pressure of pure liquids, the vapor pressure exerted by mixtures in a closed vessel at 40 ± 5 % ullage, and the initial thermal decomposition temperature of pure and mixed liquids. It is applicable to liquids that are compatible with borosilicate glass and that have a vapor pressure between 133 Pa (1.0 torr) and 101.3 kPa (760 torr) at the selected test temperatures. The test method is suitable for use over the range from ambient to 748 K. The temperature range may be extended to include temperatures below ambient provided a suitable constant-temperature bath for such temperatures is used.

NOTE 1—The isoteniscope is a constant-volume apparatus and results obtained with it on other than pure liquids differ from those obtained in a constant-pressure distillation.

1.2 Most petroleum products boil over a fairly wide temperature range, and this fact shall be recognized in discussion of their vapor pressures. Even an ideal mixture following Raoult's law will show a progressive decrease in vapor pressure as the lighter component is removed, and this is vastly accentuated in complex mixtures such as lubricating oils containing traces of dewaxing solvents, etc. Such a mixture may well exert a pressure in a closed vessel of as much as 100 times that calculated from its average composition, and it is the closed vessel which is simulated by the isoteniscope. For measurement of the apparent vapor pressure in open systems, Test Method D 2878, is recommended.

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

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Note 3, Note 4, and Note 5.

## 2. Referenced Documents

2.1 *ASTM Standards:*

D 2878 Test Method for Estimating Apparent Vapor Pressures and Molecular Weights of Lubricating Oils[2]

E 230 Temperature Electromotive Force (EMF) Tables for Standardized Thermocouples[3]

## 3. Terminology

3.1 *Definition of Term Specific to This Standard*

3.2 *ullage*—that percentage of a closed system which is filled with vapor.

3.2.1 *Discussion*—Specifically, on Fig. 1, that portion of the volume of the isoteniscope to the right of point *A* which is filled with vapor.

3.3 *Symbols:*

$C$ = temperature, °C,
$K$ = temperature, K,
$p$ = pressure, Pa or torr,
$t$ = time, s,
$P_e$ = experimentally measured total system pressure,
$P_a$ = partial pressure due to fixed gases dissolved in sample,
$P_c$ = corrected vapor pressure, Pa or torr.

$$K = C + 273.15 \tag{1}$$

## 4. Summary of Test Method

4.1 Dissolved and entrained fixed gases are removed from the sample in the isoteniscope by heating a thin layer of a sample at reduced pressure, removing in this process the minimum amount of volatile constituents from the sample.

4.2 The vapor pressure of the sample at selected temperatures is determined by balancing the pressure due to the vapor of the sample against a known pressure of an inert gas. The manometer section of the isoteniscope is used to determine pressure equality.

4.3 The initial decomposition temperature is determined from a plot of the logarithm of the vapor pressure versus the reciprocal of absolute temperature. The initial decomposition temperature is taken as that temperature at which the plot first departs from linearity as a result of the decomposition of the sample. An optional method provides for the use of isothermal rates of pressure rise for this purpose (see Annex A1). These are measured at several temperatures and the logarithm of the

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[1] This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.11 on Engineering Sciences of High Performance Fluids and Solids.

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

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

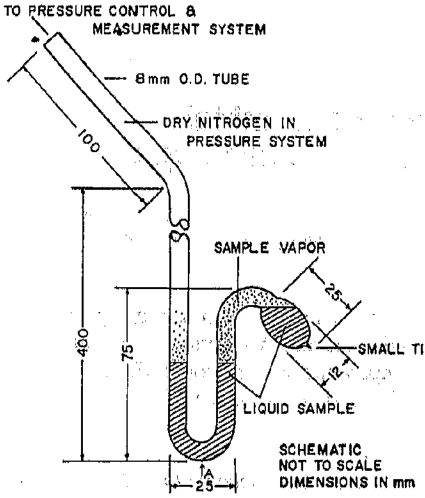


**FIG. 1 Isoteniscope**

rate of pressure rise is plotted versus the reciprocal of absolute temperature. The decomposition temperature of the sample is taken to be that temperature at which the rate of increase of pressure is sufficient to produce a rise of 185 Pa (0.0139 torr/s).

NOTE 2—Vapor pressures less than 133 Pa (1.0 torr), but greater than 13.3 Pa (0.1 torr) at a selected test temperature can be determined directly with reduced accuracy. In some cases the tendency of the sample to retain dissolved or occluded air may prevent direct determinations of vapor pressure in this range. In such cases, data points obtained at higher pressures can be extrapolated to yield approximate vapor pressures in this range.

## 5. Significance and Use

5.1 The vapor pressure of a substance as determined by isoteniscope reflects a property of the sample as received including most volatile components, but excluding dissolved fixed gases such as air. Vapor pressure, *per se*, is a thermodynamic property which is dependent only upon composition and temperature for stable systems. The isoteniscope method is designed to minimize composition changes which may occur during the course of measurement.

## 6. Apparatus

6.1 *Isoteniscope* (Fig. 1).

6.2 *Constant-Temperature Air Bath* (Fig. 2) for use over the temperature range from ambient to 748 K, controlled to ±2 K in the zone occupied by the isoteniscope beyond point "A" (Fig. 1).

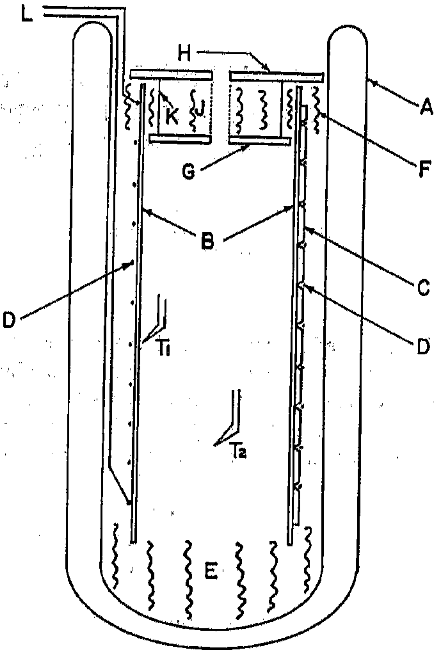
6.3 *Temperature Controller*.

6.4 *Vacuum and Gas Handling System* (Fig. 3).

6.5 *Mercury Manometer*, closed end, 0 to 101.3 kPa (0 to 760 torr) range.

NOTE 3—**Warning:** Poison. May be harmful or fatal if inhaled or swallowed. Vapor harmful; emits toxic fumes when heated. Vapor pressure at normal room temperature exceeds threshold limit value for occupational exposure. See A2.1.

6.6 *McLeod Vacuum Gage*, 0 to 2.00 kPa (0 to 15 torr), vertical primary standard type.



| | |
|---|---|
| A | Dewar, strip silvered, 110 mm ID by 400 mm deep. |
| B | Borosilicate glass tube, 90 mm OD by 320 mm long. |
| C | Glass rod, ⅛-in. in diameter by 310 mm long. Three of these heater element holders are fused along their entire length to the outer surface of Tube B at 120-deg intervals. Slots cut into the fused glass rods on ⅜-in. centers serve as guides for the heating wire D. |
| D | Resistance wire, B. and S. No. 21 gage, spirally wrapped around Tube B and its attached guides. |
| E | Glass wool pad. |
| F | Glass wool pad for centering Tube B and sealing annular opening. |
| G | Lower plate of insulated isoteniscope holder.<br>Transite disk ⅛ in. thick, loose fit in Tube B.<br>With hole for isoteniscope. |
| H | Upper plate of insulated isoteniscope holder.<br>Transite disk ⅛ in. thick, loose fit in Dewar A.<br>With hole for isoteniscope. |
| J | Glass wool insulation between plates G and H. |
| K | Plate spacer rods. |
| L | Heater leads connected to power output of temperature controller. |
| $T_1$ | Temperature-control thermocouple affixed to inside wall of Tube B. |
| $T_2$ | Temperature-indicating thermocouple affixed to isoteniscope. |

**FIG. 2 Constant-Temperature Air Bath**

6.7 *Mechanical Two-Stage Vacuum Pump*.

6.8 *Direct Temperature Readout*, either potentiometric or electronic.

6.9 *Thermocouple*, in accordance with American National Standard for Temperature Measurement Thermocouples (ANSI C96.1) from Tables E 230.

6.10 *Nitrogen*, pre-purified grade.

NOTE 4—**Warning:** Compressed gas under high pressure. Gas reduces oxygen available for breathing. See A2.2.

6.11 *Nitrogen Pressure Regulator*, single-stage, 0 to 345 kPa gage (0 to 50 psig).

6.12 *Alcohol Lamp*.

NOTE 5—**Warning:** Flammable. Denatured alcohol cannot be made nontoxic. See A2.3.

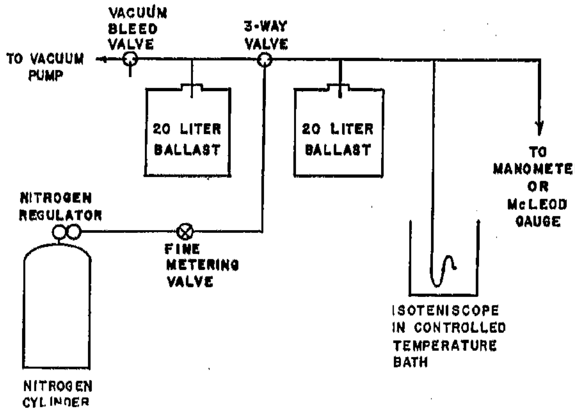


FIG. 3 Vacuum and Gas Handling System

## 7. Hazards

7.1 The procedure requires measuring pressures with devices containing mercury (**Warning**—See Note 3). Spillage of this material creates a safety hazard in the form of toxic vapor in the room. This can be prevented by use of catchment vessels under the devices. If these fail, and the ventilation of the room during occupancy is below 0.01 $m^3$ $(s{\cdot}m^2)$, 2 $ft^3/min{\cdot}ft^2$), thorough cleaning of the floor followed by inspection with a mercury vapor-detecting device is recommended. The following procedures for floor cleaning have been found effective:

7.1.1 A 5 % aqueous solution of sodium polysulfide penetrates well into porous surfaces, but should not be used on polished metal objects.

7.1.2 Sweeping with flowers of sulfur, or agricultural colloidal sulfur, is effective on nonporous floors.

7.1.3 Sweeping with granular zinc, about 20 mesh (840 µm) that has been rinsed in 3 % hydrochloric acid, is effective in catching macro-drops.

7.2 The apparatus includes a vacuum system and a Dewar flask (constant temperature air bath) that is subjected to elevated temperatures. Suitable means should be employed to protect the operator from implosion of these systems. These means include wrapping of vacuum vessels, use of safety shield in front of Dewar flask, and use of safety glasses by the operator.

## 8. Procedure

8.1 Add to the isoteniscope a quantity of sample sufficient to fill the sample bulb and the short leg of the manometer section (**Warning**—See Note 6) to point *A* of Fig. 1. Attach the isoteniscope to the vacuum system as shown in Fig. 3, and evacuate both the system and the filled isoteniscope to a pressure of 13.3 Pa (0.1 torr) as measured on the McLeod gage. Break the vacuum with nitrogen (**Warning**—See Note 7). Repeat the evacuation and purge of the system twice to remove residual oxygen.

NOTE 6—**Warning:** Poison. Can be harmful or fatal if inhaled or swallowed. Vapor harmful; emits toxic fumes when heated. Vapor pressure at normal room temperature exceeds threshold limit value for occupational exposure. See A1.1.

NOTE 7—**Warning:** Compressed gas under high pressure. Gas reduces oxygen available for breathing. See A1.2.

8.2 Place the filled isoteniscope in a horizontal position so that the sample spreads out into a thin layer in the sample bulb and manometer section. Reduce the system pressure to 133 Pa (1 torr). Remove dissolved fixed gases by gently warming the sample with an alcohol (**Warning**—See Note 8) lamp until it just boils. Continue for 1 min.

NOTE 8—**Warning:** Flammable. Denatured alcohol cannot be made nontoxic. See A2.3.

NOTE 9—During the initial evacuation of the system, it may be necessary to cool volatile samples to prevent boiling or loss of volatiles.

NOTE 10—If the sample is a pure compound, complete removal of fixed gases may readily be accomplished by vigorous boiling at 13.3 Pa (0.1 torr). For samples that consist of mixtures of substances differing in vapor pressure, this procedure is likely to produce an error due to the loss of volatile components. Gentle boiling is to be preferred in such cases. The rate of boiling during degassing may be controlled by varying both the pressure at which the procedure is carried out and the amount of heating. In most cases, satisfactory degassing can be obtained at 133 Pa (1 torr). However, extremely viscous materials may require degassing at lower pressures. Samples of high volatility may have to be degassed at higher pressures. In the event that the vapor pressure data indicate that the degassing procedure has not completely removed all dissolved gases, it may be necessary to apply a correction to the data or to disregard data points that are so affected (see 8.7). The degassing procedure does not prevent the loss of volatile sample components completely. However, the described procedure minimizes such losses, so that for most purposes the degassed sample can be considered to be representative of the original sample less the fixed gases that have been removed.

8.3 After the sample has been degassed, close the vacuum line valve and turn the isoteniscope to return the sample to the bulb and short leg of the manometer so that both are entirely filled with the liquid. Create a vapor-filled, nitrogen-free space between the bulb and the manometer in the following manner: maintain the pressure in the isoteniscope at the same pressure used for degassing; heat the drawn-out tip of the sample bulb with a small flame until sample vapor is released from the sample; continue to heat the tip until the vapor expands sufficiently to displace part of the sample from the upper part of the bulb and manometer arm into the manometer section of the isoteniscope.

8.4 Place the filled isoteniscope in a vertical position in the constant-temperature bath. As the isoteniscope approaches temperature equilibrium in the bath, add nitrogen to the gas-sampling system until its pressure equals that of the sample. Periodically adjust the pressure of the nitrogen in the gas-handling system to equal that of the sample. When the isoteniscope reaches temperature equilibrium, make a final adjustment of the nitrogen pressure to equal the vapor pressure of the sample. Pressure balance in the system is indicated by the manometer section of the isoteniscope. When the liquid levels in the manometer arms are equal in height, balance is indicated. Read and record the nitrogen pressure in the system at the balance point. Use the McLeod gage to measure pressures below 2.00 kPa (15 torr) and the mercury manometer for pressures from 2.00 kPa (15 torr) to 101 kPa (760 torr).

8.4.1 It is extremely important that adjustments of the nitrogen pressure be made frequently and carefully. If the nitrogen pressure is momentarily too great, a bubble of nitrogen may pass through the manometer and mix with the sample vapor. If the nitrogen pressure is momentarily too low, a bubble of sample vapor may escape. If either action occurs, the test is terminated immediately and restarted from 8.3.

NOTE 11—Because the densities of most samples are very much less than that of mercury, small errors in the final adjustment of the levels of the liquid level in the manometer have a negligible effect on the measured values of vapor pressure above 133 Pa (1 torr).

8.5 Increase the temperature of the constant-temperature bath 25 K. As the temperature rises, maintain pressure balance in the system in the manner described in 7.4 . When temperature equilibrium is reached, make a final adjustment of pressure to establish balance. Read and record the system pressure. Repeat at intervals of 25 K until the system pressure exceeds 101 kPa (760 torr).

8.6 Plot the logarithm and the measured vapor pressure at each temperature versus the reciprocal of the absolute temperature, $(K)^{-1}$.

NOTE 12—Three or four-cycle semilog graph paper is useful for making this type of plot.

8.7 If the slope of the vapor pressure curve at its low-temperature end indicates that the sample contains fixed gases as a result of incomplete degassing, one of three procedures must be followed. (For examples, see Fig. 4 and Fig. 5.)

8.7.1 Repeat the determination of vapor pressure in the manner described in 8.1-8.7, but employ a more vigorous degassing procedure. This procedure is recommended for pure compounds and mixtures that do not have a vapor pressure greater than 133 Pa (1 torr) at 323 K.

NOTE 13—In general, vapor pressure determinations are made after both temperature equilibrium in the air bath and pressure equilibrium in the isoteniscope and measuring system are attained. However, when a sample begins to decompose, the observed vapor pressure of the sample usually increases even at constant temperature. In such cases, the measured pressure of the system is no longer a function only of the temperature and is not a vapor pressure in the usual sense of the term. It is sometimes useful to continue to take pressure readings even after a system has become unstable. In such cases, the pressure reading is taken after temperature equilibrium is reached in the air bath, regardless of whether a stable pressure balance can be maintained.

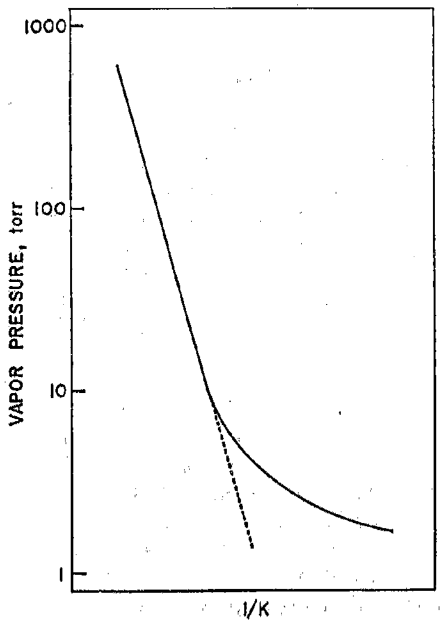


FIG. 4 Log $P_e$ versus 1/K with Linear Region

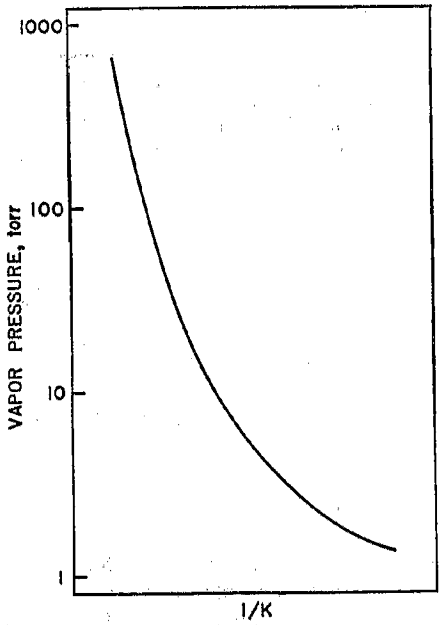


FIG. 5 Log $P_e$ versus 1/K Without Linear Region

8.7.2 In many cases, despite the presence of fixed gases in the sample, the plot of the vapor pressure may be linear over a rather wide range of temperature (see Fig. 4). Extrapolate the linear section to lower temperatures to estimate the vapor pressure even though the presence of fixed gases prevents the direct determination. Extrapolation over more than one decade of pressure is not recommended.

8.7.3 If the lack of a suitable region of linearity prevents the use of the procedure described in 8.7.2 (see Fig. 5), the following arithmetic correction procedure is used: Assume that the pressure at the lowest temperature, $K_1$, at which measurements were made is predominantly due to fixed gases. Calculate the pressure that would be developed at constant volume if this volume of fixed gases were to be heated to the temperature, $K_2$, of the next data point.

$$P_{a2} = P_{a1} \times K_2/K_1 \quad (2)$$

Repeat this procedure for each data point. Calculate the corrected vapor pressure of the sample by subtracting each value of $P_a$ from the corresponding $P_e$ for each successive data point.

$$P_c = P_e - P_a \quad (3)$$

## 9. Calculation and Report

9.1 Plot the logarithms of the calculated values of the corrected vapor pressure versus the reciprocal of the absolute temperature in the manner described in 8.6.

9.2 From the plot of the logarithm of the corrected vapor pressure versus the reciprocal of the absolute temperature, read the smoothed values of the vapor pressure at the desired temperature intervals. Report these values as the vapor pressure of the sample at the indicated temperatures.

9.3 Use the plot of the logarithm of the corrected vapor pressure versus the reciprocal of absolute temperature to determine the initial decomposition temperature of the sample. The initial decomposition temperature is that temperature at which the vapor pressure plot first deviates from linearity. Report this value as the initial decomposition temperature of the sample.

NOTE 14—The initial deviation from linearity is usually due to an increase in rate of pressure rise. A decrease in rate of pressure rise may be observed if the sample undergoes reactions such as polymerization. The vapor-pressure curve above the initial decomposition temperature is not necessarily linear or even approximately linear. Do not confuse nonlinearity due to the presence of fixed gases (see 9.3) with that caused by the decomposition of the sample. Some samples do not decompose under the conditions of the test. In those instances the vapor-pressure curve is practically linear except for low-temperature deviations due to residual quantities of fixed gases.

## 10. Precision and Bias

10.1 Because of the complex nature of Test Method D 2879 for vapor pressure-temperature relationship and because of the expensive equipment involved, there is not a sufficient number of volunteers to permit a comprehensive laboratory program for determining the precision and bias. If the necessary volunteers can be obtained, a program will be undertaken at a later date.

## 11. Keywords

11.1 decomposition temperature; initial decomposition temperature; isoteniscope; liquids; vapor pressure

# ANNEXES

## (Mandatory Information)

## A1. ALTERNATIVE METHOD FOR DETERMINATION OF DECOMPOSITION TEMPERATURE

### A1.1 Scope

A1.1.1 This annex describes a procedure for the determination of the decomposition temperature of liquids whose vapor pressure can be measured in the apparatus described in the standard method.

### A1.2 Summary of Test Method

A1.2.1 Dissolved and entrained gases are removed from the sample in the same manner described in the standard method. The isothermal rate of pressure change with respect to time is measured for several temperatures above the expected decomposition temperature of the sample. The logarithms of the rates of pressure rise are plotted against the reciprocals of the absolute temperatures at which the rates were measured. The decomposition temperature is defined as the temperature at which the rate of pressure increase of the sample is equivalent to a rise of 67 kPa (500 torr) in 10 h (1.85 Pa/s).

### A1.3 Procedure

A1.3.1 Determine the vapor pressure and initial decomposition temperature of the sample in accordance with the procedures described in Sections 8 and 9 of the standard method of test.

A1.3.2 If the sample is found to have an initial decomposition temperature that falls within the range of pressures and temperatures covered by the data in A1.3.1, fill an isoteniscope with a fresh quantity of sample and remove the dissolved fixed gas from it in accordance with the procedures described in 8.2. Prepare the isoteniscope for test as described in 8.3. Place the filled isoteniscope in the constant-temperature bath maintained at a temperature at which a rate of pressure increase greater than 1.85 Pa/s (0.0139 torr/s) will be obtained. Maintain pressure balance in the system in the manner described in 8.4 until the isoteniscope and its contents reach temperature equilibrium. As soon as temperature equilibrium is attained, measure the system pressure at selected intervals of time until a constant rate is given by successive measurements.

A1.3.3 Repeat the determination of rate of pressure rise in accordance with A1.3.2 at temperature intervals of 10 to 15 K until a total of three or four determinations have been made.

### A1.4 Calculation

A1.4.1 Plot the logarithm of the measured rates of pressure rise versus the reciprocal of the absolute temperature. Draw the best straight line through the data.

A1.4.2 Determine the temperature at which the rate of pressure rise is equal to 1.85 Pa/s (0.0139 torr/s). Report that temperature as the decomposition temperature of the sample.

A1.4.3 The interval between measurements is selected so that a minimum pressure change of approximately 2.66 kPa (20 torr) occurs during each interval.

A1.4.4 If the pressure in the sample chamber of the isoteniscope reaches 101 kPa (760 torr) as a result of the accumulation of decomposition products, the balancing gas pressure may be reduced slightly to allow some of these products to bubble through the manometer section of the isoteniscope. When the pressure has been reduced to a workable level, the system can be rebalanced and rate measurement resumed.

## A2. PRECAUTIONARY STATEMENTS

### A2.1 Mercury

**Warning**—Poison. Can be harmful or fatal if inhaled or swallowed. Vapor harmful; emits toxic fumes when heated. Vapor pressure at normal room temperature exceeds threshold limit value for occupational exposure.

Do not breathe vapor.

Keep container closed.

Use with adequate ventilation.

Do not take internally.

Cover exposed surfaces with water, if possible, to minimize evaporation.

Do not heat.

Keep recovered mercury in tightly sealed container prior to sale or purification.

Do not discard in sink or in rubbish.

### A2.2 Nitrogen

**Warning**—Compressed gas under high pressure. Gas reduces oxygen available for breathing.

Keep cylinder valve closed when not in use.

Use with adequate ventilation.

Do not enter storage areas unless adequately ventilated.

Always use a pressure regulator. Release regulator tension before opening cylinder.

Do not transfer to cylinder other than one in which gas is received.

Do not mix gases in cylinders.

Never drop cylinder. Make sure cylinder is supported at all times.

Stand away from cylinder outlet when opening cylinder valve.

Keep cylinder out of sun and away from heat.

Keep cylinder from corrosive environment.

Do not use cylinder without label.

Do not use dented or damaged cylinders.

For technical use only. Do not use for inhalation purposes.

### A2.3 Alcohol

**Warning**—Flammable. Denatured alcohol cannot be made nontoxic.

Keep away from heat, sparks, and open flame.

Keep container closed.

Use with adequate ventilation.

Avoid prolonged breathing of vapor or spray mist.

Avoid contact with eyes and skin.

Do not take internally.

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WASHINGTON, D.C.

**Designation: D 2986 – 95a (Reapproved 1999)**

An American National Standard

# Standard Practice for Evaluation of Air Assay Media by the Monodisperse DOP (Dioctyl Phthalate) Smoke Test[1]

This standard is issued under the fixed designation D 2986; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 The dioctyl phthalate (DOP) smoke test is a highly sensitive and reliable technique for measuring the fine particle arresting efficiency of an air or gas cleaning system or device. It is especially useful for evaluating the efficiency of depth filters, membrane filters, and other particle-collecting devices used in air assay work.

1.2 The technique was developed by the U.S. Government during World War II.[2] Its validity for use in evaluation of air sampling media has been well demonstrated.[3]

1.3 Although a little latitude is permissible in the associated equipment and in the operation method, experience has shown the desirability of operating within established design parameters and recognized test procedures.[4]

1.4 This practice describes the present DOP test method, typical equipment, calibration procedures, and test particles. It is applicable for use with commercially available equipment.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific safety precaution, see 6.1.

## 2. Referenced Documents

2.1 *ASTM Standards:*

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres[5]

## 3. Terminology

3.1 *Definitions*—For other definitions of terms used in this practice, refer to Terminology D 1356.

3.2 Other terms are defined as follows:

3.3 *optical owl, n*—an optical instrument for visual estimation of the particle diameter of the monodisperse aerosol by the angular dependence of light scattering, in accordance with the Mie theory.

## 4. Summary of Practice

4.1 A monodispersed aerosol of 0.3-µm diameter is continuously generated by condensation of DOP vapor under controlled conditions. By selective value arrangement, a metered portion of this aerosol is drawn through a specimen mount containing the item under test. Flow rate through the specimen is adjustable and the corresponding flow resistance is noted as part of the test.

4.2 With aerosol generation stabilized (constant particle size and concentration), aerosol concentration is measured upstream and downstream of the specimen under test by use of a linear forward light-scattering photometer.

4.3 Results are expressed as percent of DOP penetration at the flow rate used.

## 5. Apparatus

5.1 Equipment for use with this technique consists of several interoperational parts. These are indicated in proper relative arrangement by the diagrammatic sketch, Fig. 1. In Fig. 1, the letter designations refer to the same parts as described in the immediately following subsections:

5.2 *Air Supply Source* (a)—This can be a blower as shown diagrammatically or a compressed air source with stepdown regulator. In any case, the air supply source must be clean, free of entrainment, and sufficient to provide full flow against the total resistance of aerosol generator and aerosol conductor lines to the excess aerosol exhaust point.

5.3 *DOP Aerosol Generator* (b)—The generator is designed to produce uniform size liquid droplet particles of 0.3-µm diameter at a concentration of about 100 ± 20 µg/L of air. Further description of the generator is given in 8.3.

5.4 *Aging Chamber* (c)—This is simply a large vessel (usually about 20 L in volume) wherein some dwell time is provided to permit stabilization of the aerosol.

5.5 *Sample Holder* (d)—Size and design of the sample holder can be accommodated to the item under test. However, for evaluation of filter media, a circular test area of 100 cm$^2$ ± 2 % is specified. Provision is made to measure flow resistance

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[1] This practice is under the jurisdiction of ASTM Committee D-22 on Sampling and Analysis of Atmospheresand is the direct responsibility of Subcommittee D22.01on Quality Control.

Current edition approved Sept. 10, 1995. Published February 1996. Originally published as D 2986 – 71. Last previous edition D 2986 – 95.

[2] Knudson, H. W., and White, Locke, Ens. USNR, "Development of Smoke Penetration Meters," *Naval Research Laboratory Report No. P-2642*, P.B. No. 119781, September 1945.

[3] Smith, Walter, J., and Surprenant, N. F., "Properties of Various Filtering Media for Atmospheric Dust Sampling," *Proceedings*, ASTM, Vol 53, 1953, pp. 1122–1135.

[4] *Instruction Manual—Penetrometer,* Filter Testing, DOP, Q127 136-300-138B, Edgewood Arsenal, MD, July 1963.

[5] *Annual Book of ASTM Standards,* Vol 11.03.

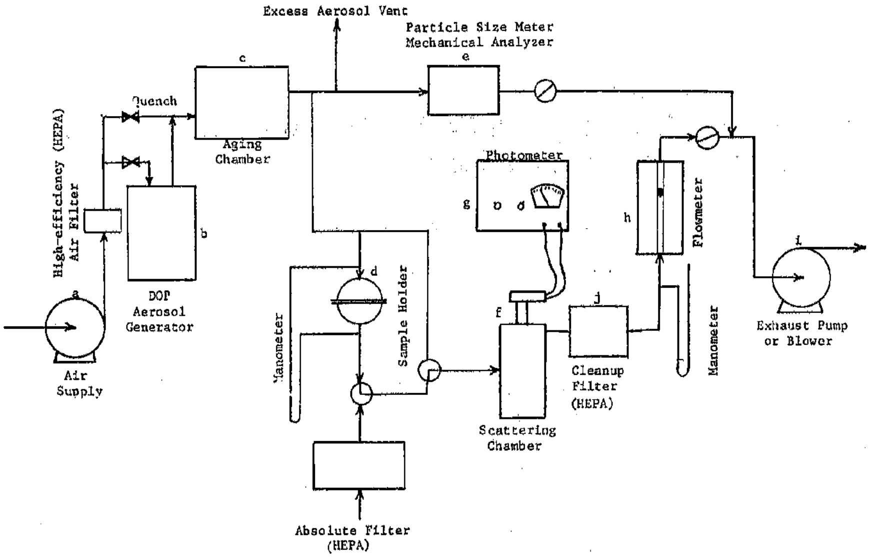


**FIG. 1 Simplified Diagram Showing Relation of Principal Parts of DOP Aerosol Test Apparatus**

across the test piece. A wire screen may be used to support the sample.

5.6 *Particle Size Analyzer* (e)—Particle size in the aerosol is indicated by the particle size analyzer. The visual owl may be used to verify the aerosol particle size. The electronic owl is an adaption designed to remove the human factor; it has proven to be highly successful. Both instruments operate by optical rotation of light scattered at a 90° angle. Paragraph 8.4 gives further detail for the optical owl.

5.7 *Scattering Chamber* (f)—The scattering chamber is used to determine concentration of aerosol either upstream or downstream of the item under test. Further detail for a typical chamber is given in 8.5.

5.8 *Photometer* (g)—This is a combination of sensitive multiplier phototube and meter. The multiplier phototube mounts on the scattering chamber and detects light forward scattered by any particles in the chamber. Further description of the photometer is given in 8.6.

5.9 *Flowmeter* (h)—A float-type flowmeter (rotameter) is used, capable of reading a flow rate well in excess of the maximum test rate to be used. A meter reading somewhat above 100 L/min is the common size. It must be protected against fouling by any DOP accumulation.

5.10 *Exhaust Pump or Blower* (i)—This can be either a positive displacement pump or blower or a multistage turbine-type blower. In any case, there must be more than sufficient capacity to draw air through the total resistance of test specimen, scattering chamber, flowmeter, and all of the related lines, valves, filters, etc., at the maximum test rate (usually 85 L/min).

5.11 *Cleanup Filter* (j)—This should be a filter of sufficiently high capacity and efficiency to remove smoke from the airstream before it passes through the flowmeter. Aerosol particles would ultimately affect the accuracy of the meter.

## 6. Reagents and Materials

6.1 *dioctyl phthalate, (DOP)*—Technical grade.

NOTE 1—DOP is under investigation as a possible carcinogen. Use only by trained personnel wearing appropriate safety equipment to avoid skin contact and inhalation.

## 7. Procedure

7.1 It is necessary to have the equipment prepared and calibrated in advance of any test work. Once prepared and in adjustment, the equipment can be turned on at any time and operated as long as desired with only occasional minor readjustment. Instruction for preparation and operation of each item of equipment is given below.

7.2 *Aerosol Generator*—Turn on the air supply and heating units of the DOP aerosol generator. Wait until the aerosol output has been stabilized; usually this will require ½ h or more from a cold start. Draw a portion of the aerosol through the particle size analyzer, verify the aerosol particle size, and adjust generator conditions until particle diameter is 0.30 µm (by adjustment of quench air temperature).

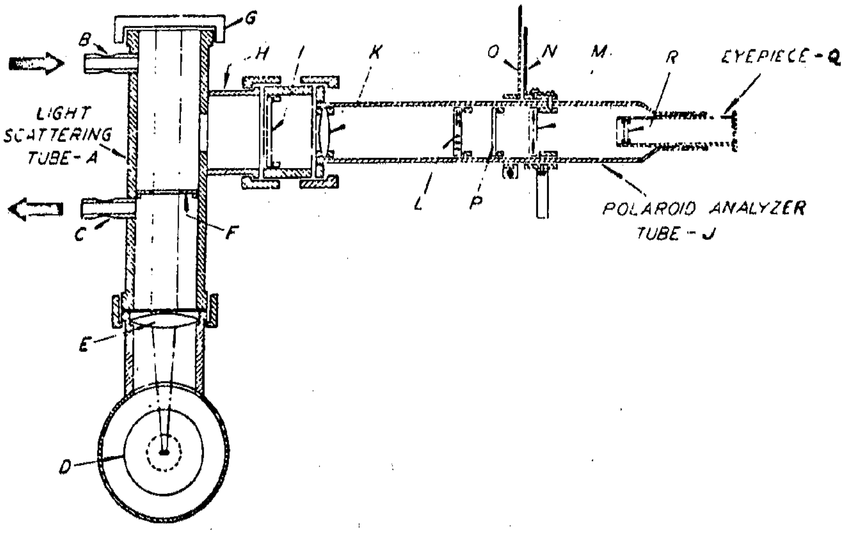
7.3 *Adjustment of Photometer*—Using the same flow rate that will be used for the test specimen (usually 32 L/min ± 2 % through 100 $cm^2$ of area ± 2 % when testing filter media), aerosol from the generator is passed directly through the scattering chamber. Adjust the *Gain* potentiometer of the galvanometer circuit in the photometer until the meter reads 100.0.

7.3.1 Draw clean filtered air through the scattering chamber. Adjust for stray light so that the photometer meter reads zero on the most sensitive scale.

7.4 *Penetration Measurement*—Mount the sample to be tested in the sample holder, making certain that all seals are tight. Draw aerosol through the test specimen. Adjust flow rate to the desired level, for example, 32 L/min. Starting with the least sensitive range, use progressively higher sensitivity until a reading can be obtained.

7.4.1 Read the photometer. Report the value as percent DOP penetration.

7.5 *Flow Resistance*—At the beginning of the penetration



A—Smoke chamber and light-scattering tube
B—Smoke inlet port
C—Smoke outlet port
D—Light source
E—Lens to form parallel beam of light through smoke chamber
F—Baffle to reduce stray light scattered from walls of chamber
G—Velvet-lined cap on chamber
H—Side arm to light scattering tube
I—Smoke-retaining window
J—Polaroid analyzer tube
K—Light collecting lens
L—Bipartite disc (split field polaroid)
M—Polaroid disc mounted in movable collar
N—Indicator on polaroid holder to show angle of displacement from verticle axis
O—Degree scale for indicator (N)
P—Green filter for obtaining monochromatic light
Q—Adjustable eyepiece
R—Lens in eyepiece

FIG. 2 "Owl" Particle Size Meter

test and after the desired flow rate has been established, the manometer is read, showing the resulting pressure drop across the test specimen. This may change after a short time due to accumulation of DOP in the test piece. Ordinarily, the reading is reported in millimetres of water pressure.

7.6 *Other Data*—Line temperature and manometer readings at the flowmeter should be noted along with the current barometer reading so that airflow rates may be reduced to standard conditions if this is required at some later time.

7.7 *Q Value*—When comparing the filter efficiency of various media, it is often useful to report filter performance in terms of the $Q$ value. Calculate $Q$ value as follows:

$$Q = [-100 \log (P/100)]/\Delta p \qquad (1)$$

where:

$P$ = DOP penetration, %, and
$\Delta p$ = airflow resistance, mm of water.

## 8. Discussion of Equipment

8.1 *Availability*—Although equipment for the DOP test is commercially available, some care must be exercised in its procurement. While the test is well developed and very reliable, the equipment is complex. It must be within certain design parameters and must be carefully fabricated. Design details are available[4] but it is strongly recommended that purchase be made of equipment from a professional fabricator.[6]

8.2 *Air Supply*—Any reliable air source may be used that is capable of supplying 120 L/min. If taken from a compressed air system, a stepdown regulator should be used, followed by a control value, and a good commercial air-line filter ahead of the high-efficiency (HEPA) filter.

8.2.1 For a mobile unit or where a compressed air line is not available, a blower can be used. A multistage blower, turbine-type, is effective and will run continuously with very little maintenance. An absolute (HEPA) type filter is used customarily in the supply line to ensure that the air is entirely clean.

8.2.2 In any case, provision must be made to either cool or heat the air as conditions may require. Commercial heat exchange equipment is satisfactory.

8.3 *Aerosol Generator*—The aerosol generator consists of a pot containing about 500 mL of DOP at about 170°C. DOP vapor is carried from the container by a small heated airstream (about 215°C) and mixed with a larger stream of quench air (about 25°C) to form the aerosol particles. The airstream temperatures determine particle size and, once established must be precisely controlled. The aerosol is generated continuously; excess aerosol is disposed of away from the test area.

8.4 *Owl*—A typical "Owl" is shown in Fig. 2. A reading of 29 ± 1° corresponds to 0.3-μm diameter DOP particles.

8.5 *Light-Scattering Chamber*—The light-scattering chamber shown diagrammatically in Fig. 3 is an essential component of the photometer system. Any airborne particles entering the chamber are strongly illuminated and the forward-scattered light intensity is detected by a multiplier phototube (H).

8.5.1 Light from the lamp bulb filament (A) is focused at the

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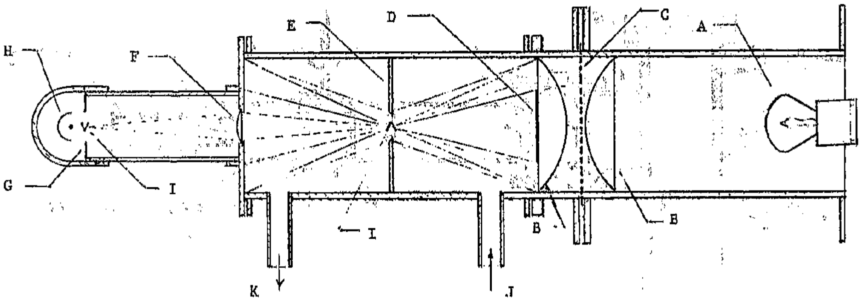
[6] Equipment suitable for the DOP test may be obtained from Air Technology, Inc., 1717 Whitehead Rd, Baltimore, MD 21207.



A—Light source
B—Front lenses
C—Optical filter or light screen
D—Opaque disk
E—Center light baffle
F—Back lens
G—Rear light baffle
H—Multiplier prototube
I—Filament image
J—Inlet port
K—Outlet port

**FIG. 3 Light-Scattering Chamber—Schematic Section Showing Optical System**

center of the light tube (E) by means of condensing lenses (B). An opaque patch (D) cemented to the inside facing of the condensing lens intercepts any direct light from the filament to the phototube.

8.5.2 The stop opening at (E) has a beveled edge, thus providing a knife edge periphery to the opening. This is important in keeping the amount of light scatter from this illuminated edge at a bare minimum.

8.5.3 Take every care to ensure that only light forward-scattered by the test aerosol is seen by the phototube. Following are points requiring special attention:

8.5.3.1 Optics must be accurately aligned with the optical axis. The light bulb filament image should be focused at the center of the light stop opening.

8.5.3.2 All lens surfaces must be perfectly clean; otherwise, light scatter will result.

8.5.3.3 All lens edges, especially if they are ground surfaces, should be painted with flat black.

8.5.3.4 No frosted or etched design or figure can be permitted on the light bulb envelop facing the condensing lenses.

8.5.3.5 The sharp edge of the light stop must be free of nicks, burrs, or even attached particles.

8.5.3.6 Light bulb current must be supplied from a voltage-stabilized circuit.

8.6 *Photometer*—Various types of photometers are in use. In most, a Type 931A multiplier phototube is operated at output currents below 30 µA to ensure stable operation. A scale switch permits the measurements down to 0.001 % or 0.0001 % penetration of DOP smoke.

## 9. Maintenance and Troubleshooting

9.1 When used routinely, the DOP test is reliable and seldom presents any serious problems. Experience will soon show the operator what steps must be followed to maintain fully satisfactory equipment performance. However, to assist the neophyte especially, the following basic suggestions are offered:

9.2 *Daily Care*:

9.2.1 Ascertain that the DOP liquid level or supply is adequate.

9.2.2 See that all temperatures are correct and that controls are functioning properly.

9.2.3 If supply air or quench air must be cooled, see that the cooling water is turned on.

9.2.4 Check aerosol particle size and make any adjustments needed to maintain 0.3-µm diameter.

9.3 *No Aerosol Generation*:

9.3.1 Make sure that air supply is working properly.

9.3.2 See that all heaters are on and working.

9.3.3 Check DOP level or supply.

9.3.4 See that both heated air and quench air are being supplied and at the proper rates.

9.4 *Particle Size Analyzer*:

9.4.1 See that the analyzer lamp is lighted.

9.4.2 Make sure that aerosol is flowing through the instrument (exhaust blower or pump turned on and the analyzer line valve open).

9.4.3 See that connection tubes to the analyzer are not pinched.

9.4.4 Adjust quench air temperature to attain correct particle size.

9.5 *Photometer Not Reading*:

9.5.1 See that the lamp is lighted in the scattering chamber.

9.5.2 See that the amplifier is plugged in and operating.

9.5.3 Make sure that aerosol is flowing through the scattering chamber (selector valve in *run* position and not *purge*).

9.5.4 See that multipler phototube is mounted on the scattering chamber and that lead wires are connected in the amplifier.

9.6 *Photometer Cannot be Adjusted for 100 % Reading*:

9.6.1 Make sure that aerosol generator is operating properly.

9.6.2 Make sure that multiplier phototube is properly adjusted.

9.7 *Photometer Cannot be Adjusted for Stray Light*:

9.7.1 The usual fault is excessive stray light in the scattering chamber. Adjust position of the light source (instrument manual) to attain minimum reading on clean air.

9.7.2 Ascertain that the amplifier is performing correctly.

9.7.3 Have the phototube and connecting leads checked.

9.7.4 Make sure there are no leaks into the filtered air supply line. Leaks will introduce particulate matter and cause a meter reading.

9.7.5 If the problem persists, the source of stray light sometimes can be detected by removing the multiplier phototube and looking into the scattering chamber. This approach should be taken only by someone thoroughly familiar with the equipment.

## 10. Quality Control

10.1 Following are steps that can be taken to help ensure a reliable bias and agreement between laboratories:

10.1.1 *Calibrated Orifice Plate*—Orifice plates are available with calibrations traceable to the National Institute of Standards and Technology (formerly NBS). The plate is inserted in the sample holder and used as a flowmeter against which the instrument flowmeter is compared. For information regarding calibrated plates, inquire of the manufacturer.[7]

10.1.2 *Leaks* in the system can be serious since they will impair the accuracy of flow rate readings. Every precaution must be taken to ensure tightness in lines, instrument filters, and fittings.

10.1.3 *Reference Filter Paper*—It is convenient to have on hand a supply of high-efficiency filter paper that has been pretested and preferably cross-checked by at least one other laboratory. An occasional test run on one of these filter samples will be reassuring and indicative that all is well. Results may be plotted on a control chart to demonstrate attainment of statistical control of the measurement process.[7]

## 11. Keywords

11.1 atmospheric analysis; air assay media; collection efficiency evaluation of filters; dioctyl phthalate, use for filter evaluation; high efficiency filters; membrane filters; particle collecting devices; smoke test for filter evaluation

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[7] Taylor, John K., "Quality Assurance of Chemical Measurements," Lewis Publishers, Inc., Chelsea, MI (1987).

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**Document Name:** ASTM D3120: Standard Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry

**CFR Section(s):** 40 CFR 80.46(a)(3)(iii)

**Standards Body:** American Society for Testing and Materials

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

**Designation: D 3120 – 96**

An American National Standard

# Standard Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry[1]

This standard is issued under the fixed designation D 3120; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method covers the determination of sulfur in the range from 3.0 to 100 ppm (μg/g) in light liquid hydrocarbons boiling in the range from 26 to 274°C (80 to 525°F).

1.2 This test method may be extended to liquid materials with higher sulfur concentrations by appropriate dilution.

1.3 The preferred units are micrograms per grams. Values stated in SI units are to be regarded as the standard. Values in inch-pound units are for information only.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see 6.3, 6.4, 6.8, and 6.10.

## 2. Summary of Test Method

2.1 A liquid sample is injected into a combustion tube maintained at about 800°C having a flowing stream of gas containing about 80 % oxygen and 20 % inert gas (for example, nitrogen, argon, etc.). Oxidative pyrolysis converts the sulfur to sulfur dioxide which then flows into a titration cell where it reacts with triiodide ion present in the electrolyte. The triiodide thus consumed, is coulometrically replaced and the total current required to replace it is a measure of the sulfur present in the sample injected.

2.2 The reaction occurring in the titration cell as sulfur dioxide enters is:

$$I_3^- + SO_2 + H_2O \rightarrow SO_3 + 3I^- + 2H^+$$

The triiodide ion consumed in the above reaction is generated coulometrically thus:

$$3I^- \rightarrow I_3^- + 2e^-$$

2.3 These microequivalents of triiodide (iodine) are equal to the number of microequivalents of titratable sample ion entering the titration cell.

## 3. Significance and Use

3.1 This test method is used to determine trace quantities of sulfur in reformer charge stocks and similar petroleum fractions where such trace concentrations of sulfur are deleterious to the performance and life of the catalyst used in the process. Higher concentrations of sulfur in products analyzed by this test method after appropriate dilution are often detrimental to the use of the product.

## 4. Interferences

4.1 This test method is applicable in the presence of total halide concentrations of up to 10 times the sulfur level and total nitrogen concentrations of up to 1000 times the sulfur level.

4.2 This test method is not applicable in the presence of total heavy metal concentrations (for example, Ni, V, Pb, etc.) in excess of 500 μg/g (ppm).

NOTE 1—To attain the quantitative detectability that the method is capable of, stringent techniques must be employed and all possible sources of sulfur contamination must be eliminated.

## 5. Apparatus[2]

5.1 *Pyrolysis Furnace*—The sample should be pyrolyzed in an electric furnace having at least two separate and independently controlled temperature zones, the first being an inlet section that can maintain a temperature sufficient to volatilize all the organic sample. The second zone shall be a pyrolysis section that can maintain a temperature sufficient to pyrolyze the organic matrix and oxidize all the organically bound sulfur. A third outlet temperature zone is optional.

5.1.1 Pyrolysis furnace temperature zones for light liquid petroleum hydrocarbons should be variable as follows:

| | |
|---|---|
| Inlet zone | up to at least 700°C |
| Center pyrolysis zone | 800 to 1000°C |
| Outlet zone (optional) | up to at least 800°C |

5.2 *Pyrolysis Tube,* fabricated from quartz and constructed in such a way that a sample, which is vaporized completely in the inlet section, is swept into the pyrolysis zone by an inert gas where it mixes with oxygen and is burned. The inlet end of the tube shall hold a septum for syringe entry of the sample and side arms for the introduction of oxygen and inert gases. The center or pyrolysis section should be of sufficient volume to ensure complete pyrolysis of the sample.

5.3 *Titration Cell,* containing a sensor-reference pair of electrodes to detect changes in triiodide ion concentration and a generator anode-cathode pair of electrodes to maintain constant triiodide ion concentration and an inlet for a

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[1] This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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[2] The apparatus described in Sections 5.1 to 5.5 inclusive, is similar in specifications to equipment available from Dohrmann Div. of Rosemount, 3240 Scott Blvd., Santa Clara, CA 95050. For further detailed discussions, in equipment, see: Preprints—Division of Petroleum Chemistry, American Chemical Society, Vol 1, No. 3, Sept. 7–12, 1969, p. B232 "Determination of Sulfur, Nitrogen, and Chlorine in Petroleum by Microcoulometry," by Harry V. Drushel.

gaseous sample from the pyrolysis tube. The sensor electrode shall be platinum foil and reference electrode platinum wire in saturated triiodide half-cell. The generator anode and cathode half-cell shall also be platinum. The titration cell shall require mixing, which can be accomplished through the use of a magnetic stirring bar, stream of inert gas, or other suitable means.

NOTE 2: **Caution**—Excessive speed will decouple the stirring bar, causing it to rise in the cell and damage the electrodes. The creation of a slight vortex is adequate.

5.4 *Microcoulometer,* having variable attenuation, gain control, and capable of measuring the potential of the sensing-reference electrode pair, and comparing this potential with a bias potential, amplifying the potential difference, and applying the amplified difference to the working-auxiliary electrode pair so as to generate a titrant. Also the microcoulometer output voltage signal shall be proportional to the generating current.

5.5 *Recorder,* having a sensitivity of at least 0.1 mV/in. with chart speeds of ½ to 1 in./min. Use of a suitable electronic or mechanical integrator is recommended but optional.

5.6 *Sampling Syringe*—A microlitre syringe of 10-μL capacity capable of accurately delivering 1 to 10 μL of sample into the pyrolysis tube. 3-in. by 24-gage needles are recommended to reach the inlet zone of the pyrolysis furnace.

NOTE 3—Since care must be taken not to overload the pyrolyzing capacity of the tube by too fast a sample injection rate, means should be provided for controlling the sample addition rate (0.1 to 0.2 μL/s).

## 6. Reagents and Materials

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[3] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Purity of Water*—The water used in preparing the cell electrolyte should be demineralized or distilled or both. Water of high purity is essential.

NOTE 4—Distilled water obtained from an all borosilicate glass still, fed from a demineralizer, has proven very satisfactory.

6.3 *Acetic Acid* (rel dens 1.05)—Glacial acetic acid ($CH_3COOH$).

NOTE 5: **Warning**—Poison. Corrosive. Combustible. May be fatal if swallowed. Causes severe burns. Harmful if inhaled.

6.4 *Argon, Helium, or Nitrogen,* high purity grade (HP),[4] used as carrier gas.

NOTE 6: **Warning**—Compressed gas under high pressure. Gas reduces oxygen available for breathing.

6.5 *Cell Electrolyte Solution*—Dissolve 0.5 g of potassium iodide (KI) and 0.6 g of sodium azide ($NaN_3$) in approximately 500 mL of high-purity water, add 5 mL of acetic acid ($CH_3COOH$) and dilute to 1000 mL.

NOTE 7—Bulk quantities of the electrolyte should be stored in a dark bottle or in a dark place and be prepared fresh at least every 3 months.

6.6 *Gas Regulators*—Two-stage gas regulators must be used on the reactant and carrier gas.

6.7 *Iodine* (I), 20 mesh or less, for saturated reference electrode.

6.8 ***Iso*octane**[5] (2,2,4-trimethylpentane).

NOTE 8: **Warning**—Extremely flammable. Harmful if inhaled. Vapors may cause flash fire.

NOTE 9—The most reliable solvent is a sulfur-free form of the sample type to be analyzed. Alternatively, use a high-purity form of cyclohexane [boiling point 80°C (176°F)], *iso*octane (2,2,4-trimethyl pentane) [boiling point, 99.3°C (211°F)], or hexadecane [boiling point, 287.5°C (549.5°F)].

6.9 *n-Butyl Sulfide* ($(CH_3CH_2CH_2CH_2)_2S$).

6.10 Oxygen, high purity grade (HP),[4] used as the reactant gas.

NOTE 10: **Warning**—Oxygen vigorously accelerates combustion.

6.11 *Potassium Iodide* (KI), fine granular.

6.12 *Sodium Azide* ($NaN_3$), fine granular.

NOTE 11: **Warning**—Toxic, causes eye and skin irritation; explosive.

6.13 *Sulfur, Standard Solution* (*approximately 30 μg/g (ppm)*)—Pipet 10 mL of sulfur stock solution (reagent 6.14) into a 100-mL volumetric flask and dilute to volume with *iso*octane.

NOTE 12—The analyst may choose other sulfur compounds for standards appropriate to sample boiling range and sulfur type which cover the concentration range of sulfur expected.

6.14 *Sulfur, Standard Stock Solution* (*approximately 300 μg/g (ppm)*)—Weigh accurately 0.5000 g of *n*-butyl sulfide into a tared 500-mL volumetric flask. Dilute to the mark with *iso*octane and reweigh.

$$\text{S, ppm } (\mu g/g) = \frac{\text{g of } n\text{-butyl sulfide} \times 0.2187 \times 10^6}{\text{g of } (n\text{-butyl sulfide} + \text{solvent})}$$

## 7. Preparation of Apparatus

7.1 Carefully insert the quartz pyrolysis tube in the pyrolysis furnace and connect the reactant and carrier gas lines.

7.2 Add the electrolyte solution to the titration cell and flush several times. Maintain an electrolyte level of ⅛ to ¼ in. (3.2 to 6.4 mm) above the platinum electrodes.

7.3 Place the heating tape on the inlet of the titration cell.

7.4 Position the platinum foil electrodes (mounted on the moveable cell head) so that the gas inlet flow is parallel to the electrodes with the generator anode adjacent to the generator cathode. Assemble and connect the coulometer and recorder (integrator optional) as designed or in accordance with the manufacturer's instructions. Figure X1.2 illustrates the typ-

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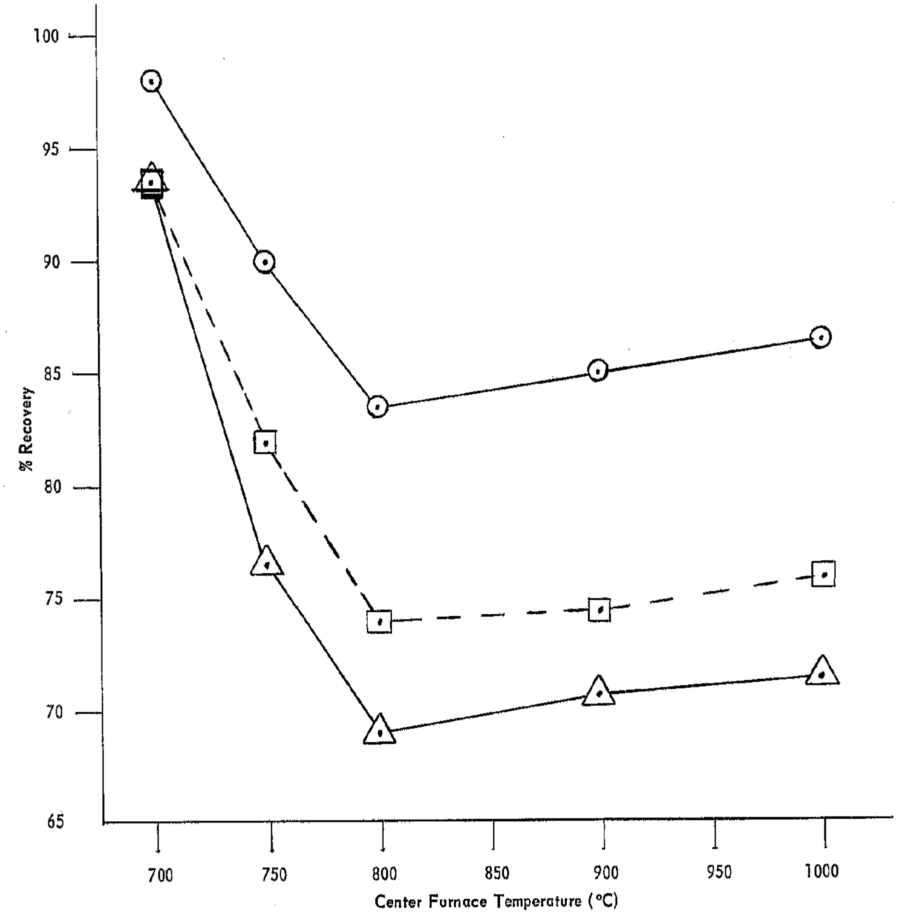
[3] *Reagent Chemicals, American Chemical Society Specifications,* American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States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

[4] High-purity grade gas has a minimum purity of 99.995 %.

[5] Pesticide test grade such as Mallinckrodt "Nano-grade" *iso*octane has been found satisfactory.



Oxidative sulfur system: Thiophene in cyclohexane (10 ppm S) using 0.06% azide electrolyte

| | Flow rate (cc/min) | | |
|---|---|---|---|
| Legend | Oxygen | Argon | $O_2$/Ar ratio |
| ⊙——⊙ | 40 | 160 | 1:4 |
| ⊡---⊡ | 100 | 100 | 1:1 |
| △——△ | 160 | 40 | 4:1 |

**FIG. 1 Percent Recovery versus Temperature (°C)**

ical assembly and gas flow through a coulometric apparatus.

7.4.1 Turn the heating tape on.

7.5 Adjust the flow of the gases, the pyrolysis furnace temperature, titration cell, and the coulometer to the desired operating conditions. Typical operational conditions are given in Table 1.

## 8. Calibration and Standardization

8.1 Prepare a series of calibration standards covering the range of sulfur concentration expected. Follow instructions in 6.13, 6.14, or dilute to appropriate level with *iso*octane.

8.2 Adjust the operational parameters (7.5).

NOTE 13—See Fig. 1 for the variance of percent recoveries with gas ratios and temperature.

8.3 The sample size can be determined either volumetrically or by mass. The sample size should be 80 % or less of the syringe capacity.

8.3.1 Volumetric measurement can be obtained by filling the syringe with about 8 µL or less of sample, being careful to eliminate bubbles, retracting the plunger so that the lower liquid meniscus falls on the 1-µL mark, and recording the volume of liquid in the syringe. After the sample has been injected, again retract the plunger so that the lower liquid meniscus falls on the 1-µL mark, and record the volume of liquid in the syringe. The difference between the two volume

**TABLE 1 Typical Operational Conditions**

| | |
|---|---|
| Reactant gas flow (oxygen), cm³/min | 160 |
| Carrier gas flow (Ar, He, N) cm³/min | 40 |
| Furnace temperature; °C: | |
| Inlet zone | 700 |
| Pyrolysis zone | 800 |
| Outlet zone | 800 |
| Titration cell | set to produce adequate mixing |
| Coulometer: | |
| Bias voltage, mV | 160 |
| Gain | low (approximately 200) |

readings is the volume of sample injected.

8.3.2 Alternatively, the sample injection device may be weighed before and after the injection to determine the amount of sample injected. This technique provides greater precision than the volume delivery method, provided a balance with a precision of ±0.00001 g is used.

8.4 Insert the syringe needle through the inlet septum up to the syringe barrel and inject the sample or standard at an even rate not to exceed 0.1 to 0.2 µL/s. If a microlitre syringe is used with an automatic injection adapter, the injection rate (volume/pulse) should be calibrated to deliver 0.1 to 0.2 µL/s.

8.5 Repeat the measurement of each calibration standard at least three times.

NOTE 14—Not all of the sulfur in the sample comes through the furnace as titratable $SO_2$. In the strongly oxidative conditions of the pyrolysis tube some of the sulfur is also converted to $SO_3$ which does not react with the titrant. Accordingly, sulfur standards of *n*-butyl sulfide in *iso*octane or sulfur standards appropriate to sample boiling range and sulfur type and sulfur concentration should be prepared to guarantee adequate standardization. Recoveries less than 75 % are to be considered suspect. Low recoveries are an indication to the operator that he should check his parameters, his operating techniques, and his coulometric system. If the instrument is being operated properly, recoveries between 75 and 90 % are to be expected. Satisfactory standard materials[6] are given in Table 2.

8.6 If the fraction of sulfur converted to $SO_2$ drops below 75 % of the standard solutions, fresh standards should be prepared. If a low conversion factor persists, procedural details should be reviewed.

## 9. Procedure

9.1 Flush the 10-µL syringe several times with the unknown sample. Determine the sulfur concentration in accordance with 8.2 to 8.6.

9.2 Sulfur concentration may require adjustment of sensitivity settings or sample volume or both.

## 10. Calculation

10.1 Calculate the sulfur content of the sample in parts per million, ppm µg/g, by mass as follows:

$$\text{Sulfur, ppm } \mu g/g = (A \times 1.99)/(R \times M \times F) \quad (1)$$

$$\text{Sulfur, ppm} = (A \times 1.99 \times 10^3)/(R \times V \times D \times F) \quad (2)$$

where:

$A$ = area under curve, in.²,
1.99 = derivation will be found in X1.3,

**TABLE 2 Satisfactory Standard Materials**

| Sample Type | Boiling Point Range °C (°F) | Sulfur Compound |
|---|---|---|
| Naphthas | 26 to 204<br>(80 to 400) | cyclohexane sulfide |
| Jet fuels and stove oil | 177 to 274<br>(350 to 525) | benzyl-thiophene |

$R$ = coulometer range switch setting, Ω,
$M$ = mass of sample, g (volume × density),
$V$ = volume of sample, µL,
$D$ = density of sample, g/mL, and
$F$ = recovery factor, fraction of sulfur in standard that is titrated, ratio of ppm sulfur determined in standard divided by the known ppm sulfur in standard.

$$F = (A \times 1.99)/(R \times M \times C_{std})$$

where:

$C_{std}$ = concentration of standard, ppm.

10.2 Derivation of the calculation equation will be found in X1.3.

NOTE 15—The calculation equation is valid only when the chart speed is 0.5 in./min and a 1-mV (span) recorder with a sensitivity of 0.1 mV/in. is used.

NOTE 16—If a disk integrator is used, see X1.3 for calculations, derivations, and equations.

NOTE 17—A more general form of the equation in 10.1 which is not dependent on the use of a particular recorder scale nor a disk integrator is as follows:

$$\text{sulfur, ppm } (\mu g/g) = \frac{(A)\,(X)\,(0.166)}{(R)\,(Y)\,(M)\,(F)}$$

where:

$A$ = area in appropriate units,
$X$ = recorder sensitivity for full-scale response (mv),

$$0.166 = \frac{(16 \text{ gS/eq})\,(10^{-3} \text{ V/mV})\,(10^6 \mu g/g)}{(96\ 500 \text{ coulombs/eq})},$$

$R$ = resistance, Ω,
$Y$ = area equivalence for a full-scale response on the recorder per second . . . area units per second,
$M$ = mass of sample, g, and
$F$ = recovery factor.

## 11. Precision and Bias

11.1 The precision of this test method as obtained by statistical examination of interlaboratory test results is as follows:

11.1.1 *Repeatability*—The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method exceed 28 % of the average value only in one case in twenty.

11.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method exceed 38 % of the average only in one case in twenty.

11.2 *Bias*—Since there is no accepted reference material suitable for determining the bias for the procedure in this test

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[6] Wallace, L. D., "Comparison of Oxidative and Reductive Methods for the Microcoulometric Determinations of Sulfur in Hydrocarbons," *Analytical Chemistry*, Vol 42, March 1970, p. 393.

method, no statement on bias is made.[7]

## 12. Keywords

12.1 light hydrocarbons; microcoulometry; sulfur

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[7] Supporting data are available from ASTM. Request RR: D02-1036.

## APPENDIX

### (Nonmandatory Information)

### X1. DERIVATION OF COULOMETRIC CALCULATIONS USED IN SECTION 10.1

X1.1 The configuration of the pyrolysis tube and furnace may be constructed as is desirable as long as the operating parameters are met. Figure X1.1 is typical of apparatus currently in use.

X1.2 A typical assembly and oxidative gas flow through a coulometric apparatus for the determination of trace sulfur is shown in Fig. X1.2.

X1.3 *Derivation of Equations:*

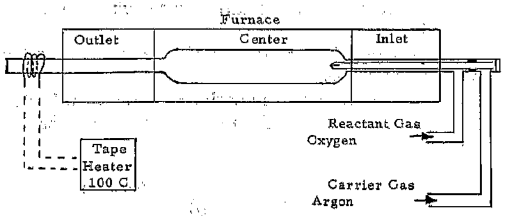

FIG. X1.1 Pyrolipis Tube

X1.3.1 The derivation of the equations used in the calculation section is based on the coulometric replacement of the triiodide (iodine) ions consumed in the microcoulometric titration cell reaction ($I_3^- + 2e^- \rightarrow 3I^-$). The quantity of the reactant formed (triiodide ions) between the beginning and the interruption of current at the end of the titration is directly proportional to the net charge transferred, $Q$.

X1.3.2 In most applications a constant current is used so that the product of current, $i$, in amperes (coulombs per second), multiplied by the time, $T$ (seconds), required to reach the end point provides a measure of the charge, $Q$ (coulombs), necessary to generate the iodine equivalent to the reactant; that is, $Q = it$. Therefore, the number of equivalents of reactant is equal to $Q/F$, where $F$ is the Faraday constant, 96 500 C per equivalent.

X1.3.3 Therefore, the expression to be solved to find the mass of reactant is:

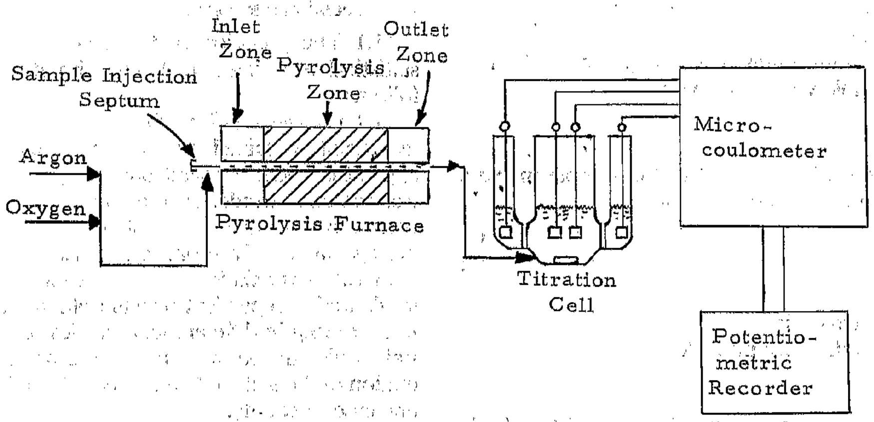

FIG. X1.2 Flow Diagram for Coulometric Apparatus for Trace Sulfur Determination

$$\text{Concentration of sulfur} = \frac{\text{mass of sulfur, g}}{\text{mass of sample, g}} = \frac{\dfrac{\dfrac{Q(\text{C})}{F\text{C}} \times \dfrac{16\ \text{g}}{\text{eq}}}{\text{eq}}}{\text{mass of sample, g}} \tag{X1.1}$$

$$\mu\text{g S} = A\ \text{in.}^2 \times \frac{\dfrac{0.1\ \text{mV}}{\text{in.}} \times \dfrac{2\ \text{min}}{\text{in.}} \times \dfrac{60\ \text{s}}{\text{min}} \times \dfrac{10^{-3}\ \text{V}}{\text{mV}} \times \dfrac{16\ \text{g}}{\text{eq}} \times \dfrac{10^{6}\ \mu\text{g}}{\text{g}}}{R(\Omega) \times \dfrac{96\,500\ \text{C}}{\text{eq}} \times \dfrac{\text{A . s}}{\text{C}} \times f)} \tag{X1.2}$$

where:

$A$ in.$^2$ = peak area measured in square inches,

0.1 mV/in. = millivolt span of upscale deflection for the recorder,

2 min/in. = chart speed in minutes per inch,

60 s/min = conversion of time in minutes to seconds,

$10^{-3}$ V/mV = conversion of volts to millivolts,

16 g/eq = gram-equivalent of sulfur,

$10^6$ μg/g = micrograms per gram conversion factor,

R(Ω) = microcoulometer range switch setting in ohms,

substituting $V/R = 1$ (amps)

$$\text{Q(A}\cdot\text{s)} = \frac{A\ \text{in.}^2 \times \dfrac{0.1\ \text{mV}}{\text{in.}} \times \dfrac{2\ \text{min}}{\text{in.}} \times \dfrac{60\ \text{s}}{\text{min}} \times \dfrac{10^{-3}\ \text{V}}{\text{mV}}}{R(\Omega)} \tag{X1.3}$$

$F$ = 96 500 C/eq

= Faraday's constant[8] (electrical equivalence of one gram-equivalent mass of any substance)

A·s/C = conversion of coulombs to ampere-seconds, and

$f$ = recovery factor (ratio of ppm S determined in standard versus known ppm S in standard)

Therefore,

$$\mu\text{g S} = \frac{A \times 12 \times 10^{-3}\ \text{A}\cdot\text{s} \times \dfrac{16\ \text{g}}{\text{eq}} \times \dfrac{10^{6}\ \mu\text{g}}{\text{g}}}{R \times \dfrac{96\ 500\ \text{C}}{\text{eq}} \times \dfrac{\text{A}\cdot\text{s}}{\text{C}} \times f} \tag{X1.4}$$

Therefore,

$$\mu\text{g S} = \frac{A \times 12 \times 10^{-3} \times 16 \times 10^{6}\ \mu\text{g}}{R \times 96\,500 \times f} \tag{X1.5}$$

Therefore,

$$\mu\text{g S} = (A \times 1.99)/(R \times f) \tag{X1.6}$$

Since ppm = μg/g:

$$\text{ppm S} = \frac{A \times 1.99}{R \times f \times \text{volume, }\mu\text{L} \times 10^{-3}\ \dfrac{\text{mL}}{\mu\text{L}} \times \text{density, } \dfrac{\text{g}}{\text{mL}}} \tag{X1.7}$$

$$\text{ppm S} = \frac{A \times 1.99 \times 10^{3}}{R \times f \times \text{volume} \times \text{density}} \tag{X1.8}$$

Since mass = volume × density

$$\text{ppm S} = (A \times 1.99)/(R \times f \times \text{mass, g}) \tag{X1.9}$$

X1.3.4 *Derivation with Disk Integrator*—$A$ in Eq X1.6 is expressed as in.$^2$ However, it may also be expressed as counts. Therefore, $A$ in.$^2$ = counts × $10^{-3}$ since 1 in.$^2$ = 1000 counts. Therefore, substituting counts × $10^{-3}$ for $A$ in Eq X1.6 gives

$$\mu\text{g S} = (\text{counts} \times 1.99 \times 10^{-3})/(R \times f)$$

Then:

$$\text{ppm S} = \frac{\text{counts} \times 1.99}{R \times \text{volume, }\mu\text{L} \times \text{density, } \dfrac{\text{g}}{\text{mL}} \times f} \tag{X1.10}$$

$$\text{ppm S} = (\text{counts} \times 1.99 \times 10^{-3})/(R \times \text{mass, g} \times f)$$

NOTE X1.1—Counts = 100 × number of integrator per full-scale excursions.

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[8] The value of the Faraday has been redetermined in 1960 by the National Bureau of Standards: the new value is 96 489 ± 2 coulombs (chemical scale).

# CERTIFICATE

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

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**Document Name:**

**CFR Section(s):**

**Standards Body:**

APPROVED

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

**Designation: D 3173 – 87 (Reapproved 1996)**

# Standard Test Method for Moisture in the Analysis Sample of Coal and Coke[1]

This standard is issued under the fixed designation D 3173; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method covers the determination of moisture in the analysis sample of coal or coke. It is used for calculating other analytical results to a dry basis. When used in conjunction with the air drying loss as determined in accordance with Method D 2013 or Practice D 346, each analytical result can be calculated to an as-received basis.

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

## 2. Referenced Documents

2.1 *ASTM Standards:*

D 346 Practice for Collection and Preparation of Coke Samples for Laboratory Analysis[2]

D 2013 Method of Preparing Coal Samples for Analysis[2]

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

D 3302 Test Method for Total Moisture in Coal[2]

## 3. Summary of Test Method

3.1 Moisture is determined by establishing the loss in weight of the sample when heated under rigidly controlled conditions of temperature, time and atmosphere, sample weight, and equipment specifications.

## 4. Significance and Use

4.1 Moisture as determined by this test method is used for calculating other analytical results to a moisture free basis using procedures in Practice D 3180. Moisture percent determined by this test method may be used in conjunction with the air-dry moisture loss determined in Method D 2013 and Test Method D 3302 to determine total moisture in coal. Total moisture is used for calculating other analytical results to "as received" basis using Practice D 3180. Moisture, ash, volatile matter, and fixed carbon percents constitute the proximate analysis of coal and coke.

## 5. Analysis Sample

5.1 The analysis sample is that sample which has been pulverized to pass 250-μm (No. 60) sieve as prepared in accordance with Practice D 346 or Method D 2013.

## 6. Apparatus

6.1 *Drying Oven*, for coal samples:

6.1.1 For determining the moisture of coal, the oven shall be so constructed as to have a uniform temperature in all parts, have a minimum of air space, and be capable of temperature regulation between the limits of 104 and 110°C. It may be of the form shown in Fig. 1. Provision shall be made for renewing the preheated air in the oven at the rate of two to four times a minute, with the air dried as defined in 7.1.

6.1.2 In the oven shown in Fig. 1, the door should contain a hole of approximately $\frac{1}{8}$ in. (3.2 mm) in diameter near the bottom to permit a free flow of air through the oven space.

6.2 *Drying Oven*, for coke samples. For determining the moisture of coke, an ordinary drying oven with openings for natural air circulation and capable of temperature regulation between limits of 104 and 110°C may be used.

6.3 *Capsules*, with covers. A convenient form, which allows the ash determination to be made on the same sample, is a porcelain capsule, $\frac{7}{8}$ in. (22 mm) in depth and $1\frac{3}{4}$ in. (44 mm) in diameter, or a fused silica capsule of similar shape. These capsules shall be used with a well-fitting flat aluminum cover, illustrated in Fig. 2. Platinum crucibles or glass capsules with ground-glass caps may also be used. They should be as shallow as possible, consistent with convenient handling.

## 7. Reagents

7.1 *Dry Air*—Air used to purge the drying oven should be dried to a moisture content of 1.9 mg/L or less. (Dew point −10°C or less.) Any desiccant or drying method capable of achieving this degree of dryness is suitable.

7.2 *Desiccants*—Materials suitable for use in the desiccator may be chosen from the following:

7.2.1 *Anhydrous Calcium Sulfate* (0.004 mg/L).

7.2.2 *Silica Gel.*

7.2.3 *Magnesium Perchlorate* (0.0005 mg/L).

7.2.4 *Sulfuric Acid, Concentrated* (0.003 mg/L).

7.2.5 The desiccant must be kept fresh enough to assure that the air in the desiccator is dry as defined in 7.1. Values in parentheses ( ) are literature values for the residual amount of moisture in air at equilibrium with these desiccants.

NOTE—**Warning:** Sulfuric acid is corrosive and can cause severe damage to eyes, skin, and clothing. Magnesium perchlorate is a strong oxidant and can react violently with organic materials.

## 8. Procedure for Sample Passing a 250-μm (No. 60) Sieve

8.1 Heat the empty capsules under the conditions at which the sample is to be dried, place the stopper or cover on the capsule, cool over a desiccant for 15 to 30 min, and

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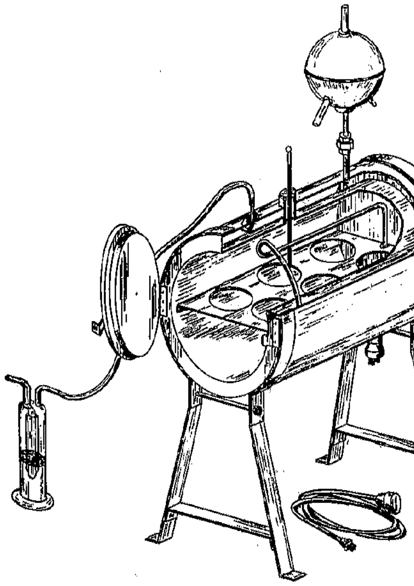
[1] This test method is under the jurisdiction of ASTM Committee D-5 on Coal and Coke and is the direct responsibility of Subcommittee D05.21 on Methods of Analysis.

Current edition approved June 8, 1987. Published August 1987. Originally published as D 3173 – 73. Last previous edition D 3173 – 85.

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



NOTE—Details in U.S. Bureau of Mines Bulletin No. 492, 1951, p 6

FIG. 1 Moisture Oven

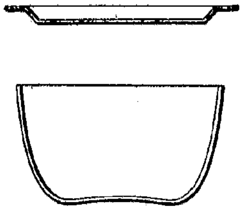


FIG. 2 Capsule for Use in Determining Moisture

weigh. Dip out with a spoon or spatula from the sample bottle approximately 1 g of the sample. Put this quickly into the capsule, close, and weigh at once to the nearest ± 0.1 mg.

8.2 An alternative procedure for weighing the sample (more subject to error) is as follows: After transferring an amount of the sample slightly in excess of 1 g, bring to exactly 1 g in weight (±0.5 mg) by quickly removing the excess weight of the sample with a spatula. The utmost dispatch must be used in order to minimize the exposure of the sample until the weight is determined.

8.3 After removing the covers, quickly place the capsules in a preheated oven (at 104 to 110°C) through which passes a current of dry air. (The current of dry air is not necessary for coke.) Close the oven at once and heat for 1 h. Open the oven, cover the capsules quickly, cool in a desiccator over desiccant, and weigh as soon as the capsules have reached room temperature.

8.4 Use the percentage of moisture in the sample passing a 250-µm (No. 60) sieve to calculate the results of the other analyses to a dry basis.

## 9. Calculations

9.1 Calculate the percent moisture in the analysis sample as follows:

$$\text{Moisture in analysis sample, } \% = [(A - B)/A] \times 100$$

where:

$A$ = grams of sample used, and
$B$ = grams of sample after heating.

## 10. Precision and Bias

10.1 The following criteria should be used for judging the acceptability of results:

10.1.1 *Repeatability*—Duplicate results by the same laboratory should not be considered suspect unless they differ by more than 0.2 % for coals having less than 5 % moisture and 0.3 % for coals having more than 5 % moisture.

10.1.2 *Reproducibility*—The results submitted by two or more laboratories should not be considered suspect unless they differ by more than 0.3 % for coals having less than 5 % moisture and 0.5 % for coals having more than 5 % moisture.

10.1.3 *Bias*—Certified standards are not available for the determination of bias by this test method.

# 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 D3178: Standard Test Method for Carbon and Hydrogen in the Analysis Sample of Coal and Coke)

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

**Standards Body:** American Society for Testing and Materials

APPROVED

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

**Designation: D 3178 – 89 (Reapproved 1997)**

# Standard Test Methods for Carbon and Hydrogen in the Analysis Sample of Coal and Coke[1]

This standard is issued under the fixed designation D 3178; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 These test methods cover the determination of total carbon and hydrogen in samples of coal or coke. Both the carbon and hydrogen are determined in one operation. These test methods yield the total percentages of carbon and hydrogen in the coal as analyzed and the results include not only the carbon and hydrogen in the organic matter, but also the carbon present in mineral carbonates and the hydrogen present in the free moisture accompanying the sample as well as hydrogen present as water of hydration of silicates.

NOTE 1—It is recognized that certain technical applications of the data derived from this test procedure may justify additional corrections. These corrections could involve compensation for the carbon present as carbonates, the hydrogen of free moisture accompanying the sample, and the calculated hydrogen present as water of hydration of silicates.

1.2 When data are converted and reported on the "dry" basis, the hydrogen value is corrected for the hydrogen present in the free moisture accompanying the sample.

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

1.4 The values stated in SI units are to be regarded as the standard.

## 2. Referenced Documents

2.1 *ASTM Standards:*

D 346 Practice for Collection and Preparation of Coke Samples for Laboratory Analysis[2]
D 1193 Specification for Reagent Water[3]
D 2013 Method of Preparing Coal Samples for Analysis[2]
D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke[2]
D 3176 Practice for Ultimate Analysis of Coal and Coke[2]
D 3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases[2]

## TOTAL CARBON AND TOTAL HYDROGEN

## 3. Summary of Test Methods

3.1 The determination of carbon and hydrogen is made by burning a weighed quantity of sample in a closed system and fixing the products of combustion in an absorption train after complete oxidation and purification from interfering substances. These test methods give the total percentages of carbon and hydrogen in the coal as analyzed, and include the carbon in carbonates and the hydrogen in the moisture and in the water of hydration of silicates.

## 4. Significance and Use

4.1 Carbon and hydrogen values are used to calculate the amount of oxygen (air) required in combustion processes, and in the calculations of efficiency of combustion processes.

4.2 Carbon and hydrogen determinations are used in material balances on coal conversion processes; also one or the other is frequently used in correlations of chemical and physical properties, such as yields of products in liquefaction, reactivity in gasification, and the density and porosity of coal.

## 5. Sample

5.1 The sample shall be the material pulverized to pass No. 60 (250-μm) sieve and well mixed according to Method D 346 or Method D 2013. It may be beneficial to grind the ash, pit ash, calcined coke and high mineral content materials to pass a No. 100 (150-μm) sieve.

5.2 The test sample shall be weighed just prior to commencing the analysis to minimize chance for moisture change. A change in moisture content would introduce error in the hydrogen analysis. In order to provide the data necessary to correct for the hydrogen present in the moisture and ensuing final calculations of both the hydrogen and carbon, a separate sample shall be weighed out at the same time for a moisture analysis, and analyzed in accordance with Test Method D 3173.

## 6. Apparatus

6.1 *Oxygen Purifying Train*, consisting of the following units arranged as listed in the order of passage of oxygen:

6.1.1 *First Water Absorber*—A container for the solid dehydrating reagent. It shall be so constructed that the oxygen must pass through a column of reagent adequate to secure water equilibrium equal to that secured in the prescribed absorption train. A container of large volume and long path of oxygen travel through the reagent will be found to be advantageous where many carbon and hydrogen determinations are made.

6.1.2 *Carbon Dioxide Absorber*—A container for solid carbon dioxide absorbing agent. It shall be constructed as described in 6.1.1 and shall provide for a column of reagent adequate to remove carbon dioxide completely.

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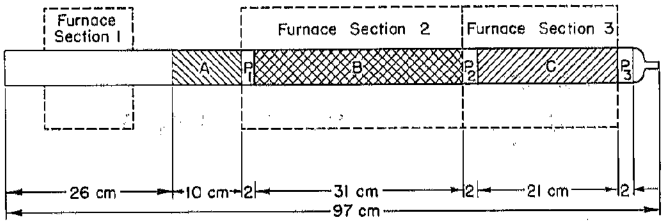
[1] These test methods are under the jurisdiction of ASTM Committee D-5 on Coal and Coke and are the direct responsibility of Subcommittee D05.21 on Methods of Analysis.

Current edition approved Sept. 29, 1989. Published February 1990. Originally published as D 3178 – 73. Last previous edition D 3178 – 84.

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

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



*A*—Clear fused quartz section (optional) when a translucent quartz tube is used.
*B*—Cupric oxide filling.
*C*—Lead chromate or silver filling.
$P_1$, $P_2$, or $P_3$—oxidized copper gauze plugs.

NOTE—All dimensions are given in centimetres. When furnace sections longer than those specified in 6.3 are to be used, changes in the above dimensions shall be in accordance with the provisions of Note 5.

**FIG. 1 Arrangement of Tube Fillings for Combustion Tube**

6.1.3 *Second Water Absorber,* same as specified in 6.1.1

6.2 *Flowmeter,* used to permit volumetric measurement of the rate of flow of oxygen during the determination. It shall be suitable for measuring flow rates within the range from 50 to 100 mL/min (standard temperature and pressure). The use of a double-stage pressure-reducing regulator with gage and needle valve preceding the first water absorber is recommended to permit easy and accurate adjustment of the rate of flow.

6.3 *Combustion Unit*—The combustion unit shall consist of three electrically heated furnace sections, individually controlled, which may be mounted on rails for easy movement; the upper part of each furnace may be hinged so that it can be opened for inspection of the combustion tube. The three furnace sections shall be as follows:

6.3.1 *Furnace Section 1,* nearest the oxygen inlet end of the combustion tube, approximately 130-mm long and used to heat the inlet end of the combustion tube and the sample. It shall be capable of rapidly attaining an operating temperature of 850 to 900°C. Combustion tube temperature shall be measured by means of a thermocouple placed immediately adjacent to the tube near the center of the tube section.

6.3.2 *Furnace Section 2,* approximately 330 mm in length and used to heat that portion of the tube filled with cupric oxide. The operating temperature shall be 850 ± 20°C. Combustion tube temperature shall be measured by means of a thermocouple placed immediately adjacent to the tube near the center of the tube section.

6.3.3 *Furnace Section 3,* approximately 230 mm-long, and used to heat that portion of the tube filled with lead chromate or silver. The operating temperature shall be 500 ± 50°C. Combustion tube temperature shall be measured by means of a thermocouple placed immediately adjacent to the tube near the center of the tube section.

6.3.4 *Combustion Tube*—The combustion tube shall be made of fused quartz or high-silica glass[4] and shall have a nominal inside diameter which may vary within the limits of 19 to 22 mm and a minimum total length of 970 mm. The exit end shall be tapered down to provide a tubulated section for connection to the absorption train. The tubulated section shall have a length of 20 to 25 mm, an internal diameter of not less than 3 mm, and an external diameter of approximately 7 mm. The total length of the reduced end shall not exceed 60 mm. If a translucent fused quartz tube is used, a transparent section 190-mm long, located 250 mm from the oxygen inlet end of the tube, will be found convenient (see Fig. 1).

6.3.5 *Combustion Boat*—This shall be either glazed porcelain, fused silica, or platinum. Boats with internal dimensions of approximately 70 by 8 by 8 mm have been found convenient.

6.4 *Absorption Train*—The absorption train shall consist of the following units arranged as listed in the order of passage of oxygen:

6.4.1 *Water Absorber,* having a capacity for 45 $cm^3$ of solid reagent and a minimum length of gas travel through the reagent of 80 mm.[5]

6.4.2 *Carbon Dioxide Absorber*—If solid reagents are used for carbon dioxide absorption the container shall be as described in 6.4.1. If a solution is used, the container shall be a Vanier bulb.

6.4.3 *Guard Tube*—A container as described in 6.4.1.

## 7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[6] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

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

7.3 *Oxygen,* 99.5 % purity or better (Note 5).

7.4 *Combustion Tube Reagents:*

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[4] Vycor has been found satisfactory for this purpose.

[5] Glass-stoppered containers such as the Nesbitt, Schwartz U-tube and the Stetser-Norton bulbs have been found satisfactory.

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

7.4.1 *Cupric Oxide* (*CuO*), wire form, dust-free.

7.4.2 *Fused Lead Chromate*, ($PbCrO_4$) approximately 2.38 to 0.84 mm size.

7.4.3 *Silver Gauze*, 99.9 % silver minimum purity, 0.84 mm, made from approximately No. 27 B&S gage wire.

7.4.4 *Copper Gauze*, 99.0 % copper minimum purity, 0.84 mm made from approximately No. 26 B&S gage wire.

7.5 *Purification and Absorption Train Reagents*:

7.5.1 *Water Absorbent*—Anhydrous magnesium perchlorate ($Mg(ClO_4)_2$) of approximately 2.38 to 0.35 mm size.

NOTE 2—Trade names of the reagents are Anhydrone and Dehydrite.

7.5.2 *Carbon Dioxide Absorbent*—If a solid reagent is used, it shall be sodium or potassium hydroxide (NaOH or KOH) impregnated in an inert carrier of approximately 2.38 to 0.84 mm size. Use of soda lime in place of the above or in admixture with them is permissible (Note 3). If a solution is used, it shall be 30 weight % potassium hydroxide (KOH).

NOTE 3—Trade names of the sodium and potassium hydroxide permissible solid carbon dioxide absorbing reagents are: Ascarite II, Caroxite, and Mikohbite. If soda lime is used in admixture with any of the foregoing, it should not exceed 30 weight % of the total reagent. In using Ascarite it may be necessary to add a few drops of water to this reagent to assure complete absorption of carbon dioxide.

## 8. Preparation of Apparatus

8.1 *Combustion Tube Packing*—To ensure complete oxidation of combustion products and complete removal of interfering substances such as oxides of sulfur, the combustion tube shall be packed with cupric oxide and lead chromate or silver. The arrangement and lengths of the tube fillings and separating plugs shall be as shown in Fig. 1. It is recommended that the tube be placed in a vertical position (constricted end downward) for packing. When filling the tube with lead chromate, any residual reagent adhering to the walls of the empty portion of the tube must be removed. When silver is used as a tube filling, the required length of filling may be prepared conveniently from three or four strips of silver gauze 150 to 200-mm long, by rolling each strip into a cylindrical plug and inserting the strips end-to-end in the tube.

NOTE 4—Longer furnaces with appropriate lengths of tube packing will be satisfactory.

8.2 *Absorption Train*:

8.2.1 *Water Absorber*—A container that is filled with a permissible solid desiccant by adding the required amount in small portions and settling each portion by gentle tapping between additions. Place a glass wool plug between the reagent and the absorber outlet to prevent loss of reagent dust.

8.2.2 *Carbon Dioxide Absorber*—If a solid reagent is used for the retention of carbon dioxide, fill the absorber as described in 8.2.1. Place in the outlet section of the container a layer or cap of desiccant that is the same as that used in the water absorber. This layer shall have a bulk volume not less than one fourth nor more than one third of the combined volume of both reagents. If a liquid absorbent is used, fill the inner tube of the Vanier bulb with the same desiccant used in the water absorber. Place a glass wool plug in the outlet section of the container to prevent loss of reagent dust.

8.2.3 *Guard Tube*, packed with equal volumes of the water absorbent and a solid carbon dioxide absorbent.

8.2.4 *Connections*—To ensure a closed system from the supply tank of oxygen to the guard tube at the end of the absorption train, it is recommended that all connections by glass-to-glass or glass-to-quartz butt joints be sealed with short lengths of flexible tubing. The connection between the purification train and the combustion tube may be made by means of a rubber stopper or other suitable device. All connections shall be gas tight. No lubricant shall be used for making tubing connections in the absorption train.

8.3 *Conditioning of Apparatus:*

8.3.1 *Newly Packed Combustion Tube*—Burn a sample of coal or coke as described in 9.4 except that the products of combustion need not be fixed in a weighed absorption train.

8.3.2 *Used Combustion Tube*—After any extended shut down, one day or more, test the combustion train under procedure conditions, but without burning a sample, for 40 min with weighed absorption bulbs connected. A variation of not more than 0.5 mg of either bulb shall be considered satisfactory.

NOTE 5—If the blank tests for flow indicate interfering impurities in the oxygen supply by consistent weight-gain in the absorption bulbs, eliminate these impurities by using a preheater furnace and tube, filled with cupric oxide. Operate this preheater furnace at 850 ± 20°C and insert in series between the supply tank of oxygen and the purification train.

8.3.3 *Absorption Train*—Condition freshly packed absorber and guard tubes by burning a sample of coal or coke as described in 9.4 except that tube weights need not be determined.

8.3.4 *Standard Checks* shall be made frequently, particularly when intermittent use of the combustion train is common or when any changes have been made in the system. A standard substance of certified analysis, such as benzoic acid or sucrose as furnished by the National Bureau of Standards shall be burned as described in Section 9. A variation from the theoretical of not more than 0.07 % for hydrogen nor more than 0.30 % for carbon shall be considered satisfactory.

## 9. Procedure

9.1 After the combustion tube and absorbers have been conditioned as prescribed in Section 8, conduct the test as follows:

9.2 *Absorption Train*—Bring the absorption tubes to room temperature near the balance for 15 to 20 min, vent momentarily to the atmosphere, wipe with a chamois or lint-free cloth in the areas where handled, and weigh to the nearest 0.1 mg.

9.3 *Sample*—Weigh approximately 0.2 g (weighed to the nearest 0.1 mg) of air-dry sample ground to pass a No. 60 (250-µm) sieve into a combustion boat.

9.4 *Sample Analysis*—With furnace (6.3.2 and 6.3.3) at specified temperatures and positioned as shown in Fig. 1, perform the following operations in rapid succession in the order listed:

9.4.1 If a conventional type of sample heating furnace is used for heating (6.3.1), place it so that its left-hand edge is about 100 mm from the oxygen inlet end of the combustion tube.

9.4.2 Attach the weighed absorption train to the tube:

9.4.3 Push the sample boat into the tube to a point within approximately 20 mm from plug $P_1$;

9.4.4 Close the tube and adjust the oxygen flow to a rate of 50 to 100 mL/min (standard temperature and pressure) being the same as used in blanking (see 8.3.2).

9.4.5 Apply full heat to heating section No. 1 to bring it to an operating temperature of 850 to 900°C as rapidly as possible. Move the heater slowly toward the boat so that it completely covers the boat and is brought into contact with heating (6.3.2) in a period of 10 to 20 min (Note 6). Allow it to remain in this position for an additional 5 to 10 min and then shut off the heat and return the sample heater to its original position. Continue to the flow of oxygen through the tube for 10 min (Note 7), close the absorbers under a positive pressure of oxygen, and detach them from the train. Remove the absorbers to the vicinity of the balance, allow them to cool to room temperature for 15 to 20 min, vent momentarily to atmosphere, wipe them with a chamois or lint-free cloth in the areas handled, and finally weigh them to the nearest 0.1 mg. While the absorbers are cooling, it is recommended that the ash remaining in the combustion boat be examined for traces of unburned carbon which, if present, will nullify the determination.

NOTE 6—Some variation in operating technique and heater manipulation may be permitted here at the discretion of the analyst, provided that it is conducive to a gradual and controlled release of volatile matter. Conditions that lead to visible burning (flame combustion) of the sample shall be avoided.

NOTE 7—Since water may condense in the cooler outlet end of the combustion tube or in the inlet arm of the water absorber, the use of an external or internal heat conducting device (a metal heat bridge) is recommended to prevent such condensation or promote reevaporation during this flushing period.

## 10. Calculation

10.1 Calculate the percentage of carbon (Note 8) in the analysis sample as follows:

$$\text{Carbon, \%} = (A \times 27.289)/B \qquad (1)$$

where:

$A$ = increase in weight of $CO_2$ absorption bulb, g, and
$B$ = grams of sample used.

NOTE 8—It is recognized that formation of oxides of nitrogen during the combustion procedure may lead to slightly high results for carbon. However, extensive study of this effect by five laboratories led to the conclusion that error so incurred would not be significant in commercial application. In certain research applications, where accuracy of a higher order is required, means of removing oxides of nitrogen prior to water and carbon dioxide absorption should be included.

10.2 *Hydrogen*—Calculate the percentage of hydrogen in the analysis sample (Note 9) as follows:

$$\text{Hydrogen, \%} = (C \times 11.19)/B \qquad (2)$$

where:

$B$ = grams of sample used, and
$C$ = increase of weight of water absorption bulb, g.

NOTE 9—The water absorbed in the water absorption tube includes not only water formed as a product of combustion, but also free water (moisture) in the sample and water of hydration of any clay minerals present.

## 11. Report

11.1 The results of the carbon and hydrogen analysis may be reported on any of a number of bases, differing from each other in the manner by which moisture is treated.

11.2 A separate portion of the analysis sample shall be analyzed for moisture content in accordance with Test Method D 3173, in order to allow calculation of the as-analyzed data to other bases.

11.3 Procedures for converting the values obtained on the analysis sample to other bases are described in Methods D 3176 and D 3180.

## 12. Precision and Bias

12.1 The permissible differences between two or more determinations shall not exceed the following values:

| | Repeatability, % | Reproducibility, % |
|---|---|---|
| Carbon | 0.3 | . . . |
| Hydrogen | 0.07 | |

12.2 The bias of this test method cannot be determined at this time.

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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 D3236: Standard Test Method for Apparent Viscosity of Hot Metal Adhesives and Coating Materials

**CFR Section(s):** 21 CFR 177.1520(b)

**Standards Body:** American Society for Testing and Materials

APPROVED

*Official Incorporator:*

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

**Designation: D 3236 – 88 (Reapproved 1999)**

An American National Standard

# Standard Test Method for Apparent Viscosity of Hot Melt Adhesives and Coating Materials[1]

This standard is issued under the fixed designation D 3236; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method covers the determination of the apparent viscosity of hot melt adhesives and coating materials compounded with additives and having apparent viscosities up to 200 000 millipascal second (mPa·s) (Note 3) at temperatures up to 175°C (347°F).

NOTE 1—Although precision has not been studied, this procedure may be adaptable to viscosities higher than the present 200 000-mPa·s limit and temperatures above 175°C (347°F). Equipment described in this procedure permits testing of materials having viscosities as high as $16 \times 10^6$ mPa·s and provides temperatures up to 260°C (500°F).

NOTE 2—For petroleum waxes and their blends having apparent viscosities below 15 mPa·s, Test Method D 445 is especially applicable.

NOTE 3—One pascal second (Pa·s) = 1000 centipoise (CP); one millipascal second (mPa·s) = one centipoise.

1.2 The values stated in acceptable metric units are to be regarded as the standard. The values in parentheses are for information only.

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

## 2. Referenced Documents

2.1 *ASTM Standards:*

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

## 3. Terminology

3.1 *Definitions:*

3.1.1 *viscosity*—the ratio of shear stress to shear rate. The viscosity of a liquid is a measure of the internal friction of the liquid in motion. The unit of dynamic viscosity is the pascal second. For a Newtonian liquid, the viscosity is constant at all shear rates. For a non-Newtonian liquid, viscosity will vary depending on shear rate.

3.1.2 *apparent viscosity*—the viscosity determined by this test method and expressed in millipascal seconds. Its value may vary with the spindle and rotational speed selected because many hot melts are non-Newtonian.

## 4. Summary of Test Method

4.1 A representative sample of the molten material to be tested is maintained in a thermally controlled sample chamber. Apparent viscosity is determined under temperature equilibrium conditions using a precision rotating spindle type viscometer. Data obtained at several temperatures can be plotted on appropriate semi-logarithmic graph paper and apparent viscosity at intermediate temperatures can be estimated.

## 5. Significance and Use

5.1 This test method distinguishes between hot melts having different apparent viscosities. It is believed that apparent viscosity determined by this procedure is related to flow performance in application machinery operating under conditions of low shear rate. Apparent viscosity as determined by this test method may not correlate well with end use applications where high shear rates are encountered.

5.2 Materials of the type described in this procedure may be quite non-Newtonian and as such the apparent viscosity will be a function of shear rate under the conditions of test. Although the viscometer described in this test method generally operates under conditions of relatively low shear rate, differences in shear effect can exist depending upon the spindle and rotational speed conditions selected for the test program. Maximum correlation between laboratories, therefore, depends upon testing under conditions of equivalent shear.

5.3 Approximate shear rates using various spindles are shown in Table A1.1 in the Annex to this procedure.

## 6. Apparatus

6.1 *Viscometer*, rotating spindle type with leveling stand.[3]

6.2 *Viscometer Spindles*, stainless steel.[3]

6.3 *Sample Chamber*, with precision proportional temperature controller[3],[4] that provides control accuracy of ±1.0°C

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[1] This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.10.0A on Physical and Chemical Properties.

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

[3] Suitable viscometers and accessories can be obtained from Brookfield Engineering Laboratories, Inc., Stoughton, MA 02072.

[4] A suitable temperature controller can be obtained from Athena Controls, Inc., 2 Union Road, West Conshohocken, PA 19428.

(1.8°F) or better through the range from 100 to 200°C (212 to 392°F).

6.4 *Graph Paper*, semi-logarithmic.

## 7. Calibration

7.1 The viscometer is precalibrated using Newtonian fluids by the manufacturer. No zero adjustment is provided since experience has shown that the zero point will not vary due to changes in the spring. The viscometer and spindles are precision equipment and should be kept from undue shock and mishandling. Physical damage to the instrument will often reveal itself as erratic or no oscillation of the pointer when the instrument, with or without the spindle in place, is operated in air. When operating normally, the pointer will be stable and have free oscillation about the zero point in air.

7.2 The instrument may be further calibrated using standard reference fluids. Suitable fluids are available in nominal viscosities up to 15 000 mPa·s at 149°C (300°F).[5] The procedure for instrument calibration using standard reference fluids is that encompassed by this test method. Results obtained using standard reference fluids should not deviate from the nominal viscosity by more than 2 %.

7.3 The temperature controller of the type recommended for this procedure is factory calibrated and has control capability of ±0.5 % of the control point (±1.0°C at 175°C). To further check the controller and further establish controller settings, use the following procedure: Place a sufficient quantity of low viscosity (500 mPa·s or less) hot melt in the sample container to permit immersion of the appropriate ASTM thermometer to the proper depth. Do not permit the thermometer bulb to rest on the bottom of the sample container. Suitable thermometers are shown in Table 1.

TABLE 1 Suitable ASTM Thermometers

| Temperature Range | Immersion, mm | Scale Error, max | ASTM Thermometer Number |
|---|---|---|---|
| 90°C to 170°C | 51 | 0.2°C | 35C-62 |
| 194°F to 338°F | 51 | 0.5°F | 35F-62 |
| 145°C to 205°C | 76 | 0.4°C | 100C-68 |

NOTE 4—Particular care must be taken not to overflow the sample chamber when using the 100°C, 76-mm immersion thermometer.

7.3.1 Insert the thermometer through the insulating cover of the sample container and hold it in place at the point required for proper immersion depth. Adjust the thermal controller to provide the desired test temperature. Rotate the thermometer during temperature reading to minimize the effect of thermal gradients in the sample. Continue temperature readings and controller adjustment until minimum deviation from test temperature is obtained. Minimum deviation may vary between laboratories, depending upon the controller, but should in no case exceed ±0.5°C (0.9°F). Repeat this procedure for any test temperature desired within the scope of this procedure.

## 8. Procedure

8.1 *Selection of Spindle*—From the estimated viscosity of the sample and Table A1.1 in the Annex, select a viscometer and spindle combination that will produce readings in the desired range.

NOTE 5—Use only the spindle shown to be appropriate for the viscometer to be used.

8.1.1 Where more than one spindle is available for the range selected, choose the spindle that produces results nearest the midpoint of the measurable viscosity range. Viscometer scale readings must be within the 10 to 95 range.

NOTE 6—Care must be taken in the storage and handling of spindles and assemblies. Protect them from dust, corrosive deposits, and mechanical abuse. Avoid touching the calibrated section of the spindle with the hands. Clean the spindle and sample chamber thoroughly after each use. A recommended cleaning procedure is included in Annex A2.

8.2 *Preparation of Sample*—Place the required amount of representative sample (see Table 2) measured to the nearest 0.005 g (or 0.05 mL if handled in the molten state) in the sample chamber. Melt the sample in an oven set at the desired test temperature or in the thermo-container preheated to the desired test temperature. Avoid excessive or prolonged heating of the sample to minimize thermal and oxidative effects. Use a fresh sample for each temperature for which a determination is to be made.

8.3 *System Alignment and Spindle Insertion*—After the sample is completely melted, lower the properly aligned and leveled viscometer until the tips of the alignment bracket just touch the top of the thermo-container, making contact directly behind the locating ring. Raise the viscometer, positioning the tips of the alignment bracket 2 mm (1⁄16 in.) above the top of the thermo-container. Using both hands, gently slide the thermo-container base until the tips of the alignment bracket *just touch* the locating ring. *Do not* forcibly displace the alignment bracket (see Fig. 1). Screw the link coupling nut onto the viscometer coupling nut (note left-hand thread). Connect the coupling link to the spindle (and the coupling nut). Lower the spindle into the sample chamber and connect the link coupling nut to the viscometer coupling nut, noting the left-hand thread. Pick up the insulating cap and place it over the sample chamber (see Fig. 1).

8.4 *Viscosity Determination*—Ensure that the material in the sample chamber is completely molten and that temperature controller settings are proper. Turn on the viscometer and allow the spindle to rotate at the lowest spindle speed available to

TABLE 2 Sample Size Requirement

| Spindle | Approximate Volume, mL | Approximate Sample Weight, g[A] |
|---|---|---|
| SC 4-18 | 8.00 | 6.40 |
| SC 4-21 | 8.00 | 6.40 |
| SC 4-27 | 10.50 | 8.40 |
| SC 4-28 | 11.50 | 9.20 |
| SC 4-29 | 13.00 | 10.40 |
| SC 4-31 | 10.00 | 8.00 |
| SC 4-34 | 9.50 | 7.60 |

[A] Based on typical molten specific gravity of 0.800. If the specific gravity of the material to be tested varies greatly from this value, sample size must be adjusted to ensure proper liquid level on the spindle shaft.

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[5] Suitable calibration fluids may be obtained from Brookfield Engineering Laboratories, Inc., Stoughton, MA 02072 or Cannon Instrument Co., P. O. Box 16, State College, PA 16801.

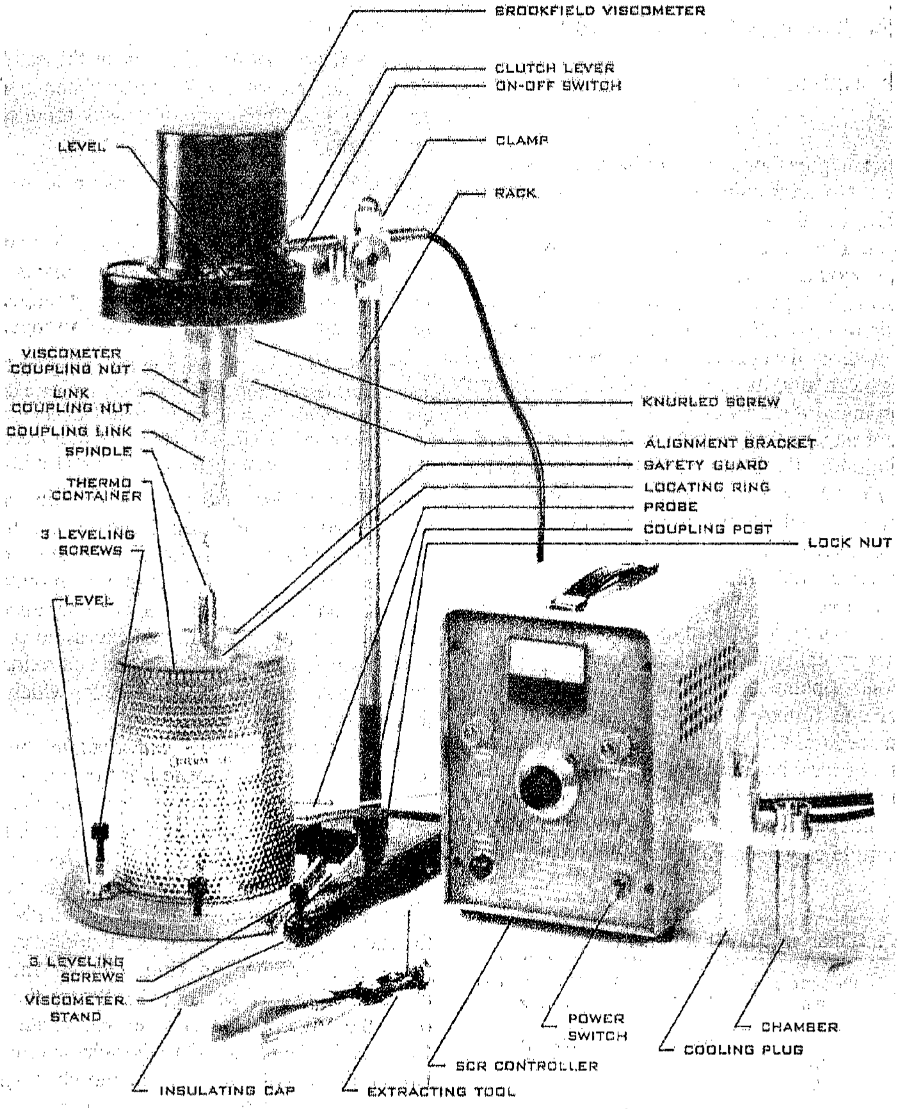

FIG. 1 Apparatus for Viscosity Determination

minimize temperature gradients in the sample as well as possible shear effects. When temperature equilibrium is indicated, turn off the viscometer, remove the insulating cap, raise the viscometer and spindle, and inspect the liquid level on the spindle shaft. It should extend about 3 mm (⅛ in.) up the spindle shaft beyond the upper, tapered portion of the spindle. If the liquid level varies significantly from this, add or remove sample to provide this level. Replace the insulating cap, and allow the unit to reestablish temperature equilibrium with the spindle rotating at the lowest available speed. Continue spindle rotation for 15 min after apparent equilibrium. Increase the spindle speed to that required to produce a scale reading nearest the midpoint of the scale, but in no case outside the 10 to 95 unit range. Engage the pointer clutch and stop the viscometer motor when the pointer is in view. Record the scale reading. Restart the viscometer motor, and allow at least five additional revolutions of the spindle. Engage the pointer clutch and stop the viscometer motor with the pointer in view. Record the second dial reading. Repeat the above operation until three consecutive scale readings are obtained which differ by no more than 0.5 unit.

## 9. Calculation

9.1 Determine the average of the three consecutive scale readings which differ by no more than 0.5 scale unit. To convert to millipascal seconds, multiply this value by the appropriate factor taken from either the instrument instruction manual or Table A1.2 in the Annex. Repeat this for each temperature.

NOTE 7—If it is necessary to interpolate for viscosity values at intermediate temperatures, plot a series of observed apparent viscosity values on the logarithmic scale and the corresponding test temperatures on the linear scale of appropriate semi-logarithmic paper, using a series of at least three different temperatures. From the plot, determine the apparent

TABLE 3 Summary of Precision Estimates, Total Round-Robin Data

| Sample No. | Average Viscosity, mPa·s | Sa | deg freedom | Sa + b | deg freedom | Sa % | Sa + b % |
|---|---|---|---|---|---|---|---|
| MI69-28 | | | | | | | |
| 100°C | 65.2 | 2.02 | 11 | 3.64 | 10 | 3.10 | 5.58 |
| 125°C | 38.7 | 1.07 | 10 | 2.39 | 9 | 2.76 | 6.18 |
| 150°C | 25.2 | 0.27 | 10 | 2.20 | 9 | 1.07 | 8.73 |
| MI69-29 | | | | | | | |
| 100°C | 170.2 | 4.39 | 10 | 19.7 | 9 | 2.58 | 11.58 |
| 125°C | 93.4 | 2.54 | 9 | 9.10 | 8 | 2.72 | 9.74 |
| 150°C | 55.8 | 1.00 | 9 | 4.23 | 8 | 1.79 | 7.59 |
| MI69-30 | | | | | | | |
| 125°C | 232,100 | 8540 | 6 | 9040 | 5 | 3.68 | 3.88 |
| 150°C | 128,167 | 4280 | 6 | 7380 | 5 | 3.34 | 5.76 |
| 175°C | 74,021 | 1840 | 7 | 5310 | 6 | 2.49 | 7.17 |
| MI69-31 | | | | | | | |
| 125°C | 3416 | 117 | 11 | 207 | 10 | 3.43 | 6.06 |
| 150°C | 1456 | 43.2 | 11 | 70.0 | 10 | 2.96 | 4.81 |
| 175°C | 756 | 16.7 | 11 | 46.2 | 10 | 2.21 | 6.11 |
| MI69-32 | | | | | | | |
| 125°C | 66,560 | 2850 | 9 | 7410 | 8 | 4.28 | 11.13 |
| 150°C | 26,800 | 1130 | 9 | 2750 | 8 | 4.22 | 10.26 |
| 175°C | 11,850 | 449 | 9 | 1030 | 8 | 3.79 | 8.69 |
| MI69-33 | | | | | | | |
| 125°C | 165,300 | 3730 | 7 | 7320 | 6 | 2.26 | 4.43 |
| 150°C | 74,590 | 1860 | 8 | 2650 | 7 | 2.52 | 3.78 |
| 175°C | 35,840 | 1820 | 9 | 2420 | 8 | 5.07 | 6.75 |

*Pooled Data:*

Sa (overall) = 3.14 % at 162 deg freedom
3.14 × 2.80 = 8.8 % relative

Sa + b (overall) = 7.60 % at 7 deg freedom
7.60× 3.34 = 25.4 % relative

TABLE 4 Summary of Precision Estimates, Selected Shear Equalized Data

| Sample No. | Average Viscosity, mPa·s | Sa | deg freedom | Sa + b | deg freedom | Sa % | Sa + b % |
|---|---|---|---|---|---|---|---|
| MI69-28 | | | | | | | |
| 100°C | 64.4 | 1.33 | 7 | 2.15 | 6 | 2.07 | 3.34 |
| 125°C | 38.0 | 0.56 | 5 | 0.75 | 4 | 1.47 | 1.97 |
| 150°C | 24.1 | 0.51 | 6 | 0.47 | 5 | 2.12 | 1.95 |
| MI69-29 | | | | | | | |
| 100°C | 163.2 | 0.63 | 6 | 4.09 | 5 | 0.38 | 2.51 |
| 125°C | 90.3 | 0.75 | 5 | 1.90 | 4 | 0.90 | 2.11 |
| 150°C | 53.7 | 0.83 | 5 | 1.30 | 4 | 1.55 | 2.42 |
| MI69-30 | | | | | | | |
| 125°C | 229,900 | 10,240 | 4 | 15,700 | 3 | 4.59 | 7.04 |
| 150°C | 130,900 | 5200 | 5 | 5200 | 4 | 3.97 | 3.97 |
| 175°C | 74,640 | 830 | 5 | 4750 | 4 | 1.11 | 6.36 |
| MI69-31 | | | | | | | |
| 125°C | 3429 | 40 | 6 | 77.6 | 5 | 1.17 | 2.26 |
| 150°C | 1474 | 12.3 | 6 | 28.3 | 5 | 0.83 | 1.92 |
| 175°C | 770 | 15.6 | 5 | 21.0 | 4 | 2.03 | 2.73 |
| MI69-32 | | | | | | | |
| 125°C | 68,680 | 1450 | 5 | 3440 | 4 | 2.11 | 5.00 |
| 150°C | 28,000 | 255 | 6 | 1670 | 5 | 0.91 | 5.96 |
| 175°C | 12,350 | 361 | 6 | 911 | 5 | 2.92 | 7.38 |
| MI69-33 | | | | | | | |
| 125°C | 167,700 | 1730 | 5 | 5000 | 4 | 1.03 | 2.98 |
| 150°C | 75,700 | 756 | 7 | 1645 | 6 | 1.00 | 2.17 |
| 175°C | 37,350 | 685 | 5 | 1070 | 4 | 1.83 | 2.86 |

*Pooled Data:*

Sa (overall) = 1.83 % at 99 deg freedom
1.83 × 2.82 = 5.16 % relative

Sa + b (overall) = 3.81 % at 4 deg freedom
3.81 × 3.92 = 14.93 % relative

viscosity at any temperature requested, within the range of test temperatures.

## 10. Report

10.1 Report the apparent viscosity at a given temperature along with the particulars of the instrument model, the spindle number and rotational speed. *Example:* Apparent viscosity at 125°C (RVT, SC 4-28, 20 rpm)—20 000 mPa·s.

NOTE 8—If it is desired to report the shear rate corresponding to the instrument/spindle/speed combination, refer to Table A1.1 for the appropriate calculation.

## 11. Precision and Bias

11.1 The precision of this test method as determined by statistical examination of interlaboratory results is as follows:

11.1.1 *Repeatability*— The difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the normal and correct operation of the test method, exceed the following values in one case in twenty:

8.8 % of the mean of the two results. (1)

11.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories in identical test material would, in the long run, exceed the following value only in one case in twenty:

25.4 % of the mean of the two results. (2)

NOTE 9—The precision of this test method is based on a round-robin conducted using six wax-based hot melt materials that are believed to be representative of the class. Tests were conducted at three temperatures by seven to eleven laboratories using the Brookfield viscometer model and spindle combination available to that laboratory. This encompassed a total of four viscometer models (Models LVF, LVT, RVT, and HBT) and seven different spindles, each appropriately tailored to the viscometer used. The effect of shear rate was disregarded.

11.1.3 A review of that portion of the data which can be considered comparable at equal shear rates indicates that those laboratories capable of comparing data at equal shear rates can expect improvement in reproducibility. It is estimated that under conditions of equal shear rate reproducibility the values would in the long run, exceed the following in one case in twenty:

15 % of the mean of the two results. (3)

11.1.4 A summary of data generated in this round-robin program is shown in Table 3 and Table 4.

11.2 *Bias*—The procedure in this test has no bias because the value of apparent viscosity can be defined only in terms of a test method.

## 12. Keywords

12.1 adhesives; apparent viscosity; coating materials; hot melt adhesives; viscosity

## ANNEXES

(Mandatory Information)

### A1. APPARATUS AND EQUIPMENT SET-UP

A1.1 *Viscometer and Stand*—Set up the viscometer stand on a firm, level surface convenient to a 15-A, 115-V, 60-Hz a-c electrical service and a cooling water supply and drain. Connect the coupling post to the rack, and screw both posts into the V-shaped base, leaving the lock nut loose. Place the three leveling screws in position in the base. Attach the viscometer to the stand, inserting it into the clamp on the rack. The viscometer must be leveled and centered on the viscometer base. Lock the posts tightly to the stand with the lock nut on the coupling post. Raise the viscometer to the highest position on the stand. Making certain that the power switch is off, plug in the viscometer power cord.

A1.2 *Alignment Bracket*—With the viscometer raised to the highest position on the stand and the dial directly in front, attach the alignment bracket to the back of the viscometer pivot cup, securing it tightly with the knurled screw.

A1.3 *Thermo-container, Sample Chamber, and Safety Guard* —Level the red thermo-container base using the three leveling screws in the base. Slide the perforated safety guard over the top of the thermo-container, sliding it past the power cord flush against the red base. Using the extracting tool, insert the sample chamber into the thermo-container. Rotate the sample chamber until it drops and locks in place preventing further rotation.

A1.4 *Controller and Probe*—Place the controller on the level surface adjacent to the thermo-container. Insert the three-pronged male plug from the thermo-container braided cord into the socket on the controller. **Caution:** This plug must be connected to the controller only. Insert the 4-in. stainless steel probe into the hole in the thermo-container located directly above the braided cord. Plug the other end of the probe into the connector on the controller. Making certain that the controller power switch is in the OFF position, plug the controller power cord "into" a 115-V, 60-Hz, grounded a-c power source.

**TABLE A1.1 Viscometer-Spindle Data**

LV Series Viscometers

| Spindle | Viscosity Range, mPa·s | | | Shear Rate, $s^{-1}$ | Sample Volume, mL | Approximate Sample Weight, g |
|---|---|---|---|---|---|---|
| | LVT | LVF | 5 x LVT | | | |
| SC 4-18 | 5–10 000 | 5–500 | 25–50 000 | 1.32 (N)[A] | 8.0 | 6.4 |
| SC 4-31 | 50–100 000 | 50–5 000 | 250–500 000 | 0.34 (N) | 10.0 | 8.0 |
| SC 4-34 | 100–200 000 | 100–10 000 | 500–1 000 000 | 0.28 (N) | 9.5 | 7.6 |

RV Series Viscometers

| Spindle | Viscosity Range, mPa·s | | | Shear Rate, $s^{-1}$ | Sample Volume, mL | Approximate Sample Weight, g |
|---|---|---|---|---|---|---|
| | RVT | RVF | RVF–100 | | | |
| SC 4-21 | 50–100 000 | 250–25 000 | 50–5 000 | 0.93 (N) | 8.0 | 6.4 |
| SC 4-27 | 250–500 000 | 1 250–125 000 | 250–25 000 | 0.34 (N) | 10.5 | 8.4 |
| SC 4-28 | 5001 000 000 | 2 500–250 000 | 500–50 000 | 0.28 (N) | 11.5 | 9.2 |
| SC 4-29 | 1 000–2 000 000 | 5 000–500 000 | 1 000–100 000 | 0.25 (N) | 13.0 | 10.4 |

HA Series Viscometers

| Spindle | Viscosity Range, mPa·s | | Shear Rate, $s^{-1}$ | Sample Volume, mL | Approximate Sample Weight, g |
|---|---|---|---|---|---|
| | HAT | HAF | | | |
| SC 4-21 | 100–200 000 | 1 000–100 000 | 0.93 (N) | 8.0 | 6.4 |
| SC 4-27 | 500–1 000 000 | 5 000–500 000 | 0.34 (N) | 10.5 | 8.4 |
| SC 4-28 | 1 000–2 000 000 | 10 000–1 000 000 | 0.28 (N) | 11.5 | 9.2 |
| SC 4-29 | 2 000–4 000 000 | 20 000–2 000 000 | 0.25 (N) | 13.0 | 10.4 |

HB Series Viscometers

| Spindle | Viscosity Range, mPa·s | | Shear Rate, $s^{-1}$ | Sample Volume, mL | Approximate Sample Weight, g |
|---|---|---|---|---|---|
| | HBT | HBF | | | |
| SC 4-21 | 400–800 000 | 4 000–400 000 | 0.93 (N) | 8.0 | 6.4 |
| SC 4-27 | 2 000–4 000 000 | 20 000–2 000 000 | 0.34 (N) | 10.5 | 8.4 |
| SC 4-28 | 4 000–8 000 000 | 40 000–4 000 000 | 0.28 (N) | 11.5 | 9.2 |
| SC 4-29 | 8 000–16 000 000 | 80 000–8 000 000 | 0.25 (N) | 13.0 | 10.4 |

[A] $N$ = rpm at which dial readings are taken

Example: Model RVT Viscometer/SC 4-28 spindle at 20 rpm

$$\text{Shear Rate Factor} \times \text{Spindle Speed in rpm} = \text{Shear Rate in } s^{-1}$$

$$0.28 \times 20 = 5.6\ s^{-1}$$

A1.5 *System Alignment and Spindle Insertion*—Level the viscometer stand base and the thermo-container and base. Lower the viscometer until the tips of the alignment bracket *just touch* the top of the thermo-container, making contact directly behind the locating ring. Raise the viscometer, positioning the tips of the alignment bracket about 2 mm (1⁄16 in.) above the top of the thermo-container. Using both hands, gently slide the thermo-container base until the tips of the alignment bracket *just touch* the locating ring. *Do not* forcibly displace the alignment bracket. Screw the link coupling nut onto the viscometer coupling nut, noting the left-hand thread. Connect the coupling link to the spindle. Lower the spindle into the sample chamber and connect the spindle and link to the link coupling nut on the viscometer. Place the insulating cap over the sample chamber inlet, thus capping the system.

**TABLE A1.2 Viscometer-Spindle Factor Data**

Note 1—To calculate viscosity in millipascal seconds (mPa·s) multiply the dial reading by the factor, corresponding to the viscometer, spindle, and speed combination utilized.

| | LV Series Viscometer Spindle Factors | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Speed, rpm | LVT | | | LVF | | | 5 × LVT | | |
| | SC4-18 | SC4-31 | SC4-34 | SC4-18 | SC4-31 | SC4-34 | SC4-18 | SC4-31 | SC4-34 |
| 60 | 0.5 | 5 | 10 | 0.5 | 5 | 10 | 2.5 | 25 | 50 |
| 30 | 1.0 | 10 | 20 | 1.0 | 10 | 20 | 5 | 50 | 100 |
| 12 | 2.5 | 25 | 50 | 2.5 | 25 | 50 | 12.5 | 125 | 250 |
| 6 | 5 | 50 | 100 | 5 | 50 | 100 | 25 | 250 | 500 |
| 3 | 10 | 100 | 200 | | | | 50 | 500 | 1M |
| 1.5 | 20 | 200 | 400 | | | | 100 | 1M | 2M |
| 0.6 | 50 | 500 | 1M | | | | 250 | 2.5M | 5M |
| 0.3 | 100 | 1M | 2M | | | | 500 | 5M | 10M |

| | RV Series Viscometer Spindle Factors | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Speed, rpm | RVT | | | | RVF | | | | RVF-100 | | | |
| | SC4-21 | SC4-27 | SC4-28 | SC4-29 | SC4-21 | SC4-27 | SC4-28 | SC4-29 | SC4-21 | SC4-27 | SC4-28 | SC4-29 |
| 00 | 5 | 25 | 50 | 100 | ... | ... | ... | ... | 5 | 25 | 50 | 100 |
| 50 | 10 | 50 | 100 | 200 | ... | ... | ... | ... | 10 | 50 | 100 | 200 |
| 20 | 25 | 125 | 250 | 500 | 25 | 125 | 250 | 500 | 25 | 125 | 250 | 500 |
| 10 | 50 | 250 | 500 | 1M | 50 | 250 | 500 | 1M | 50 | 250 | 500 | 1M |
| 5 | 100 | 500 | 1M | 2M | ... | ... | ... | ... | | | | |
| 4 | ... | ... | ... | ... | 125 | 625 | 1.25M | 2.5M | | | | |
| 2.5 | 200 | 1M | 2M | 4M | ... | ... | ... | ... | | | | |
| 2 | ... | ... | ... | ... | 250 | 1.25M | 2.5M | 5M | | | | |
| 1 | 500 | 2.5M | 5M | 10M | ... | ... | ... | ... | | | | |
| 0.5 | 1M | 5M | 10M | 20M | ... | ... | ... | ... | | | | |

| | HA Series Viscometer Spindle Factors | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Speed, rpm | HAT | | | | HAF | | | |
| | SC4-21 | SC4-27 | SC4-28 | SC4-29 | SC4-21 | SC4-27 | SC4-28 | SC4-29 |
| 100 | 10 | 50 | 100 | 200 | ... | ... | ... | ... |
| 50 | 20 | 100 | 200 | 400 | ... | ... | ... | ... |
| 20 | 50 | 250 | 500 | 1M | ... | ... | ... | ... |
| 10 | 100 | 500 | 1M | 2M | 100 | 500 | 1M | 2M |
| 5 | 200 | 1M | 2M | 4M | 200 | 1M | 2M | 4M |
| 2.5 | 400 | 2M | 4M | 8M | ... | ... | ... | ... |
| 2 | ... | ... | ... | ... | 500 | 2.5M | 5M | 10M |
| 1 | 1M | 5M | 10M | 20M | 1M | 5M | 10M | 20M |
| 0.5 | 2M | 10M | 20M | 40M | ... | ... | ... | ... |

| | HB Series Viscometer Spindle Factors | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Speed, rpm | HBT | | | | HBF | | | |
| | SC4-21 | SC4-27 | SC4-28 | SC4-29 | SC4-21 | SC4-27 | SC4-28 | SC4-29 |
| 100 | 40 | 200 | 400 | 800 | ... | ... | ... | ... |
| 50 | 80 | 400 | 800 | 1.6M | ... | ... | ... | ... |
| 20 | 200 | 1M | 2M | 4M | ... | ... | ... | ... |
| 10 | 400 | 2M | 4M | 8M | 400 | 2M | 4M | 8M |
| 5 | 800 | 4M | 8M | 16M | 800 | 4M | 8M | 16M |
| 2.5 | 1.6M | 8M | 16M | 32M | ... | ... | ... | ... |
| 2 | ... | ... | ... | ... | 2M | 10M | 20M | 40M |
| 1 | 4M | 20M | 40M | 80M | 4M | 20M | 40M | 80M |
| 0.5 | 8M | 40M | 80M | 160M | ... | ... | ... | ... |

## A2. CLEANING OF EQUIPMENT

A2.1 The spindle and sample chambers are made from stainless steel and may be cleaned with most commercial chlorinated or hydrocarbon solvents. If the solvents are heated, adequate precautions must be taken to avoid toxicity, flammability, or explosive hazards. Spindles and cham-bers must not come in contact with sulfuric acid, hydrofluoric acid, hydrochloric acid, and ferric chloride. Care must also be exercised to avoid scratching or deforming the spindles.

# 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 D3246: Standard Test Method for Sulfur in Petroleum Gas by Oxidative Microcoulometry

**CFR Section(s):** 40 CFR 60.335(b)(10)(ii)

**Standards Body:** American Society for Testing and Materials

APPROVED

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

**Designation: D 3246 – 96**

An American National Standard

# Standard Test Method for Sulfur in Petroleum Gas by Oxidative Microcoulometry[1]

This standard is issued under the fixed designation D 3246; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method covers determination of sulfur in the range from 1.5 to 100 mg/kg (ppm by mass) by weight in hydrocarbon products that are gaseous at normal room temperature and pressure.

NOTE 1—The test method has been tested cooperatively only on high-purity ethylene gas. Precision data have not been developed for other products.

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

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

## 2. Referenced Documents

2.1 *ASTM Standards:*

D 1265 Practice for Sampling Liquified Petroleum (LP) Gases—Manual Method[2]

D 1193 Specification for Reagent Water[3]

D 3120 Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry[4]

F 307 Practice for Sampling Pressurized Gas for Gas Analysis[5]

2.2 *Other Standards:*

Compressed Gas Association Booklets G-4 and G-4-1 on the Use of Oxygen.[6]

## 3. Summary of Test Method

3.1 A sample is injected into a combustion tube maintained at about 800°C having a flowing stream of gas containing about 80 % oxygen and 20 % inert gas (for example, nitrogen, argon, etc.). Oxidative pyrolysis converts the sulfur to sulfur dioxide which then flows into a titration cell where it reacts with triiodide ion present in the electrolyte. The triiodide thus consumed, is coulometrically replaced and the total current required to replace it is a measure of the sulfur present in the sample injected.

3.2 The reaction occurring in the titration cell as sulfur dioxide enters is:

$$I_3^- + SO_2 + H_2O \rightarrow SO_3 + 3I^- + 2H^+ \tag{1}$$

The triiodide ion consumed in the above reaction is generated coulometrically thus:

$$3I^- \rightarrow I_3^- + 2e^- \tag{2}$$

3.3 These microequivalents of triiodide (iodine) are equal to the number of microequivalents of titratable sample ion entering the titration cell.

3.4 A liquid blend containing a known amount of sulfur is used for calibration.

## 4. Significance and Use

4.1 Trace quantities of sulfur compounds in hydrocarbon products can be harmful to many catalytic chemical processes in which these products are used. Maximum permissible levels of total sulfur are normally included in specifications for such hydrocarbons. It is recommended that this test method be used to provide a basis for agreement between two laboratories when the determination of sulfur in hydrocarbon gases is important.

4.2 On liquefied petroleum gas, total volatile sulfur is measured on an injected gas sample. For such material a liquid sample must be used to measure total sulfur.

## 5. Interferences

5.1 This test method is applicable in the presence of total halide concentrations of up to 10 times the sulfur level and total nitrogen content of up to 1.0 %. Free nitrogen does not interfere.

5.2 This test method is not applicable in the presence of total heavy metal concentrations (for example, Ni, V, Pb, etc.) in excess of 500 mg/kg.

NOTE 2—To attain the quantitative detectability that the method is capable of, stringent techniques should be employed and all possible sources of sulfur contamination must be eliminated.

## 6. Apparatus[7,8]

6.1 *Pyrolysis Furnace*—The sample should be pyrolyzed

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[1] This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.D 0.02 on C3 Test Methods.

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

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

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

[5] *Annual Book of ASTM Standards*, Vol 15.03.

[6] Available from Compressed Gas Association, 1235 Jefferson Davis Hwy., Arlington, VA 22202.

[7] The apparatus described in 6.1 to 6.5 inclusive, is similar in specifications to equipment available from Tekmar-Dohrmann, 7143 E. Kemper Rd., Cincinnati, OH 524549. For further detailed discussions, in equipment, see: Preprints—Division of Petroleum Chemistry, American Chemical Society, Vol 1, No. 3, Sept. 7–12, 1969, p. B232 "Determination of Sulfur, Nitrogen, and Chlorine in Petroleum by Microcoulometry," by Harry V. Drushel.

[8] Tekmar-Dohrmann is the sole source of supply of the apparatus known to the committee at this time. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

in an electric furnace having at least two separate and independently controlled temperature zones, the first being an inlet section that can maintain a temperature sufficient to volatilize all the organic sample. The second zone shall be a pyrolysis section that can maintain a temperature sufficient to pyrolyze the organic matrix and oxidize all the organically bound sulfur. A third outlet temperature zone is optional.

6.1.1 Pyrolysis furnace temperature zones for light liquid petroleum hydrocarbons should be variable as follows:

| | |
|---|---|
| Inlet zone | up to at least 700°C |
| Center pyrolysis zone | up to at least 1000°C |
| Outlet zone (optional) | up to at least 800°C |

6.2 *Pyrolysis Tube*, fabricated from quartz and constructed in such a way that a sample, which is vaporized completely in the inlet section, is swept into the pyrolysis zone by an inert gas where it mixes with oxygen and is burned. The inlet end of the tube shall hold a septum for syringe entry of the sample and side arms for the introduction of oxygen and inert gases. The center or pyrolysis section should be of sufficient volume to assure complete pyrolysis of the sample.

6.3 *Titration Cell*, containing a sensor-reference pair of electrodes to detect changes in triiodide ion concentration and a generator anode-cathode pair of electrodes to maintain constant triiodide ion concentration and an inlet for a gaseous sample from the pyrolysis tube. The sensor electrode shall be platinum foil and the reference electrode platinum wire in saturated triiodide half-cell. The generator anode and cathode half-cell shall also be platinum. The titration cell shall require mixing, which can be accomplished through the use of a magnetic stirring bar, stream of inert gas, or other suitable means.

NOTE 3: **Caution**—Excessive speed will decouple the stirring bar, causing it to rise in the cell and damage the electrodes. The creation of a slight vortex is adequate.

6.4 *Microcoulometer*, having variable attenuation gain control, and capable of measuring the potential of the sensing-reference electrode pair, and comparing this potential with a bias potential, amplifying the potential difference, and applying the amplified difference to the working-auxiliary electrode pair so as to generate a titrant. Also the microcoulometer output voltage signal shall be proportional to the generating current.

6.5 *Recorder*, having a sensitivity of at least 0.1 mV/25 mm with chart speeds of 12 to 25 mm/min. Use of a suitable electronic or mechanical integrator is recommended but optional.

6.6 *Sampling Syringe for Liquid*—A microlitre syringe of 10-µL capacity capable of accurately delivering 1 to 10 µL of liquid blend into the pyrolysis tube 75 mm by 24-gage needles are recommended to reach the inlet zone of the pyrolysis furnace.

NOTE 4—Since care should be taken not to overload the pyrolyzing capacity of the tube by too fast a sample injection rate, means should be provided for controlling the sample addition rate (0.1 to 0.2 µL/s).

6.7 *Sampling Syringe for Gas*—A gas syringe capable of delivering up to 5 $cm^3$ of gas sample into the pyrolysis furnace. A 25 mm by 28-gage needle should be attached to the syringe.

6.8 *Exit Tube Insert*, with quartz wool.

## 7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[9] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—The water used in preparing the cell electrolyte should be demineralized or distilled or both. Water of high purity is essential. See Specification D 1193 for reagent water.

NOTE 5—Distilled water obtained from an all borosilicate glass still, fed from a demineralizer, has proven very satisfactory.

7.3 *Acetic Acid* (rel dens 1.05)—Concentrated acetic acid ($CH_3COOH$).

NOTE 6: **Warning**—May cause burns. See Annex A1.1.

7.4 *Argon, Helium, or Nitrogen*, high-purity grade (HP),[10] used as the carrier gas.

NOTE 7: **Warning**—Hazardous pressure. See Annex A1.2.

7.5 *Cell Electrolyte Solution*—Dissolve 0.5 g of potassium iodide (KI) and 0.6 g of sodium azide ($NaN_3$) in approximately 500 mL of high-purity water, add 5 mL of acetic acid ($CH_3COOH$) and dilute to 1000 mL.

NOTE 8—Bulk quantities of the electrolyte should be stored in a dark bottle or in a dark place and be prepared fresh at least every 3 months.

7.6 *Gas Regulators*—Two-stage gas regulators must be used on the reactant and carrier gas.

7.7 *Iodine* ($I_2$), 20 mesh or less, for saturated reference electrode.

NOTE 9: **Warning**—Toxic fumes. See A1.3.

7.8 *Isooctane*[11] *(2,2,4-trimethyl pentane).*

NOTE 10 **Warning**—Combustible, very harmful. See Annex A1.4.

NOTE 11—The most reliable solvent is a sulfur-free form of the sample type to be analyzed. Alternatively, use a high-purity form of cyclohexane [boiling point 80°C (176°F)], *iso*octane (2,2,4-trimethyl pentane) [boiling point, 99.3°C (211°F)], or hexadecane [boiling point, 287.5°C (549.5°F)].

7.9 *n-Butyl Sulfide* ($(CH_3CH_2CH_2CH_2)_2S$).

7.10 *Oxygen*, high-purity grade (HP),[9] used as the reactant gas.

NOTE 12: **Warning**—Oxygen accelerates combustion. See Annex A1.5.

7.11 *Potassium Iodide* (KI), fine granular.

7.12 *Sodium Azide* ($NaN_3$), fine granular.

NOTE 13: **Warning**—Highly toxic. Can react violently with shock, friction or heat.

7.13 *Sulfur, Standard Solution (approximately 30*

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

[10] High-purity grade gas has a minimum purity of 99.995 %.

[11] A high purity isooctane of pesticide quality has been found satisfactory.

*mg/kg*)—Pipet 10 mL of sulfur stock solution (reagent 7.14) into a 100-mL volumetric flask and dilute to volume with *iso*octane.

NOTE 14—The analyst may choose other sulfur compounds for standards appropriate to sample boiling range and sulfur type which cover the concentration range of sulfur expected.

7.14 *Sulfur, Standard Stock Solution* (*approximately 300 ppm* (*µg/g*))—Weigh accurately 0.5000 g of *n*-butyl sulfide into a tared 500-mL volumetric flask. Dilute to the mark with *iso*octane and reweigh.

$$\text{S, mg/kg} = \frac{\text{g of } n\text{-butyl sulfide} \times 0.2187 \times 10^6}{\text{g of } (n\text{-butyl sulfide} + \text{solvent})} \qquad (3)$$

## 8. Sampling

8.1 Supply samples to the laboratory in high-pressure sample cylinders, obtained using the procedures described in Practice D 1265 and Practice F 307.

8.2 Because of the reactivity of most sulfur compounds, it has been found desirable to use TFE-fluorocarbon-coated cylinders or other specially treated sample containers. Test samples as soon as possible after receipt.

## 9. Preparation of Apparatus

9.1 Carefully insert the quartz pyrolysis tube in the pyrolysis furnace and connect the reactant and carrier gas lines.

9.2 Add the electrolyte solution to the titration cell and flush several times. Maintain an electrolyte level of ⅛ to ¼ in. (3.2 to 6.4 mm) above the platinum electrodes.

9.3 Place the heating tape on the inlet of the titration cell.

9.4 Place an exit tube insert packed loosely with about 1 in. (25 mm) of quartz wool into the exit end of the pyrolysis tube. The quartz wool end of the exit tube should be in the hot zone of the pyrolysis tube.

9.5 Depending upon the instrumentation used, set up the titration cell to allow for adequate mixing of its contents and connect the cell inlet to the outlet end of the pyrolysis tube. Position the platinum foil electrodes (mounted on the movable cell head) so that the gas inlet flow is parallel to the electrodes with the generator anode adjacent to the generator cathode. Assemble and connect the coulometer and recorder (integrator optional) as designed or in accordance with the manufacturer's instructions. Figure X1.2 illustrates the typical assembly and gas flow through a coulometric apparatus.

9.5.1 Turn the heating tape on.

9.6 Adjust the flow of the gases, the pyrolysis furnace temperature, titration cell, and the coulometer to the desired operating conditions. Typical operational conditions are given in Table 1.

## 10. Calibration and Standardization

10.1 Prepare a series of calibration standards covering the range of sulfur concentration expected. Follow instructions in 7.13, 7.14, or dilute to appropriate level with *iso*octane.

10.2 Adjust the operational parameters (9.5).

NOTE 15—A ratio of 80 % oxygen to 20 % inert gas gives an acceptable recovery, and permits the use of a larger sample and a more rapid-charging rate.

TABLE 1 Typical Operational Conditions

| | |
|---|---|
| Reactant gas flow (oxygen), cm³/min | 160 |
| Carrier gas flow (Ar, He, N), cm³/min | 40 |
| Furnace temperature; °C: | |
| Inlet zone | 700 |
| Pyrolysis zone | 800 |
| Outlet zone | 800 |
| Titration cell | set to produce adequate mixing |
| Coulometer: | |
| Bias voltage, mV | 160 |
| Gain | low (approximately 200) |

10.3 The sample size can be determined either volumetrically or by mass. The sample size should be 80 % or less of the syringe capacity.

10.3.1 Volumetric measurement can be obtained by filling the syringe with about 8 µL or less of sample, being careful to eliminate bubbles, retracting the plunger so that the lower liquid meniscus falls on the 1-µL mark, and recording the volume of liquid in the syringe. After the sample has been injected, again retract the plunger so that the lower liquid meniscus falls on the 1-µL mark, and record the volume of liquid in the syringe. The difference between the two volume readings is the volume of sample injected.

10.3.2 Alternatively, the sample injection device can be weighed before and after the injection to determine the amount of sample injected. This test method provides greater precision than the volume delivery method, provided a balance with a precision of ±0.01 g is used.

10.4 Insert the syringe needle through the inlet septum up to the syringe barrel and inject the sample or standard at an even rate not to exceed 0.1 to 0.2 µL/s. When a microlitre syringe is used with an automatic injection adapter, the injection rate (volume/pulse) should be calibrated to deliver 0.1 to 0.2 µL/s.

10.5 Repeat the measurement of each calibration standard at least three times.

NOTE 16—Not all of the sulfur in the sample comes through the furnace as titratable $SO_2$. In the strongly oxidative conditions of the pyrolysis tube some of the sulfur is also converted to $SO_3$ which does not react with the titrant. Accordingly, sulfur standards of *n*-butyl sulfide in *iso*octane or sulfur standards appropriate to sample boiling range and sulfur type and sulfur concentration should be prepared to guarantee adequate standardization. Recoveries less than 75 % are to be considered suspect. Low recoveries are an indication to the operator that he should check his parameters, his operating techniques, and his coulometric system. If the instrument is being operated properly, recoveries between 75 and 90 % are to be expected.

10.6 Calculate the percent sulfur found by the coulometer. For a 1-mV (span) recorder with a sensitivity of 0.1 mV/in. and a speed of 0.5 in./min:

$$\text{Sulfur recovered, \%} = [(A \times 1.99)/(R \times S_o \times V_L/1000)] \times 100 \qquad (4)$$

where:

$A$ = area, cm²,

$R$ = coulometer range setting, Ω,

$S_o$ = known concentration of sulfur in the standard blend, µg/mL, and

$V_L$ = volume standard blend charged, µL.

10.6.1 *For a disk integrator:*

$$\text{Sulfur recovered, \%} = [(C \times 1.99 \times 10^{-3})/(R \times S_o \times V_L/1000)] \times 100 \qquad (5)$$

where:

$C$ = 100 × number of integrator pen full scale excursions. Derivation of equations is given in Appendix X1.

10.6.2 *For an electronic integrator:*

$$\text{Sulfur Recovered, \%} = \frac{A}{B} \times 100 \quad \text{(using consistent sample sizes)} \qquad (6)$$

where:
$A$ = integrator result, mg/kg, and
$B$ = known concentration of sulfur in standard blend, mg/kg.

NOTE 17—For further explanation of the derivation of the calculation, see Test Method D 3120.

10.7 If the fraction of sulfur converted to $SO_2$ drops below 75 % of the standard solutions, fresh standards should be prepared. If a low conversion factor persists, procedural details should be reviewed.

10.8 Calculate the average calibration factor, $F$, µg $S$/cm², as follows:

$$F = (S_o \times V_L/1000)/A \qquad (7)$$

## 11. Procedure

11.1 Place a silicone rubber septum in a bushing and connect to the valve on the sample cylinder containing the gaseous sample (for liquefied gas samples, see Note 5). Crack the cylinder valve so as to flush the air from all connections and then turn the bushing down to hold slight back pressure on the septum. Close the cylinder valve until the gas syringe is ready for filling.

NOTE 18: **Warning**—Samples are extremely flammable. See Annex A1.7.

11.2 Crack the valve on the sample cylinder until slight flow of gas is detected around the septum. Insert the gas syringe in the septum carefully.

NOTE 19: **Warning**—High pressure. See Annex A1.8.

11.3 Withdraw the plunger and allow the gas to flow through the syringe. After sufficient time to flush the syringe with sample, withdraw the plunger so as to contain no less than 5 cm³ of gas.

11.4 Insert the tip of the needle barely through the septum. Inject 5.0 cm³ of gas into the instrument at a constant rate so that 15 s is required for the injection. Determine the sulfur concentration by the procedure described in 10.2 to 10.7.

11.5 Sulfur concentration can require adjustment of sample volume.

11.6 Report a needle blank with test results.

## 12. Calculation

12.1 Calculate the sulfur content of the sample in parts per million (ppm) by weight as follows:

$$\text{Sulfur, mg/kg} = (A \times F)/W \qquad (8)$$

where:
$A$ = area under curve, taking into account the area of the needle blank, in square centimetres using same range (Ω) as calibration,
$W$ = weight of sample, g, and
$F$ = calibration factor, µg S/cm²

For gases:

$$W = \frac{V_g \times 273 \times P \times M}{(273 + C) \times 760 \times 22410} \qquad (9)$$

where:
$V_g$ = gas, cm³
$P$ = barometric pressure, mm Hg
$M$ = molecular weight of gas, g/mol, and
$C$ = temperature, gas, °C.

For ethylene at 23°C and 760 mm Hg:

$$W = V_g \times 0.001154 \qquad (10)$$

For liquid:

$$W = V_L/1000 \times d \qquad (11)$$

where:
$V_L$ = volume, µL, and
$d$ = density, g/mL.

## 13. Precision and Bias

13.1 The following criteria should be used for judging the acceptability of results:

13.1.1 *Repeatability*—The difference between successive test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, and in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

| Range or Sample Type | Repeatability |
|---|---|
| 0 to 10 mg/kg | 0.4 mg/kg |

13.1.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators working in different laboratories on identical test material would, in the long run, and in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

| Range or Sample Type | Reproducibility |
|---|---|
| 0 to 10 mg/kg | 5 mg/kg |

13.2 *Bias*—The bias of the procedure of this test method cannot be determined since an appropriate standard reference material containing trace sulfur level in ethylene is not available.

## 14. Keywords

14.1 microcoulometer; oxidate microcoulometry; petroleum gas; pyrolysis furnace; sulfur; sulfur dioxide

## ANNEX

### (Mandatory Information)

## A1. PRECAUTIONARY STATEMENTS

### A1.1 Acetic Acid

**Warning**—May produce severe burns to skin and eyes.

Prolonged breathing of concentrated vapor may be harmful.

Avoid contact with skin, eyes, and clothing.

Use with adequate ventilation.

### A1.2 Compressed Gases Argon, Helium, Nitrogen

**Warning**—Compressed gas under high pressure.

Gas reduces oxygen available for breathing.

Keep container closed.

Use with adequate ventilation.

Do not enter storage areas unless adequately ventilated.

Always use a pressure regulator.

Release regulator tension before opening cylinder.

Do not transfer to cylinder other than one in which gas is received.

Do not mix gases in cylinders.

Do not drop cylinder.

Make sure cylinder is supported at all times.

Stand away from cylinder outlet when opening cylinder valve.

Keep cylinder out of sun and away from heat.

Keep cylinders from corrosive environment.

Do not use cylinder without label.

Do not use dented or damaged cylinders.

For Technical Use only.

Do not use for inhalation purposes.

### A1.3 Iodine

**Warning**—Fumes highly toxic.

Can cause irritation and burning of eyes, nose, and throat.

Avoid heating and prolonged breathing of vapors.

Avoid contact with skin.

### A1.4 Isooctane

**Warning**—Extremely flammable.

Harmful if inhaled.

Vapors may cause flash fire.

Keep away from heat, sparks, and open flame.

Keep container closed.

Use with adequate ventilation.

Avoid build-up of vapors and eliminate all sources of ignition, especially nonexplosion proof electrical apparatus and heaters.

Avoid prolonged breathing of vapor or spray mist.

Avoid prolonged or repeated skin contact.

### A1.5 Oxygen

**Warning**—Oxygen vigorously accelerates combustion.

Keep oil and grease away.

Do not use oil or grease on regulators, gauges, or control equipment.

Use only with equipment conditioned for oxygen service by careful cleaning to remove oil, grease, and other combustibles.

Keep combustibles away from oxygen and eliminate ignition sources.

Keep surfaces clean to prevent ignition or explosion, or both, on contact with oxygen.

Always use a pressure regulator.

Release regulator tension before opening cylinder valve.

All equipment and containers used must be suitable and recommended for oxygen service.

Never attempt to transfer oxygen from cylinder in which it is received to any other cylinder.

Do not mix gases in cylinders.

Do not drop cylinder.

Make sure cylinder is secured at all times.

Keep cylinder valve closed when not in use.

Stand away from outlet when opening cylinder valve.

For technical use only.

Do not use for inhalation purposes.

Keep cylinder out of sun and away from heat.

Keep cylinders from corrosive environment.

Do not use cylinder without label.

Do not use dented or damaged cylinders.

See Compressed Gas Association booklets G-4 and G-4.1 for details of safe practice in the use of oxygen.

### A1.6 Sodium Azide

**Warning**—Highly toxic.

Inhalation may cause nausea, shortness of breath, dizziness, and headaches.

Contact with dust may cause eye irritation.

Avoid breathing dust or vapors from acidified solutions.

Avoid contact with skin, eyes, and clothing.

Wash thoroughly after handling.

### A1.7 Flammable Gas

**Warning**—Extremely flammable (liquified) gas under pressure.

Keep away from heat, sparks, and open flame.

Use with adequate ventilation.

Never drop cylinder.

Make sure cylinder is supported at all times.

Keep cylinder out of sun and away from heat.

Always use a pressure regulator.

Release regulator tension before opening cylinder.

Do not transfer cylinder contents to another cylinder.

Do not mix gases in cylinder.

### A1.8 Flammable Gas

**Warning**—Keep cylinder valve closed when not in use.

Do not inhale.

Do not enter storage areas unless adequately ventilated.

Stand away from cylinder outlet when opening cylinder valve.

Keep cylinder from corrosive environment.

Do not use cylinder without label.

Do not use dented or damaged cylinders.

For technical use only.

Do not inhale.

# APPENDIX

## (Nonmandatory Information)

## X1. DERIVATION OF COULOMETRIC CALCULATIONS USED IN PARAGRAPH 12.1

X1.1 The configuration of the pyrolysis tube and furnace may be constructed as is desirable as long as the operating parameters are met. Figure X1.1 is typical of apparatus currently in use.

X1.2 A typical assembly and oxidative gas flow through a coulometric apparatus for the determination of trace sulfur is shown in Fig. X1.2.

X1.3 *Derivation of Equations:*

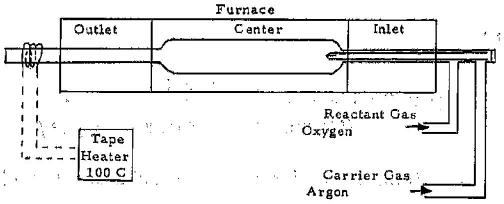

**FIG. X1.1 Pyrolysis Tube**

X1.3.1 The derivation of the equations used in the calculation section is based on the coulometric replacement of the triiodide (iodine) ions consumed in the microcoulometric titration cell reaction ($I_3^- \rightarrow 3I^- + H^+$). The quantity of the reactant formed (triiodide ions) between the beginning and the interruption of current at the end of the titration is directly proportional to the net charge transferred, $Q$.

X1.3.2 In most applications a constant current is used so that the product of current, $i$, in amperes (coulombs per second), multiplied by the time, $T$ (seconds), required to reach the end point provides a measure of the charge, $Q$ (coulombs), necessary to generate the iodine equivalent to the reactant; that is, $Q = it$. Therefore, the number of equivalents of reactant is equal to $Q/F$, where $F$ is the Faraday constant, 95 500°C per equivalent.

X1.3.3 Therefore, the expression to be solved to find the mass of reactant is:

$$\text{Concentration of sulfur} = \frac{\text{mass of sulfur, g}}{\text{mass of sample, g}} = \frac{\dfrac{\dfrac{Q(C)}{FC}}{\text{eq}} \times \dfrac{16\text{ g}}{\text{eq}}}{\text{mass of sample, g}} \tag{X1.1}$$

$$\mu\text{g S} = A\text{ cm}^2 \times \frac{\dfrac{0.1\text{ mV}}{\text{cm}} \times \dfrac{2\text{ min}}{\text{cm}} \times \dfrac{60\text{ s}}{\text{min}} \times \dfrac{10^{-3}\text{ V}}{\text{mV}} \times \dfrac{16\text{ g}}{\text{eq}} \times \dfrac{10^6\ \mu\text{g}}{\text{g}}}{R\ (\Omega) \times \dfrac{96\,500°\text{C}}{\text{eq}} \times \dfrac{\text{A}\cdot\text{s}}{\text{C}} \times f)} \tag{X1.2}$$

where:

$A$ cm$^2$ = peak area measured in square inches,

0.1 mV/cm = millivolt span of upscale deflection for the recorder,

2 min/cm = chart speed in minutes per inch,

60 s/min = conversion of time in minutes to seconds,

$10^{-3}$ V/mV = conversion of volts to millivolts,

16 g/eq = gram-equivalent of sulfur,

$10^6$ µg/g = micrograms per gram conversion factor,

$R$ (Ω) = microcoulometer range switch setting in ohms,

substituting $V/R = I$(amps)

$$Q(A\cdot s) = \frac{A\text{ cm}^2 \times \dfrac{0.1\text{ mV}}{\text{cm}} \times \dfrac{2\text{ min}}{\text{cm}} \times \dfrac{60s}{min} \times \dfrac{10^{-3}\ V}{mV}}{R(\Omega)}$$

$F$ = 96 500°C/eq

= Faraday's constant[8] (electrical equivalence of one gram-equivalent mass of any substance)

A·s/°C = conversion of coulombs to ampere-seconds, and

$f$ = recovery factor (ratio of ppm S determined in standard versus known ppm S in standard).

Therefore,

$$\mu\text{g S} = \frac{A \times 12 \times 10^{-3}\text{ A}\cdot\text{s} \times \dfrac{16\text{g}}{\text{eq}} \times \dfrac{10^6\ \mu\text{g}}{\text{g}}}{R \times \dfrac{96\,500°\text{C}}{\text{eq}} \times \dfrac{\text{A}\cdot\text{s}}{\text{C}} \times f} \tag{X1.3}$$

Therefore,

$$\mu\text{g S} = \frac{A \times 12 \times 10^{-3} \times 16 \times 10^6\ \mu\text{g}}{R \times 96\,500 \times f} \tag{X1.4}$$

Therefore,

$$\mu\text{g S} = (A \times 1.99)/(R \times f) \tag{X1.5}$$

Since ppm = µg/g:

$$\text{ppm S} = \frac{A \times 1.99}{R \times f \times \text{volume, }\mu\text{L} \times 10^{-3}\ \dfrac{\text{mL}}{\mu\text{L}} \times \text{density, }\dfrac{\text{g}}{\text{mL}}} \tag{X1.6}$$

$$\text{ppm S} = \frac{A \times 1.99 \times 10^3}{R \times f \times \text{volume} \times \text{density}} \tag{X1.7}$$

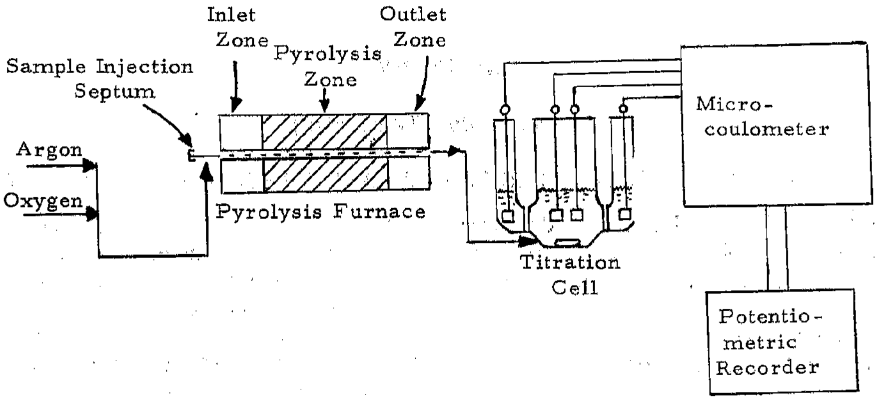

FIG. X1.2 Flow Diagram for Coulometric Apparatus for Trace Sulfur Determination

Since mass = volume × density

$$\text{ppm S} = (A \times 1.99)/(R \times F \times \text{mass, g}) \qquad \text{(X1.8)}$$

X1.3.4 *Derivation with Disk Integrator*—$A$ in Eq X1.5 is expressed as in.$^2$ However, it may also be expressed as counts. Therefore, $A$ in.$^2$ = counts × $10^{-3}$ since 1 in.$^2$ = 1000 counts. Therefore, substituting counts × $10^{-3}$ for $A$ in Eq 5 gives

$$\mu\text{g S} = (\text{counts} \times 1.99 \times 10^{-3})/(R \times f) \qquad \text{(X1.9)}$$

Then:

$$\text{ppm S} = \frac{\text{counts} \times 1.99}{R \times \text{volume, } \mu\text{L} \times \text{density, } \frac{\text{g}}{\text{mL}} \times f} \qquad \text{(X1.10)}$$

$$\text{ppm S} = (\text{counts} \times 1.99 \times 10^{-3})/(R \times \text{mass, } g \times f)$$

NOTE X1.1—Counts = 100 × number of integrator per full-scale excursions.

# CERTIFICATE

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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 Gross Calorific Value of Coal and Coke by the Isoperibol Bomb Calorimeter[1]

This standard is issued under the fixed designation D 3286; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

## 1. Scope

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

1.2 The values stated in SI units are to be regarded as the standard unless otherwise designated. The values given in parentheses are for information only.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Section 8.

## 2. Referenced Documents

2.1 *ASTM Standards:*

D 121 Terminology of Coal and Coke[2]
D 346 Practice for Collection and Preparation of Coke Samples for Laboratory Analysis[2]
D 1193 Specification for Reagent Water[3]
D 2013 Method of Preparing Coal Samples for Analysis[2]
D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke[2]
D 3177 Test Methods for Total Sulfur in the Analysis Sample of Coal and Coke[2]
D 3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases[2]
D 4239 Test Method for Sulfur in the Analysis Sample of Coal and Coke Using High Temperature Tube Furnace Combustion Methods[2]
E 1 Specification for ASTM Thermometers[4]
E 144 Practice for Safe Use of Oxygen Combustion Bombs[5]

## 3. Terminology

3.1 *Definitions:*

3.1.1 *calorific value, n*—the heat produced by combustion of a unit quantity of a test specimen under specific conditions.

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

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

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

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

3.2 *Descriptions of Terms Specific to this Standard:*

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

3.2.1.1 *Discussion*—Temperature is measured in degrees Celsius. Thermometer corrections shall be applied. Temperatures may be recorded in ohms or other arbitrary units as the equivalent of degrees. Consistent units shall be used in standardization and the actual calorific value determination. If arbitrary units other than degrees Celsius are used, the temperature interval over which all tests are made shall not vary so much that an error greater than 0.001°C would result.

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

NOTE 1—Conversion to other units is discussed in Appendix X2. Time is expressed in minutes. Mass is expressed grams.

## 4. Summary of Test Method

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

4.2 Oxidation after sampling of susceptible low-rank coal or lignite may result in a reduction of calorific value.

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[1] This test method is under the jurisdiction of ASTM Committee D-5 on Coal and Coke and is the direct responsibility of Subcommittee D05.21 on Methods of Analysis.

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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.

Unnecessary exposure of the sample to air from the time of sampling or delay in analysis shall be avoided.

## 5. Significance and Use

5.1 When mutually agreed upon between the buyer and the seller, the gross calorific value may be used to compute the total calorific content of the quantity of coal represented by the sample for payment purposes.

5.2 The gross calorific value can be used to determine if the coal meets the regulatory requirement for industrial fuels.

5.3 The gross calorific value can be used for evaluating the effectiveness of benefaction process, or for research purposes.

## 6. Apparatus and Facilities

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

6.2 *Combustion Bomb,* shall be constructed of materials that are not affected by the combustion process or products sufficiently to introduce measurable heat input or alteration of end products. The bomb shall be designed so that all liquid combustion products can be completely recovered by washing the inner surfaces. There shall be no gas leakage during a test. The bomb shall be capable of withstanding a hydrostatic pressure test of 20 MPa (3000 psig) at room temperature without stressing any part beyond its elastic limit.

6.3 *Balance*—A laboratory balance having the capability to weigh the sample to the nearest 0.0001 g. The balance should be checked periodically to determine its accuracy.

6.4 *Calorimeter Vessel,* made of metal with a tarnish-resistant coating, and with all outer surfaces highly polished. Its size shall be such that the bomb will be completely immersed in water when the calorimeter is assembled. It shall have a device for stirring the water thoroughly and at a uniform rate but with minimum heat input. Continuous stirring for 10 min shall not raise the calorimeter temperature more than 0.01°C starting with identical temperatures in the calorimeter, room, and jacket. The immersed portion of the stirrer shall be coupled to the outside through a material of low-heat conductivity.

6.5 *Jacket,* a double-walled, air, or water-filled jacket. The calorimeter shall be insulated from the jacket by an air space. The sides, top, and bottom of the calorimeter vessel shall be approximately 10 mm from the inner wall of the jacket to minimize convection currents. Mechanical supports for the calorimeter vessel shall provide as little thermal conduction as possible. The jacket shall be capable of maintaining the temperature constant to within ±0.1°C of room temperature at a calorimeter temperature 2°C below, and 2°C or more above room temperature throughout the determination. If a water-filled jacket is used, it shall have a device for stirring the water at a uniform rate with minimum heat input.

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

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

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

6.6.3 *Other Thermometers,* of precision equal to or better than 0.001°C, such as platinum resistance or linear thermistor thermometers are satisfactory and may be used if properly calibrated. A Wheatstone bridge and galvanometer capable of measuring resistance to 0.0001 Ω are necessary for use with 25 Ω platinum resistance thermometers.

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

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

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

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

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

6.12 *Automated Controller and Temperature Measuring Accessories,* may be used for measuring temperatures before, during, and after combustion of the sample; ignition of the sample; and calculation of results provided that they meet the minimal functional specifications in Sections 6 and 10.

## 7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specification of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[6] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

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

7.3 *Benzoic Acid* ($C_6H_5COOH$), shall be NIST certified benzoic acid. The crystals shall be pelletized before use. Commercially prepared pellets may be used provided they are made from NIST certified benzoic acid or made from benzoic acid that has been calibrated against NIST certified benzoic acid. The value of heat of combustion of the benzoic acid for use in the calibration calculations shall be in accordance with the value listed in the NIST certificate issued with the standard.

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

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

7.6 *Sodium Carbonate Standard Solution,* sodium carbonate ($Na_2CO_3$) should be dried for 24 h at 105°C. Dissolve 3.76 g in water and dilute to 1 L. One millilitre of this solution is equivalent to 1.0 cal in the nitric acid ($HNO_3$) titration.

## 8. Hazards

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

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

8.3 Inspect the bomb parts carefully after each use and, after 3000 firings, check the bomb for thread wear on any closures. If an inspection reveals any wear, return the parts to the factory for further testing or replacement of the defective parts. It is good practice to return the bomb to the manufacturer for inspection at yearly intervals.

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

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

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

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

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

## 9. Sample

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

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

9.3 Sulfur analysis shall be made in accordance with Test Methods D 3177 or D 4239.

## 10. Standardization

10.1 The calorimeter shall be standardized by combustion of benzoic acid.

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

10.3 *Procedure:*

10.3.1 Regulate the weights of the pellets of benzoic acid in each series to yield approximately the same temperature rise as that obtained with the coals tested in the same laboratory. The usual range of masses is from 0.9 to 1.3 g. Weigh the pellet to the nearest 0.1 mg in the sample holder in which it is to be burned, and record the weight as the mass.

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

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

**TABLE 2 Standard Deviations for Calorimeter Standardization**[A]

| Standardization Number | Column A | Column B | Column C |
|---|---|---|---|
| | Energy Equivalent (cal/°C) | Code to 2449 (Column A-2449) | (Column B)$^2$ |
| 1 | 2450 | 1 | 1 |
| 2 | 2448 | −1 | 1 |
| 3 | 2453 | 4 | 16 |
| 4 | 2449 | 0 | 0 |
| 5 | 2447 | −2 | 4 |
| 6 | 2448 | −1 | 1 |
| 7 | 2446 | −3 | 9 |
| 8 | 2452 | 3 | 9 |
| 9 | 2450 | 1 | 1 |
| 10 | 2447 | −2 | 4 |
| SUM | 241 490 | 0 | 46 |

Average $= \bar{X} = 2449 \cdot 24\,490/10$

$$\text{Variance} = s^2 = \frac{\Sigma \text{ Column C} - [(\Sigma\text{Column B})^2/n]}{n-1} = 5.11$$

Standard deviation $= s = \sqrt{\text{variance}} = \sqrt{5.11} = 2.26$

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

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

10.3.4 Assemble the bomb and charge it with oxygen to a consistent pressure between 2.5 to 3 MPa (25 to 30 atm). This pressure must remain the same for each calibration and each calorific-value determination. Admit the oxygen slowly into the bomb so as not to blow powdered material from the sample holder. If the pressure exceeds the specified pressure, do not proceed with the combustion. Instead, detach the filling connection and exhaust the bomb in the usual manner, and discard the sample.

10.3.5 Fill the calorimeter vessel (bucket) with the measured (or weighed) quantity of water adjusted from 1.0 to 5.0°C below the jacket temperature, but not lower than 20°C. Use the same mass of water in each test weighed to ±0.5 g. For 2000-mL calorimeters, the proper quantity can be obtained by use of a volumetric flask calibrated to deliver 1980 to 2020 mL with ±0.5 mL repeatability. As the density of water varies with temperature, make suitable corrections if the water temperature varies from the temperature at which the flask was calibrated. Place the assembled bomb in the calorimeter vessel. Check that no oxygen bubbles are leaking from the bomb. Place the calorimeter vessel in the jacket; connect the electrodes; place the stirrers, thermometers, and cover in position. Start the stirrer(s) and continue to operate it (them) throughout the determination. Examine the thermometers for liquid separation and correct any separation before proceeding. The starting temperature shall be within ±0.5°C of that used in the analysis of coal or coke samples.

10.3.5.1 The initial temperature adjustment will ensure a final temperature slightly above that of the jacket for 2000-mL calorimeters. Some operators prefer a lower initial temperature so that the final temperature is slightly below that of the jacket. This procedure is also satisfactory. Whichever procedure is used, the same procedure shall be used in all tests, including standardization. A small heater may be built into the calorimeter so that the desired starting temperature can be easily attained.

NOTE 2—Check all liquid-in-glass thermometers at least daily for any defects, for example, cracked glass, etc.

10.3.6 Allow 5 min for attainment of equilibrium; then record the calorimeter temperature at 1-min intervals for 5 min or until the rate of change has been nearly constant for 5 min. Use a magnifier when using ASTM Bomb Calorimeter Thermometers 56C, and estimate all of the readings (except those during the rapid-rise period) to the nearest 0.002°C. Estimate ASTM Thermometers 115C, 116C, or 117C readings to 0.001°C, and 25 Ω resistance thermometer readings to the nearest 0.0001 Ω. Tap mercury thermometers (for instance with a pencil) just before reading to avoid errors caused by mercury sticking to the walls of the capillary. Ignite the charge at the start of the sixth minute and record the time, *i*, and the thermometer reading, $t_i$ (Note 6). Take the next two readings 0.5 min and 1 min after firing because of the rapid rise. Record subsequent readings at 1-min intervals on the minute until the difference between successive readings has been constant for 5 min. If the final temperature is above the bath temperature, the temperature rises to a maximum and then begins to fall. Record the time, *f*, and the thermometer reading, $t_f$, after the rate of change has become uniform. The calorimeter water temperature shall be at the same temperature (±0.05°C) for every determination, at the time of firing, if the Bureau of Mines method for radiation correction is to be used. See Annex A1.5.

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

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

10.4 *Calculation:*

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

$$t = t_f - t_i + C_e + C_s + C_r \tag{1}$$

where:

$t$ = corrected temperature rise, °C,
$t_i$ = initial temperature reading at time of firing,
$t_f$ = final temperature reading, °C,
$C_e$ = thermometer, emergent stem correction, if required (see 10.4.1.1 and Annex A1.4),
$C_s$ = thermometer setting correction, if required (see 10.4.1.1 and Annex A1.3), and
$C_r$ = radiation correction (see 10.4.1.1 and Annex A1.5).

10.4.1.1 With all mercury-in-glass thermometers, it is necessary to make corrections if the total calorific value is altered by 2.7 cal/g (5 Btu/lb) or more. This represents a change of 0.001°C in a calorimeter using approximately 2000 g of water. Beckmann thermometers also require a setting correction and an emergent stem correction (see Annex A1.3 and A1.4). Solid-stem ASTM Thermometer 56C does not require emergent stem corrections if all tests, including standardization, are performed within the same 5.5°C interval. If operating temperatures range beyond this limit, a differential emergent stem correction (see Annex A1.4) must be applied to the corrected temperature rise, *t*, in all tests, including standardization. A radiation correction must be made in all tests, including standardization.

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

$e_1$ = correction for the heat of formation of $HNO_3$, cal. Each millilitre of standard $Na_2CO_3$ is equivalent to 1.0 cal, and
$e_2$ = correction for heat of combustion of firing wire, cal (Note 2).
= 0.23 cal/mm (1.4 cal/mg) for 0.16-mm diameter (No. 34 B & S gage) Chromel C wire.
= 0.27 cal/mm (1.8 cal/mg) for 0.16-mm diameter (No. 34 B & S gage) iron wire.

NOTE 3—There is no correction for platinum or palladium wire provided the ignition energy is constant.

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

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

where:

$E$ = calorimeter energy equivalent,
$H$ = heat of combustion of benzoic acid, as stated in the NIST certificate, cal/g in air,
$g$ = mass (weight in air) of benzoic acid, g,
$e_1$ = titration correction (10.4.2),
$e_2$ = fuse wire correction (10.4.2), and
$t$ = corrected temperature rise (10.4.1).

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

## 11. Restandardization

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

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

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

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

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

TABLE 3 Summary of Numerical Requirements

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

| Number of Runs | Maximum Range of Results | Maximum Difference between $\bar{X}_1$, and $\bar{X}_2$[B] |
|---|---|---|
| | cal/°C | cal/°C |
| 1 | . . . | ±4 |
| 2 | 5 | ±3 |
| 4 | 8 | ±2 |
| 6 | 10 | ±2 |
| 10 | 12 | ±1 |

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

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

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

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

## 12. Procedure for Coal and Coke Samples

12.1 Thoroughly mix the analysis sample of coal or coke in the sample bottle and carefully weigh approximately 1 g ± 0.1 mg of it into the sample holder. Make each determination in accordance with the procedure described in 10.3.2 through 10.3.8.

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

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

12.4 Determine the sulfur content of the sample by any of the procedures described in Test Methods D 3177 or D 4239.

## 13. Calculation (Note 1)

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

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

$e_1$ = correction for the heat of formation of $HNO_3$, cal. Each millilitre of standard sodium carbonate is equivalent to 1.0 cal,

$e_2$ = correction for heat of combustion of ignition wire, cal,
= 0.23 cal/mm (1.4 cal/mg) for 0.16-mm diameter (No. 34 B & S gage) Chromel C wire,
= 0.27 cal/mm (1.8 cal/mg) for 0.16-mm diameter (No. 34 B & S gage) iron wire (Note 3), and
$e_3$ = correction for difference between heat of formation of $H_2SO_4$ from the heat of formation $HNO_3$, cal,
= 13.17 times percent of sulfur in sample times weight of sample, g.

## 14. Calorific Value (Note 4)

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

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

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

NOTE 4—This calculation gives calorific value in calories per gram. To obtain calorific value in joules per gram or British thermal units per pound, see Appendix X2.

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

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

where:
$Q_p$ (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 and oxygen include hydrogen and oxygen in sample moisture, %.

NOTE 5—Example for converting from the as-determined (air-dried) sample basis to the as-received net calorific value basis:[7]

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

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

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

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

$$H_{ar} = 5.37$$

$$\begin{aligned} Q_p \text{ (net)}_{ar} &= 7056 - 5.72\ (5.37 \times 9) \\ &= 7056 - 276 \\ &= 6780 \text{ cal/g (International Table Calories)} \\ &= 12204 \text{ Btu/lb} \\ &= 28382 \text{ J/g} \\ &= 28.38 \text{ MJ/kg} \end{aligned}$$

## 15. Report

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

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

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

## 16. Precision and Bias

16.1 The following criteria should be used for judging the acceptability of results (95 % probability) on split 250-µm (No. 60) samples.

16.1.1 *Repeatability*—Duplicate results by the same laboratory using the same operator and equipment, should not be considered suspect unless they differ by more than 28 cal/g (50 Btu/lb) on a dry basis.

16.1.2 *Reproducibility*—The results submitted by two or more laboratories (different equipment, operators, date of test, and different portions of the same pulp) should not be considered suspect unless the two results differ by more than 56 cal/g (100 Btu/lb) on a dry basis.

16.1.3 *Bias*—The equipment used in this test method for measuring gross calorific value has no bias because the equipment is standardized with a compound having a known heat of combustion. Since there is no acceptable reference material for determining the bias for the procedure in this test method, bias has not been determined.

## 17. Keywords

17.1 bomb calorimeter; calorific value; calorimeter; isoperibol bomb calorimeter

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[7] For a comprehensive derivation of calculations for converting gross calorific value at constant volume to net calorific value at constant pressure, refer to Research Report D05-1013.

## ANNEX

### (Mandatory Information)

## A1. THERMOMETRIC CORRECTIONS

### A1.1 Thermometer Corrections

A1.1.1 It is necessary to make the following individual corrections if not making the corrections would result in an equivalent change of 28 cal/g (5.0 Btu) or more.

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

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

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

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

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

where:

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

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

Differential stem correction, $C_e$

$$= 0.00016\,(28 - 24)\,(28 + 24 - 16 - 26)$$
$$= 0.0064°\text{C}.$$

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

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

where:

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

A1.1.5 *Radiation Corrections*—These are used to calculate heat loss to the water jacket. They are based on the Dickinson formula,[8] the Regnault-Pfaundler formula,[9] or the U.S. Bureau of Mines method.[10] The same method of determining the radiation correction must be used consistently in calibration and test measurements.

A1.1.5.1 *Dickinson Formula:*

$$C_r = -\,r_1\,(b - i) - r_2\,(f - b) \qquad (\text{A1.3})$$

where:

$C_r$ = radiation correction,
$r_1$ = rate of rise in temperature per minute in the preliminary period, °C,
$r_2$ = rate of rise of temperature per minute in the final period (if temperature is falling, $r_2$ is negative), °C,
$t_i$ = firing temperature, °C,
$t_f$ = final temperature, being the first temperature after which the rate of change is constant, °C,
$i$ = time at temperature, $t_i$, min,
$b$ = time at temperature, $t_i + 0.60\,(t_f - t_i)$, min, and
$f$ = time at temperature, $t_f$, min.

A1.1.5.2 *Regnault-Pfaundler Formula:*

$$C_r = nr_1 + kS \qquad (\text{A1.4})$$

where:

$C_r$ = radiation correction,
$n$ = number of minutes in the combustion period,
$k$ = $(r_1 - r_2)/(t'' - t')$,
$S$ = $t_n - 1 + (1/2)\,(t_i + t_f)\,nt'$,
$t'$ = average temperature during the preliminary period, °C,
$t''$ = average temperature during the final period, °C,
$t_1, t_2, t_3 \ldots\ldots t_n$ = successive temperature recorded during the combustion period, °C, and
$t_n - 1$ = sum of $t_1, t_2, t_3 \ldots\ldots\ldots t_n - 1$.

A1.1.5.3 *Bureau of Mines Method*—A table of radiation correction can be established so that only the initial and final readings are required to determine the heat value of any fuel. This may be done by carrying out a series of tests utilizing the procedure described in Section 10, using the following conditions. Regulate the amount of sample burned so that a series of determinations is made in which different temperature rises are obtained. For all determinations, keep the water jacket temperature constant, fire the bomb at the same initial temperature, and have the same time, $f - i$, elapse (±2 s) between the initial and final readings. Determine the radiation corrections for each of the series of temperature rises using the Dickinson method (see A1.1.5.1), or the Regnault-Pfaundler method (see A1.1.5.2). These corrections are constant for a given temperature rise. From the

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[8] Dickinson, H. C., *Bulletin,* National Bureau of Standards, Vol 11, 1951, p. 189.

[9] Pfaundler, L., *Annalen der Physik* (Leipzig), Vol 129, 1866, p. 102.

[10] "Methods of Analyzing and Testing Coal and Coke" *Bulletin 638,* U.S. Bureau of Mines, 1967, pp. 16–17.

series of readings a table or graph is plotted to show radiation correction versus temperature rise. Once the table or graph is established, the radiation corrections can be obtained from it until there is a major change in the equipment.

## APPENDIXES

### (Nonmandatory Information)

## X1. THERMOCHEMICAL CORRECTIONS

X1.1 *Energy of Formation of Nitric Acid*—A correction, $e_1$, (10.4.2 and 13.2) is applied for the acid titration. This correction is based on the assumptions (*1*) that all the acid titrated is $HNO_3$ formed by the following reaction: ½ $N_2$ (gas) + 5⁄4 $O_2$ (gas) + ½ $H_2O$ (liquid) = $HNO_3$ (in 500 mol $H_2O$), and (*2*) that the energy of formation of $HNO_3$ in approximately 500 mol of water under bomb conditions is −59.0 kJ/mol.[11]

X1.1.1 A convenient concentration of $Na_2CO_3$ is 3.76 g $Na_2CO_3$/1000 mL which gives $e_1 = V$, where $V$ is the volume of $Na_2CO_3$ in millilitres. (One millilitre of this solution is equivalent to 1.0 cal in the acid titration.) This value (V = mL) is to be used for calculating calorific value in calories per gram. For other units see Table X2.1. When $H_2SO_4$ is also present, a part of the correction for $H_2SO_4$ is contained in the $e_1$ correction and the remainder in the $e_3$ correction.

X1.2 *Energy of Formation of Sulfuric Acid*—By definition (see Terminology D 121) the gross calorific value is obtained when the product of the combustion of sulfur in the sample is $SO_2$ (in grams). However, in actual bomb combustion processes, all the sulfur is found as $H_2SO_4$ in the bomb washings. A correction $e_3$ (see 13.2) is applied for the sulfur that is converted to $H_2SO_4$. This correction is based upon the energy of formation of $H_2SO_4$ in solutions, such as will be present in the bomb at the end of a combustion. This energy is taken as −295.0 kJ/mol.[12] A correction of 2 times 59.0 kJ/mol of sulfur was applied in the $e_1$ correction, so the additional correction necessary is 295.0 − (2 times 59.0) = 177 kJ/mol, or 5.52 kJ/g of sulfur in the sample (55.2 J times weight of sample in grams times percent sulfur in sample). This causes $e_3$ to be 23.7 times weight of samples in grams times percent sulfur in sample for calculating calorific value in British thermal units per pound. The factor 13.17 for $e_e$ (see 13.2) is to be used for calculating calorific value in calories per gram. For other units, see Appendix X2. The values above are based on a coal containing about 5 % sulfur and about 5 % hydrogen. The assumption is also made that the $H_2SO_4$ is dissolved entirely in the water condensed during combustion of the sample.[13]

X1.2.1 If a 1-g sample of such a fuel is burned, the resulting $H_2SO_4$ condensed with water formed on the walls of the bomb will have a ratio of about 15 mol of water to 1 mol of $H_2SO_4$. For this concentration the energy of the reaction $SO_2$ (gas) + ½ $O_2$ (gas) + $H_2O$ (liquid) = $H_2SO_4$ (in 15 mol of $H_2O$) under the conditions of the bomb process is −295 kJ/mol.[12] Basing the calculation upon a sample of comparatively large sulfur content reduces the possible overall errors, because, for small percents of sulfur, the correction is smaller.

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

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

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

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

## X2. REPORTING RESULTS IN OTHER UNITS

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

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

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

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

$$E' = [(gH') + e_1' + e_2']/t \qquad \text{(X2.1)}$$

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

$E'$ = energy equivalent, with units of joules per temperature unit,
$H'$ = heat of combustion of reference material, with units of joules per gram weight in air (J/g from the certificate for the NIST benzoic acid),
$g$ = mass (weight in air) of benzoic acid, g,
$t$ = corrected temperature rise (see 10.4.1), and
$e_1'$, $e_2'$, and $e_3'$ = corrections, with units of joules (see Table X2.1).

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

$$Q_v \text{ (gross)} = [(tE') - e_1' - e_2' - e_3')]/g \qquad \text{(X2.2)}$$

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, with units of joules per temperature unit, and
$e_1'$, $e_2'$, and $e_3'$ = corrections, with units of joules (see Table X2.1).

X2.1.5 *Precision:*

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

| Correction | Multiplication Factor | Multiply By |
|---|---|---|
| $e_1'$ ($HNO_3$) | 20 J/mL | mL of 0.34 *N* $Na_2CO_3$ |
| $e_3'$ ($H_2SO_4$) | 55.2 J/cgS | percent of sulfur in sample times mass of sample in grams |
| $e_2'$ (fuse wire) | 0.95 J/mm | length (mm) of 0.16-mm diameter (No. 34 B & S gage) Chromel C wire |
| or | | |
| $e_2'$ (fuse wire) | 1.14 J/mm | length (mm) of 0.16-mm diameter (No. 34 B & S gage) iron wire |
| $e_2'$ (fuse wire) | 6.0 J/mg | mass (mg) of Chromel C wire |
| or | | |
| $e_2'$ (fuse wire) | 7.4 J/mg | mass (mg) of iron wire |

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

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

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

# 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 D3371: Standard Test Method for Nitriles in Aqueous Solution by Gas-Liquid Chromatography

**CFR Section(s):** 40 CFR 136.3(a) Table IF

**Standards Body:** American Society for Testing and Materials

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

**Designation: D 3371 – 95**

# Standard Test Method for Nitriles in Aqueous Solution by Gas-Liquid Chromatography [1]

This standard is issued under the fixed designation D 3371; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method covers nitriles that can be separated and detected quantitatively at a limit of approximately 1 mg/L by aqueous injection on a selected gas-liquid chromatographic column.

1.2 This test method utilizes the procedures and precautions as described in Practice D 2908.

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

## 2. Referenced Documents

2.1 *ASTM Standards:*

D 1129 Terminology Relating to Water[2]

D 2908 Practice for Measuring Volatile Organic Matter in Water by Aqueous-Injection Gas Chromatography[3]

## 3. Terminology

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

## 4. Significance and Use

4.1 Nitriles at concentrations of a few milligrams per litre are potentially toxic to aquatic life. Nitriles in waste water discharges should be detected and controlled.

4.2 Gas-liquid chromatography (GLC) can detect and determine mixtures of nitriles at levels where wet chemical procedures are not applicable.

## 5. Special Comments

5.1 It is recommended that samples that cannot be analyzed immediately, be quick frozen for preservation. Samples should be neutralized to pH 7 at the time of collection to minimize hydrolysis of the nitrile groups.

5.2 Samples of nitriles to be employed as standards should be considered to be unstable. Storage in a freezer is recommended.

5.3 It is not always practical to translate operating conditions directly from one GLC instrument to another. An operator should optimize his instrument to a particular procedure, for example, injection and detection temperature, flow rates, etc.

## 6. Typical Chromatograms

6.1 The following instrument parameters were used to obtain the typical chromatograms (See Fig. 1 and Fig. 2).

6.1.1 *Column*—⅛ in. outside diameter stainless steel, 8 ft long packed with a porous styrene divinylbenzene polymer.

NOTE 1—"Chromosorb" 101, 50/60 mesh, was used for the typical chromatograms.

6.1.2 *Detector*, flame ionization.

6.1.3 *Temperatures*:

| | |
|---|---|
| Injection port | 240°C |
| Detector | 240°C |
| Oven, isothermal | 130°C |
| Oven, programmed at 10°C/min | 110°C to max of 200°C |

6.1.4 *Carrier Gas*, helium at 25 mL/min.

6.1.5 *Sample Size*:

isothermal 5 μL

programmed 3 μL

6.1.6 *Recorder*, ¾ in./min chart speed and 1 mV full-scale response.

6.2 *Kovats Index Values:*[4]

| Compounds | Relative Retention | Kovats Index |
|---|---|---|
| Acetonitrile | 1.00 | 470 |
| Acrylonitrile | 1.25 | 512 |
| Proprionitrile | 1.67 | 570 |
| Methoxyacetonitrile | 2.21 | 635 [5] |
| Butyronitrile | 2.50 | 678 |
| Isovaleronitrile | 3.04 | 740 [5] |
| Valeronitrile | 3.38 | 783 |
| Hexanenitrile | 4.25 | 905 [5] |
| Benzonitrile | 5.42 | 990 |

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[1] This test method is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D 19.06 on Methods for Analysis for Organic Substances in Water.

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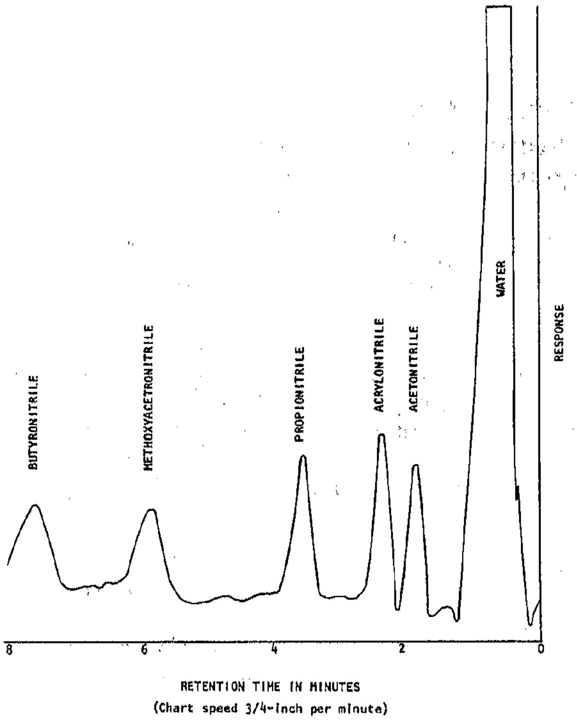
[2] *Annual Book of ASTM Standards*, Vol 11.01.

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

[4] *Gas Chromatographic Data Compilation, ASTM AMD25A*, 1967.



Column Packing - Chromosorb 101, 50/60 mesh
Carrier Gas - Helium at 25 mL/min
Temperature - Isothermal operation of the column at 130°C
Sample Size - 5 microlitres containing 10 mg/L of each nitrile

**FIG. 1 Isothermal Chromatographic Analysis of Nitriles in Aqueous Solution**

## 7. Precision and Bias

7.1 An interlaboratory study was conducted in 1972 with participation from four laboratories and seven operators. Triplicate analyses of three concentrations in distilled water were contributed by all operators; see Table 1 for statistics from distilled water data. Three operators also did triplicate recoveries of three concentrations spiked into a river water of their choice; see Table 2 for the statistics from the river water recovery data.

7.2 The precision of this test method within the range from 10 to 60 mg of standards/L in distilled water may be expressed as follows:

| Compound | |
|---|---|
| Acetonitrile | $S_t = 0.182x + 0.194$ |
| | $S_o = 0.023x + 0.038$ |
| Proprionitrile | $S_t = 0.100x - 0.817$ |
| | $S_o = 0.020x + 0.348$ |
| Methoxyacetonitrile | $S_t = 0.260x + 0.263$ |
| | $S_o = 0.026x + 0.671$ |
| Butyronitrile | $S_t = 0.107x - 0.457$ |
| | $S_o = 0.036x + 0.202$ |

where:
$S_t$ = overall precision,
$S_o$ = single operator precision, and
$x$ = concentration of the specification compound, mg/L.

## 8. Keywords

8.1 flame ionization; gas-liquid chromatography; GLC; isothermal chromatographic analysis; Kovats index

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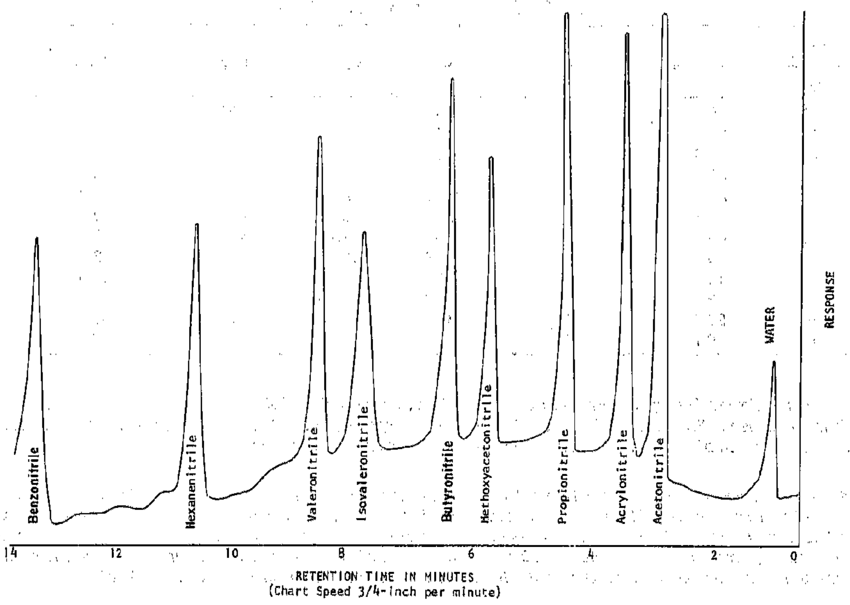
[5] Kovats index values estimated from relative retention data because standard compound was not readily available.



Column Packing - Chromosorb 101, 50/60 mesh
Carrier Gas - Helium at 25 mL/min
Temperature - Programmed operation at 10°C/min from 110°C to a maximum of 200°C
Sample Size - 3 microlitres containing 1 500 mg/L of each nitrile

FIG. 2 Proposed Temperature Chromatographic Analysis of Nitriles in Aqueous Solution

TABLE 1 Recovery for Reagent Water

| Compound | Amount Added, mg/L | Amount Found, mg/L | *n* | $S_o$ | $S_t$ | Bias | % Bias | Statistical Significance, 95 % CL |
|---|---|---|---|---|---|---|---|---|
| Acetonitrile | 60 | 50.7 | 21 | 1.37 | 11.0 | −9.3 | −15.5 | yes |
| | 30 | 24.4 | 21 | 1.10 | 5.90 | −5.6 | −18.7 | yes |
| | 10 | 8.42 | 21 | 0.57 | 1.86 | −1.58 | −15.8 | yes |
| Proprionitrile | 60 | 56.6 | 15 | 1.54 | 5.20 | −3.4 | −5.7 | yes |
| | 30 | 28.8 | 15 | 0.96 | 1.35 | −1.2 | −4.0 | yes |
| | 10 | 9.66 | 15 | 0.54 | 0.56 | −0.34 | −3.4 | yes |
| Methoxyacetonitrile | 60 | 62.8 | 18 | 2.21 | 15.6 | 2.8 | 4.7 | no |
| | 30 | 31.6 | 18 | 1.48 | 8.65 | 1.6 | 5.3 | no |
| | 10 | 9.88 | 18 | 0.91 | 2.50 | −0.12 | −1.2 | no |
| Butyronitrile | 60 | 57.9 | 21 | 2.43 | 6.08 | −2.1 | −3.5 | no |
| | 30 | 28.9 | 21 | 1.12 | 2.48 | −1.1 | −3.7 | no |
| | 10 | 9.31 | 21 | 0.66 | 0.78 | −0.69 | −6.9 | yes |

**TABLE 2 Recovery for River Water**

| Compound | Amount Added, mg/L | Amount Found, mg/L | $n$ | $S_o$ | $S_t$ | Bias | % Bias | Statistical Significance, 95 % CL |
|---|---|---|---|---|---|---|---|---|
| Acetonitrile | 60 | 38.7 | 9 | 2.83 | 17.4 | −21.3 | −35.5 | yes |
| | 30 | 16.3 | 9 | 1.59 | 9.94 | −13.7 | −45.7 | yes |
| | 10 | 4.32 | 9 | 1.12 | 4.58 | −5.68 | −56.8 | yes |
| Proprionitrile | 60 | 57.8 | 9 | 1.25 | 3.11 | −2.2 | −3.7 | no |
| | 30 | 29.6 | 9 | 0.64 | 2.67 | −0.4 | −1.3 | no |
| | 10 | 9.77 | 9 | 0.24 | 0.45 | −0.23 | −2.3 | no |
| Methoxyacetonitrile | 60 | 85.4 | 9 | 1.63 | 21.7 | 25.4 | 42.3 | yes |
| | 30 | 44.4 | 9 | 1.83 | 12.65 | 14.4 | 46.7 | yes |
| | 10 | 14.3 | 9 | 0.88 | 5.36 | 4.3 | 43.0 | yes |
| Butyronitrile | 60 | 62.5 | 9 | 1.68 | 5.73 | 2.5 | 4.2 | yes |
| | 30 | 29.9 | 9 | 0.76 | 1.38 | −0.1 | −0.3 | yes |
| | 10 | 9.75 | 9 | 0.64 | 0.90 | −0.25 | −2.5 | yes |