EXHIBIT 150
PART 10

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 D5257: Standard Test Method for Dissolved Hexavalent Chromium in Water by Ion Chromatography

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

Standards Body: American Society for Testing and Materials

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

Designation: D 5257 – 97

Standard Test Method for Dissolved Hexavalent Chromium in Water by Ion Chromatography[1]

This standard is issued under the fixed designation D 5257; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers procedures for the determination of dissolved hexavalent chromium in waste water, surface water, and drinking water.

1.2 The precision and bias of this test method has been tested in reagent water and industrial waste water and has been found suitable over the range of approximately 1 to 1000 µg/L. See Table 1 for details. Higher levels can be determined by appropriate dilution.

1.3 Samples containing very high levels of anionic species (that is, chloride, sulfate, etc.) may cause column overload. Samples containing high levels of reducing species (that is, sulfides, sulfites, etc.) may cause reduction of Cr(VI) to Cr(III). This can be minimized by buffering the sample to a pH of 9 to 9.5, filtering it, storing it at 4°C and analyzing it within 24 h.

1.4 The values stated in SI units are to be regarded as the standard.

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

TABLE 1 Determination of Precision and Bias for Hexavalent Chromium

Water Matrix	Amount Added, µg/L	Amount Found, µg/L	S_t	S_o[A]	Bias, %
Reagent	1.2	1.40	0.16	0.15	+ 16.6
	1.6	1.87	0.65	...	+ 16.9
	6.0	6.68	1.03	0.53	+ 11.3
	8.0	8.64	1.10	...	+ 8.0
	16.0	17.4	2.25	0.77	+ 8.8
	20.0	21.4	2.31	...	+ 7.0
	100	101	1.91	3.76	+ 1.0
	140	143	5.52	...	+ 2.1
	800	819	24.3	12.7	+ 2.4
	960	966	18.5	...	+ 7.3
Waste	6.0	5.63	1.17	0.55	–6.2
	8.0	7.31	1.91	...	–8.6
	16.0	15.1	2.70	1.85	–5.6
	20.0	19.8	1.01	...	–1.0
	100	98.9	4.36	3.31	–1.1
	140	138	8.39	...	–1.4
	800	796	60.6	27.1	–0.5
	960	944	72.1	...	–1.7

[A] Each Youden pair was used to calculate one lab data point, S_o.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1066 Practice for Sampling Steam[2]

D 1129 Terminology Relating to Water[2]

D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits[2]

D 1193 Specification for Reagent Water[2]

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

D3370 Practices for Sampling Water from Closed Conduits

2.2 *EPA Standard*:

EPA Method 218.6 Determination of Dissolved Hexavalent Chromium in Drinking Water, Groundwater and Industrial Wastewater Effluents by Ion Chromatography[3]

3. Terminology

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

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *eluant*— the ionic mobile phase used to transport the sample through the ion exchange column.

3.2.2 *resolution*—the ability of a column to separate constituents under specified test conditions.

4. Summary of Test Method

4.1 A fixed volume of buffered and filtered sample, typically 100 µL, is injected into the eluant flow path and separated by anion exchange using an ammonium sulfate based eluant.

4.2 After separation, the sample is reacted with an acidic solution of diphenylcarbohydrazide. Hexavalent chromium reacts selectively with this reagent to form the characteristic violet colored complex.

4.3 The eluant stream passes through a photometric detector

---

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

Current edition approved Dec. 10, 1997. Published December 1998. Originally published as D 5257 – 92. Last previous edition D 5257 – 93.

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

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

for detection of the chromium diphenylcarbohydrazide complex by visible absorbance at 530 nm. Absorbance is proportional to the hexavalent chromium concentration.

5. Significance and Use

5.1 Hexavalent chromium salts are used extensively in the metal finishing and plating industries, in the leather industry as a tanning agent, and in the manufacture of paints, dyes, explosives, and ceramics. Trivalent chromium salts are used as mordants in textile dying, in the ceramic and glass industry, and in photography. Chromium, in either oxidation state, may be present in waste water from these industries and may also be discharged from chromate-treated cooling waters.

5.2 Hexavalent chromium is toxic to humans, animals, and aquatic life. It can produce lung tumors when inhaled and readily induces skin sensitization. It is not known whether cancer will result from ingestion of chromium in any of its valence states.

5.3 Ion chromatography provides a means of separating the hexavalent chromium from other species present in the sample, many of which interfere with other detection methods. The combination of this separation with a sensitive colorimetric detection method provides a selective and sensitive analytical method for hexavalent chromium with minimal sample preparation.

6. Interferences

6.1 By virtue of the chromatographic separation essentially all interfering species are removed from the hexavalent chromium before detection.

6.2 Interferences may result from overloading of the analytical column capacity with high concentrations of anionic species in the sample. Concentrations of chloride ion or sulfate ion up to the equivalent of 1 % NaCl and 3 % Na_2SO_4 do not affect the separation or detection when using an anion exchange column and a 100 µL sample loop.

6.3 The response of 1 mg/L of hexavalent chromium is not affected by 1 g/L of chromic ion.

6.4 Reducing species may reduce hexavalent chromium in acidic matrices. Preservation at a pH 9 to 9.5 will minimize the effect of these species.

6.5 Trace amounts of Cr are sometimes found in reagent grade salts. Since a concentrated buffer solution is used in this test method to adjust the pH of samples, reagent blanks should be analyzed to assess the potential for Cr(VI) contamination. Contamination can also come from improperly cleaned glassware or contact with caustic or acidic reagents with chromium containing stainless steel or pigmented materials.

7. Apparatus

7.1 *Ion Chromatograph*—An ion chromatograph having the following components configured as shown in Fig. 1.

7.1.1 *Pump*, capable of delivering a constant flow in the range of 1 to 5 mL/min at a pressure of 200 to 2000 psi.

7.1.2 *Injection Valve*— A high pressure, low dead volume valve that allows introduction of 50 to 250 µL of sample into the eluant stream at up to 2000 psi.

7.1.3 *Guard Column*— A column placed before the separator column to protect the separator column from fouling by particles or strongly absorbed organic constituents.

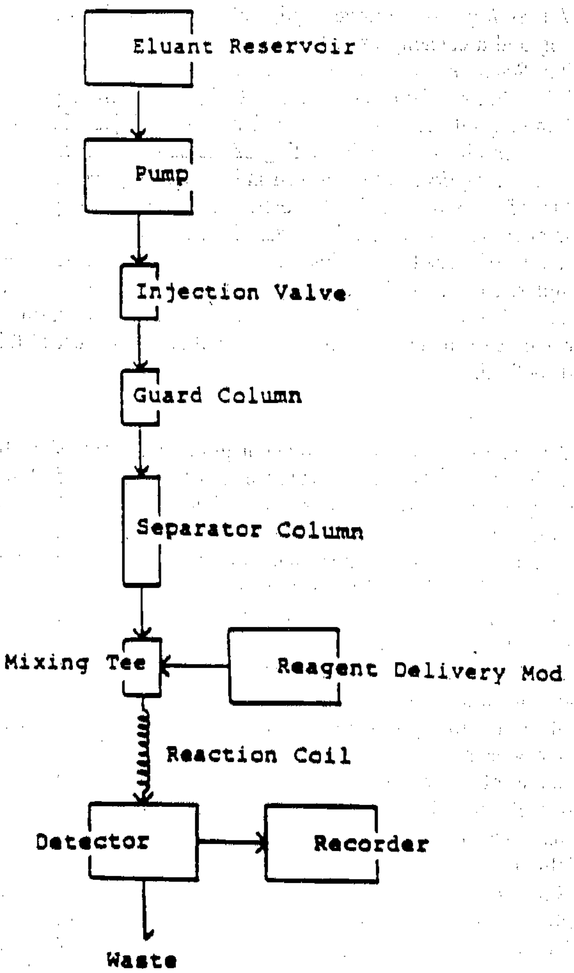


FIG. 1 Diagram of an Ion Chromatograph Using Post-Column Reagent Addition and Photometric Detection

7.1.4 *Analytical Column*—A liquid chromatographic column packed with a polymeric anion exchange resin capable of separating chromate from other anions in a sample containing high total dissolved solids (for example 3 % Na_2SO_4).

7.1.5 *Reagent Delivery Module*—A device capable of delivering 0 to 2 mL/min of reagent against a backpressure of up to 60 psi.

7.1.6 *Mixing Tee and Reaction Coil*—A device capable of mixing two flowing streams providing a sufficient reaction time for post column reaction with minimal band spreading.

7.1.7 *Detector*—A low-volume, flow-through UV-visible absorbance detector with a non-metallic flow path. The recommended detection wavelength for hexavalent chromium is 530 nm.

7.2 *Recorder, Integrator, Computer*—A device compatible with detector output, capable of recording detector response as a function of time for the purpose of measuring peak height or area.

7.3 *Eluant Reservoir*— A container suitable for storing eluant.

7.4 *Syringe*—A syringe equipped with a male luer type fitting and a capacity of at least 1 mL.

7.5 *Summary of Column Requirements*:

7.5.1 *Guard Column*— A short liquid chromatographic column capable of removing organics from the injected sample so as to minimize organic fouling of the separator column.

7.5.2 *Analytical Column*—An anion exchange column capable of providing suitable retention and chromatographic efficiency for chromate ion even in the presence of high amounts of dissolved solids that can occur in waste water samples. Note that high capacity columns will tolerate higher dissolved solids before becoming overloaded. See Section 13 for details of the columns used in the collaborative test of this test method.

8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[4] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*— Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193, Type I. Other reagent water types may be used provided it is first ascertained that the water is of sufficiently high purity to permit its use without adversely affecting the bias and precision of the test method. Type II water was specified at the time of round robin testing of this test method.

8.3 *Chromium Solution, Stock* (1000 mg Cr/L)—Dissolve 0.2828 g of potassium dichromate ($K_2Cr_2O_7$ that has been dried at 105°C for 1 h) in water. Add 0.1 mL of eluant concentrate (8.6) to ensure analyte stability. Dilute to 100 mL in a volumetric flask.

8.4 *Chromium Solution, Standard* (1000 µg Cr/L)—Pipet 1.00 mL of chromium stock solution (see 8.3) and 1 mL of eluant concentrate into a 1 L volumetric flask. Dilute to volume with water.

8.5 *Reagent Blank*— Add 1 mL of eluant concentrate (8.6) to a 1 L flask and dilute to volume with the water used to prepare the chromium standards.

8.6 *Eluant Concentrate* (2.5 *M* $(NH_4)_2SO_4$, 1.0 *M* NH_4OH)—Dissolve 330 g of ammonium sulfate $(NH_4)_2SO_4$ in about 500 mL of water. Add 65 mL of concentrated ammonium hydroxide (NH_4OH to sp gr 0.90). Mix well and dilute to 1 L in a volumetric flask.

8.7 *Eluant*—Two different analytical anion exchange columns proved satisfactory in the collaborative test that is summarized in Section 13. Accordingly, the eluant appropriate for each column is described in 8.7.1 and 8.7.2. Eluants should be filtered through a 0.45-µm filter and degassed.

8.7.1 *Eluant for IonPac AS7 Column* (0.250 *M* $(NH_4)_2SO_4$, 0.1 *M* NH_4OH)—Add 100 mL of eluant concentrate (8.6) to a 1 L volumetric flask and dilute to volume with water.

8.7.2 *Eluant for IC Pac Anion HC Column* (0.025 *M* $(NH_4)_2SO_4$, 0.01 *M* NH_4OH)—Add 10 mL of eluant concentrate (8.6) to a 1 L volumetric flask and dilute to volume with water.

8.8 *Diphenylcarbohydrazide Reagent*—Dissolve 0.5 g of 1,5-diphenylcarbohydrazide in 100 mL of reagent grade methanol. Add to about 500 mL of water containing 28 mL of concentrated sulfuric acid. Dilute with water, while stirring, to 1 L in a volumetric flask. Filter and degas if necessary to ensure reliable delivery.

9. Sampling

9.1 Collect the sample in accordance with the applicable ASTM Standards as follows: Practice D 1066, Specification D 1192, or Practices D 3370.

9.2 Filter samples and adjust pH immediately upon sampling to minimize any interconversion between Cr III and Cr VI species. Filter the sample through a 0.45 µm filter. Collect the filtrate and adjust its pH to 9 to 9.5 using the eluant concentrate (see 8.6). Ship and store samples at 4°C. Bring to ambient temperature prior to analysis. Analyze this stabilized filtrate within 24 h. Adjust final calculations to account for sample dilution.

10. Calibration

10.1 Prepare at least three levels of standards for each decade of the concentration range of interest. For standards of 1 to 1000 µg/L, prepare by diluting measured volumes of the standard chromium solution (see 8.4) with water in separate volumetric flasks.

10.2 Determine the chromium response for each of the standards and blank using the procedure defined in Section 11.

10.3 Prepare a calibration curve by using a linear plot of the peak height or area as a function of standard concentration. Do not force the calibration curve through zero. The response of the reagent blank should be less than 0.1 µg/L hexavalent chromium.

10.4 Prepare a new calibration curve when new reagents are made or the hardware is altered.

11. Procedure

11.1 Set up the ion chromatograph in accordance with the manufacturer's instructions.

11.2 Adjust the eluant flow rate to 1.5 mL/min. Increase the flow of the post-column reagent until the flow rate from the detector outlet line is 2.0 mL/min. so as to have a reagent flow of 0.5 mL/min under operating conditions. Measure the pH of the detector effluent to confirm it is 2 or lower.

11.3 After the flow rates are adjusted, allow the system to equilibrate for about 15 min.

11.4 If using a fixed volume sample loop (typically 100 µL), load at least 1 mL of sample through the sample port using an appropriate syringe. Inject the sample into the eluant stream and record the chromatogram (see Fig. 2). If using a variable volume injector, inject the desired sample volume into the eluant stream and record the chromatogram.

---

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

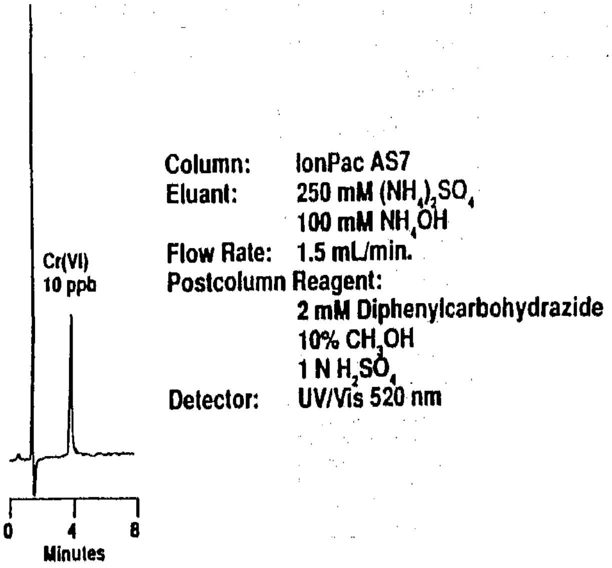


FIGURE 2 ION CHROMATOGRAPHIC DETERMINATION OF HEXAVALENT CHROMIUM

FIG. 2 Ion Chromatographic Determination of Hexavalent Chromium

12. Calculation

12.1 Refer the hexavalent chromium peak height or peak area to the calibration curve to determine the hexavalent chromium concentration of the injected sample in µg/L.

12.2 For samples that have been diluted, calculate the original hexavalent chromium concentration in µg/L by:

$$\mu g\,Cr(VI)/L = C \times F / V,$$

where:

C = µg Cr(VI)/L read from the calibration curve,
F = volume of diluted sample, in mL, and
V = volume of undiluted sample in mL.

13. Precision and Bias

13.1 The precision and bias data presented in this test method meet the requirements of Practice D 2777 (see Annex A1 for details).

13.2 The following separator columns were used in the collaborative test high capacity separator column[5] and low capacity separator column.[6]

13.3 The collaborative test of this test method was performed in reagent water and waste water by fifteen laboratories using one operator each. For reagent water the test used ten levels of concentration comprised of five Youden pairs ranging from 1.2 to 960 µg/L of hexavalent chromium. For waste water the test used eight levels of concentration comprised of four Youden pairs ranging from 6 to 960 µg/L of hexavalent chromium. The precision and bias data are presented in Table 1. See the Annex for a detailed description of the collaborative test.

13.4 The results of this collaborative test can also be summarized as follows:

Number of laboratories: 15
Range tested: 1.2 to 960 µg/L
Matrix: Reagent Water:
$S_o = 0.033x + 0.106$
$S_t = 0.050x + 0.559$
Mean Recovery = $1.04x + 0.183$
Matrix: Wastewater:
$S_o = 0.041x + 0.039$
$S_t = 0.059x + 1.05$
Mean Recovery = $0.989x + -0.41$

14. Keywords

14.1 analysis; hexavalent chromium; ion chromatography; wastewater; water

---

[5] Model IonPac A57 column, available from Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94088, has been found suitable for this purpose.

[6] Model IC Pac Anion HC, available from Millipore Corporation (Waters Division), 34 Maple Street, Milford, MA 01757.

ANNEX

(Mandatory Information)

A1. DUPLICATION OF QUALITY CONTROL MEASURES

A1.1 The precision and bias data cited in this test method were the result of a collaborative test designed and executed jointly by ASTM Committee D-19 on Water and the U.S. EPA Environmental Monitoring and Support Laboratory (Cincinnati). Participants were required to use this method or EPA Method 218.6, or both. These two methods are technically equivalent. The eleven reagent water samples consisted of a reagent water blank and five Youden pairs. The nine wastewater samples consisted of a waste-water blank and four Youden pairs. The following is a duplication of the test instructions that included the quality control measures that were part of this test method:

A1.2 Preparation

A1.2.1 *Calibration Standard Preparation*:

A1.2.1.1 A standard concentrate (green label) has been furnished with this study to minimize calibration standard biases. The Cr(VI) concentration contained within the standard concentrate ampul and the study range are listed in Table A1.1.

A1.2.1.2 Prepare a calibration curve according to 9.1 of

TABLE A1.1 Standard Ampul Concentration and Study Range

Analyte	MDL, µg/L	STANDARD Ampul, µg/L	Study Range, µg/L
Cr(VI)	0.4	100,000	1–1000

EPA Method 218.6, revision 3.2 using a series of calibration standards prepared from the standard concentrate. The calibration curve must range from 1.0 µg/L to 1000 µg/L.

A1.2.2 *Matrix Blanks*:

A1.2.2.1 An analysis of each matrix water is required to determine potential background concentrations of Cr(VI). These blanks are referred to as *reagent water blank* and *wastewater blank*. The wastewater blank should be adjusted to pH 9.0 to 9.5 with the buffer solution (section 7.9, EPA Method 218.6) and passed through a 0.45 µm filter before analysis. Analyze a portion of the wastewater solution prepared in A1.2.4.2 as the blank.

A1.2.3 *Quality Control Sample Preparation*:

A1.2.3.1 Prepare the QC sample (laboratory fortified blank (LFB) as described in section 10.3.2, Method 218.6, revision 3.2) by pipetting a 1.0 mL aliquot from the QC sample concentrate ampul (blue label) and diluting to 100 mL with reagent water. The Cr(VI) concentration in the QC sample and the acceptance limits that are to be used for this study are presented in Table A1.2.

A1.2.4 *Sample Preparation*:

A1.2.4.1 *Reagent Water Samples*:

(a) Prepare the reagent water samples by transferring a 1.0 mL aliquot from each ampul labelled reagent water (yellow labels) to individual 100 mL volumetric flasks and dilute to volume with reagent water. These samples are now ready for analysis.

A1.2.4.2 *Wastewater Samples*:

(a) Collect at least 1 liter of a wastewater of your choice. Filter the wastewater matrix through a 0.45 µm filter then adjust the pH of the filtrate to 9.0 to 9.5 by adding dropwise a solution of the buffer (8.2, EPA Method 218.6). Prepare the individual wastewater samples by transferring a 1.0 mL aliquot from each ampul labelled wastewater (orange labels) to individual 100 mL volumetric flasks and dilute to volume with the pH adjusted wastewater. These samples are now ready for analysis. The wastewater matrix is not to be diluted prior to spiking regardless of the Cr(VI) background concentration.

A1.3 Sample Analyses

A1.3.1 Analyze each prepared sample in the order defined in Table A1.3. The sample names and numbers in Table A1.3 are the same as those on the data report forms. Be certain that the sample data is entered under the correct sample name.

TABLE A1.2 Quality Control Sample Acceptance Limits

Analyte	True Value (T.V.) µg/L	Acceptance Limits [A] µg/L
Cr(VI)	40.0	36–44

[A] Defined as T.V. ± 10 %.

TABLE A1.3 EPA Method Study 218.6 Injection Order

Sample Name and Sample Order
QC Sample
Reagent Water Blank
Reagent Water—Sample #1
Reagent Water—Sample #2
Reagent Water—Sample #3
Reagent Water—Sample #4
Reagent Water—Sample #5
Reagent Water—Sample #6
Reagent Water—Sample #7
Reagent Water—Sample #8
Reagent Water—Sample #9
Reagent Water—Sample #10
QC Sample
Wastewater Blank
Wastewater—Sample #11
Wastewater—Sample #12
Wastewater—Sample #13
Wastewater—Sample #14
Wastewater—Sample #15
Wastewater—Sample #16
Wastewater—Sample #17
Wastewater—Sample #18
QC Sample

A1.4 Quality Control (QC)

A1.4.1 The QC sample is used to perform regular checks on the calibration curve. Only one QC sample need be prepared. However, three analyses of this QC sample will be required; one immediately following the last calibration standard, another immediately following the reagent water sample series, and the third immediately following the wastewater sample series. If the Cr(VI) concentration in the QC sample falls outside of the acceptance limits found in Table A1.2, the analyst should reanalyze the QC sample. If the Cr(VI) concentration falls within the acceptance limits, continue with the sample analyses. If the Cr(VI) concentration is still outside of the acceptance limits, a new calibration curve is required and must be confirmed by a successful QC analysis before sample analyses can continue.

A1.5 Data Report Forms

A1.5.1 Analytical values reported on the data report forms must not be corrected for matrix background concentrations. Report measured concentrations of Cr(VI) as µg/L to three significant figures (that is, 2.35, 23.5, or 235).

A1.6 Questionnaire

A1.6.1 Operate your ion chromatograph according to manufacturer specifications and recommendations found in EPA Method 218.6 (revision 3.2) and the equivalent Test Method D 5257. A questionnaire is enclosed to record your specific operating conditions and equipment type.

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 D5373: Standard Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Laboratory Samples of Coal and Coke

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

Standards Body: American Society for Testing and Materials

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

Designation: D 5373 – 93 (Reapproved 1997)

Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Laboratory Samples of Coal and Coke[1]

This standard is issued under the fixed designation D 5373; 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 instrumental determination of carbon, hydrogen, and nitrogen in laboratory samples of coal and coke prepared in accordance with Test Methods D 2013 and D 346.

1.2 Within the limitations outlined below, these test methods are applicable to either the air-dry or moisture-free laboratory sample, or both.

1.2.1 For instrumental systems in which the moisture and waters of hydration in the sample are liberated with (and only with) the oxidation products upon combustion, the analyses can be performed on a test specimen of the air-dry sample (Note 1). Concentrations determined on this air-dried basis represent the total carbon (including that present as carbonate), total hydrogen (including that present as water), and total nitrogen.

NOTE 1—These systems are also satisfactory for determining the subject materials in the moisture-free sample.

1.2.2 For systems in which the moisture and hydrates are otherwise liberated, the analysis shall be performed on the moisture-free sample. Values obtained on this basis represent the total carbon, organic hydrogen, and total nitrogen.

1.3 These test methods can be used to provide for the requirements specified in Practice D 3176 for the ultimate analysis.

1.4 The values stated in SI units shall be regarded as the standard.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in 8.3.1.

2. Referenced Documents

2.1 *ASTM Standards:*

D 346 Test Method for Collection and Preparation of Coke Samples for Laboratory Analysis[2]

D 2013 Test Method for Preparing Coal Samples for Analysis[2]

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

D 3174 Test Method for Ash in the Analysis Sample of Coal and Coke from Coal[2]

D 3176 Practice for Ultimate Analysis of Coal and Coke[2]

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

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

D 5142 Test Methods for the Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures[2]

3. Summary of Test Methods

3.1 Carbon, hydrogen, and nitrogen are determined concurrently in a single instrumental procedure. In some systems, the procedure consists of simply weighing a test specimen, placing the test portion into the instrument, and initiating the (subsequently automatic) analytical process. In other systems, the analytical process may be controlled manually to some degree.

3.2 The actual process can vary substantially from instrument to instrument because a variety of means can be used to effect the primary requirements of the test methods. These test methods provide for the following: (*1*) conversion of the subject materials in an oxygen stream in their entirety to carbon dioxide, water vapor, nitrogen oxides, and ash, respectively; and (*2*) subsequent, quantitative determination of the gases in an appropriate reference gas stream.

3.2.1 The conversion of the subject materials to their corresponding gases occurs largely during combustion of the sample at an elevated temperature in an atmosphere of purified oxygen. The gases that are produced include the following:

3.2.1.1 Carbon dioxide from the oxidation of organic and elemental carbon and the decomposition of carbonate minerals;

3.2.1.2 Hydrogen halides from organic halides (and organic hydrogen, as required);

3.2.1.3 Water vapor from the oxidation of (the remaining) organic hydrogen and the liberation of moisture and waters of hydration;

3.2.1.4 Nitrogen and nitrogen oxides from the oxidation of organic nitrogen and the decomposition of nitrates; and

3.2.1.5 Sulfur oxides from the oxidation of organic sulfur, and the decomposition of sulfide and sulfate minerals.

(*1*) In some systems, sulfurous and sulfuric acids can also be obtained from a combination of the sulfur oxides and the water vapor.

3.2.2 For hydrogen and nitrogen, the required conversion is completed in a two-step process consisting of the following:

---

[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 March 15, 1993. Published May 1993.

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

3.2.2.1 Removal of the halides and sulfur oxides and liberation of the associated hydrogen (as water), by conducting the combustion gases through a series of absorption traps containing appropriate absorbing materials.

3.2.2.2 Reduction of the nitrogen oxides to elemental nitrogen (see Note 2) by passing the resultant gases over copper at an elevated temperature. The carbon dioxide, water vapor, and nitrogen may then be determined via one of several satisfactory detection schemes.

NOTE 2—In this process, residual oxygen is also removed.

3.2.3 In one configuration, the gases are conducted through a series of thermal conductivity detectors and gas absorbers aligned so that, at the water vapor detector level, the gases pass through the sample side of the detector, a water vapor absorber, and the reference side of the detector. At the carbon dioxide detector level, the gases are then conducted through the sample side of the detector, a carbon dioxide absorber, and the reference side of the detector. Finally, the resultant gases, which contain only nitrogen and the carrier gas, pass through the sample side of the nitrogen detector and are vented. At this detector level, high-purity carrier gas is used as the reference gas. In these ways, the detectors determine the thermal conductivities solely of the specified components.

3.2.4 In a second configuration, the carbon dioxide and water vapor are determined by infrared detection, using an aliquot of the combustion gases from which only the halides and sulfur oxides have been removed. These detectors determine the infrared absorption of the pertinent gases at precise wavelength windows so that the absorbances result from only the specified components. In these systems, nitrogen is determined by thermal conductivity, using a second aliquot of the gases, additionally treated to also reduce the nitrogen oxides to nitrogen and to remove the residual oxygen, carbon dioxide, and water vapor.

3.2.5 In a third configuration, which is essentially a modified gas chromatographic system, the nitrogen, carbon dioxide, and water vapor in the treated combustion gases are eluted from a chromatographic column and determined (at appropriate retention times) by thermal conductivity detection.

3.3 In all cases, the concentrations of carbon, hydrogen, and nitrogen are calculated as functions of the following:

3.3.1 Measured instrumental responses,

3.3.2 Values for response per unit mass for the elements (established via instrument calibration), and

3.3.3 Mass of the sample.

3.4 Or to the following: the instrument response is proportional to the gas density, which has been calibrated against a gas density of known concentration.

3.5 A capability for performing these computations automatically can be included in the instrumentation used for these test methods.

4. Significance and Use

4.1 Carbon and hydrogen values are used to determine the amount of oxygen (air) required in combustion processes and for the calculations of efficiency of combustion processes.

4.2 Carbon and hydrogen determinations are used in material balance calculations on coal conversion processes; also, one or the other is used frequently in correlations of chemical and physical properties, such as yields of products in liquefaction, reactivity in gasification and the density and porosity of coal.

4.3 Nitrogen data are required to fulfill the requirements of the ultimate analysis, Practice D 3176. Also, the data obtained can be used to evaluate the potential formation of nitrogen oxides as a source of atmospheric pollution.

4.4 Nitrogen data are used for comparing coals and in research. If the oxygen content of coal is estimated by difference, it is necessary to make a nitrogen determination.

5. Apparatus

5.1 Because a variety of instrumental components and configurations can be used satisfactorily for these test methods, no specifications are presented here with respect to overall system design.

5.2 Functionally, however, the following requirements are specified for all approved instruments (Note 3):

NOTE 3—The approval of an instrument with respect to these functions is paramount to these test methods, since such approval tacitly provides approval of both the materials and the procedures used with the system to provide for these functions.

5.2.1 The conditions for combustion of the sample shall be such that (for the full range of applicable samples) the subject components shall be converted completely to carbon dioxide, water vapor (except for hydrogen associated with volatile halides), and nitrogen or nitrogen oxides. Generally, instrumental conditions that effect complete combustion include (*1*) availability of the oxidant, (*2*) temperature, and (*3*) time.

5.2.2 Representative aliquots of the combustion gases shall then be treated for the following reasons:

5.2.2.1 To liberate (as water vapor) hydrogen present as hydrogen halides and sulfur oxyacids; and

5.2.2.2 To reduce (to the element) nitrogen present as nitrogen oxides.

(*1*) The water vapor and nitrogen so obtained shall be included with the materials originally present in these aliquots.

5.2.3 Additional treatment of the test specimens (prior to detection) depends on the detection scheme used for the instrument (Note 4).

NOTE 4—The additional treatments can be provided by the instrumental components used to satisfy 5.2.2.

5.2.3.1 For the configuration described in 3.2.3, the halides proper, sulfur oxides, and residual oxygen shall be removed from the single test specimen in which the water vapor, carbon dioxide, and nitrogen are determined sequentially.

5.2.3.2 For the configuration described in 3.2.4, the test specimen in which the water vapor and carbon dioxide are determined, only the halides and sulfur oxides shall be removed from the gas stream in which the water vapor and carbon dioxide are determined. For combusted gases in which the nitrogen is determined, the water, carbon dioxide, and residual oxygen shall also be removed.

5.2.3.3 For the configuration described in 3.2.5, the halides and sulfur oxides shall be removed from the combusted gases obtained from the single test specimen.

5.2.4 The detection system (in its full scope) shall determine the analytical gases individually and without interference. Additionally, for each analyte, either of the following applies:

5.2.4.1 The detectors themselves shall provide linear responses that correlate directly to concentration over the full range of possible concentrations from the applicable samples, or

5.2.4.2 The system shall include provisions for evaluating nonlinear responses appropriately so that the nonlinear responses can be correlated accurately with these concentrations.

(*1*) Such provisions can be integral to the instrumentation, or they can be provided by (auxiliary) computation schemes.

5.2.5 Finally, except for those systems in which the concentration data are output directly, the instrument shall include an appropriate readout device for the detector responses.

6. Reagents

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 *Helium, Carrier Gas*, as specified by the instrument manufacturer.

6.3 *Oxygen*, as specified by the instrument manufacturer.

6.4 *Additional Reagents*, as specified by the instrument manufacturer. This specification refers to the reagents used to provide for the functional requirements cited in 5.2.2 through 5.2.3.3. These reagents can vary substantially for different instruments; in all cases, however, for systems that are functionally satisfactory (and therefore approved), the reagents recommended by the manufacturer are also tacitly approved. Consequently, these reagents shall be those recommended by the manufacturer.

7. Preparation of Analysis Sample

7.1 The samples shall initially be prepared in accordance with Test Methods D 2013 or D 346.

7.2 If required by characteristics of the instrumental system, reduce the air-dry samples (7.1) typically to pass 75 μm (No. 200 U.S.A. Standard Sieve Series) to obtain test units of the analysis sample in the size range recommended by the instrument manufacturer. If required by characteristics of the instrumental system, as specified in 1.2.2, treat the test specimens in accordance with Test Method D 3173 to provide moisture-free materials solely appropriate for these systems. In this and all subsequent sample handling steps, exercise care to minimize changes in moisture content resulting from exposure to the atmosphere.

8. Instrument Preparation

8.1 Assemble the instrumental system in accordance with the manufacturer's instructions.

8.2 *Adjustment of Response of Measurement System*—Weigh an appropriate test portion of standard reference material (SRM), calibrating agent, or reference coal. Analyze the test portion (see 9.1). Repeat this procedure. Adjust instrument response, as recommended by the manufacturer, until the absence of drift is indicated.

8.3 *Calibration*—Select coal SRMs or other calibrating agents and materials specified by the manufacturer that have certified carbon, hydrogen, and nitrogen values in the range of samples to be analyzed. At least three such SRMs or calibrating agents are recommended for each range of carbon, hydrogen, and nitrogen values to be tested. When possible, two of the SRMs or calibrating agents shall bracket the range of carbon, hydrogen, and nitrogen to be tested, with the third falling within the range.

8.3.1 All coal SRMs should be in accordance with 7.1 and shall be supplied by or have traceability to an internationally recognized certifying organization. **CAUTION:** An indicated problem with linearity of the instrument during calibration can result from contamination of the SRM or calibrating agent as the container becomes depleted. It is therefore recommended that the SRM or calibrating agent be discarded when less than five grams remain in the container.

8.3.2 *Calibration Procedure*—Analyze, as samples, portions of an SRM, reference coal, or calibrating agent chosen to represent the level of carbon, hydrogen, and nitrogen in the samples to be tested. If not required by the characteristics of the instrumental system, use the "as-determined" carbon, hydrogen, and nitrogen values for calibration. These values must have been calculated previously from the certified "dry basis" carbon, hydrogen, and nitrogen values and residual moisture determined using either Test Methods D 3174 or D 5142. Continue analyzing until the results from five consecutive determinations fall within the repeatability interval (see 12.2.1) of these test methods. Calibrate the instrument according to the manufacturer's instructions using these values. Analyze, as samples, two SRMs reference coals or calibrating agents that bracket the range of values to be tested. The results obtained for these samples must be within the stated precision limits of the SRM, reference coal, or calibrating agent, or the calibration procedure must be repeated. Records for all calibrations must be in accordance with Guide D 4621.

8.3.3 *Periodic Calibration Verification and Recalibration*—In accordance with Guide D 4621, analyze a control sample on a periodic basis. Results obtained for the control sample must be within established limits, or all results obtained since the last successful control check must be rejected and the calibration procedure repeated.

9. Procedure

9.1 Analyze a test specimen of the analysis sample in accordance with the manufacturer's instructions.

---

[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.

10. Calculation

10.1 Calculate the concentrations of carbon, hydrogen, and nitrogen, on the appropriate sample basis, as follows:

$$A = \frac{(B \times C)}{D} \times 100$$

where:

A = % of the analyte,

B = detector response for that analyte,

C = unit mass per detector response established for the analyte during calibration, and

D = mass of test specimen, g.

The calculations can be provided automatically by the instrumental system used for these test methods.

11. Report

11.1 Report results from the carbon, hydrogen, and nitrogen determinations on any of the several common bases that differ solely with respect to moisture. Procedures for converting the as-determined concentrations to the other bases are specified in Practices D 3176 and D 3180.

12. Precision and Bias

12.1 These test methods are highly dependent on the calibration of the equipment.

12.2 The precision of these test methods for the determination of carbon, hydrogen, and nitrogen was calculated from data obtained from coal and coke with the following concentration ranges: carbon (dry-basis) from 48.6 to 90.6 %, hydrogen (dry-basis) from 0.14 to 5.16 %, and nitrogen (dry-basis) from 0.69 to 1.57 %.

12.2.1 *Repeatability*—The difference, in absolute value, between two test results, conducted on portions of the same analysis sample, in the same laboratory, by the same operator, using the same apparatus, shall not exceed the repeatability interval $I(r)$ in more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the repeatability interval, there is reason to question one, or both, of the test results. The repeatability intervals for carbon, hydrogen, and nitrogen are given in Table 1.

TABLE 1 Repeatability and Reproducibility

% Dry Basis	$I(r)$	$I(R)$
Carbon	0.64	2.51
Hydrogen	0.16	0.30
Nitrogen	0.11	0.17

12.2.2 *Example*—Duplicate analyses for carbon exhibited values of 73.26 and 73.62 %. The absolute difference between the two test results is 0.36 %. Since this value does not exceed the $I(r)$ value of 0.64 %, these duplicate analyses are acceptable at the 95 % confidence level.

12.2.3 *Reproducibility*—The difference, in absolute value, between the averages of duplicate determinations conducted in different laboratories on representative samples prepared from the same bulk sample after reducing to 100 % through a 250 Mm (No. 60 U.S.A. Standard Sieve Series) sieve shall not exceed the reproducibility internal $I(R)$ in more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the reproducibility interval, there is reason to question one, or both, of the test results. The reproducibility intervals for carbon, hydrogen, and nitrogen are given in Table 1.

12.2.4 *Example*—Duplicate analysis for hydrogen in one laboratory revealed an average value of 5.15 %, and a value of 4.93 % was obtained in a different laboratory. The difference between the different laboratory value is 0.22 %. Since the laboratory difference is less than the $I(R)$, the two laboratory results are acceptable at the 95 % confidence level.

12.3 *Bias*—Bias is eliminated when the apparatus is calibrated properly against certified reference standards. Proper calibration includes comparison of test data on NIST SRM 1632 or other reagents and materials that have certified carbon, hydrogen, and nitrogen values.

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:

CFR Section(s):

Standards Body:

APPROVED

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

Designation: D 5489 – 96a

Standard Guide for Care Symbols for Care Instructions Textile Products[1]

This standard is issued under the fixed designation D 5489; 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 guide provides a uniform system of symbols for the disclosure of care instructions on textile products such as apparel, piece goods, and household and institutional articles, hereinafter referred to as "textile," or "textile product."

1.2 This guide provides a comprehensive system of symbols to represent care instructions in order to reduce language-dependent care instructions.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 123 Terminology Relating to Textile Materials[2]

D 3136 Terminology Relating to Care Labels for Textile and Leather Products Other than Textile Floor Coverings and Upholstery[2]

D 3938 Guide for Determining or Confirming Care Instructions for Apparel and Other Textile Consumer Products[3]

2.2 *AATCC Standard:*

A Glossary of AATCC Standard Terminology, Current Edition[4]

2.3 *Other Standards:*

Federal Trade Commission Amendment to Trade Regulation Rule Concerning Care Labeling of Textile Wearing Apparel, and Certain Piece Goods, *Federal Register*, Vol 48, No. 99, May 20, 1983 (cited as 16 CFR 423).[5]

The National Standard of Canada—Care Labelling of Textiles (CAN/CGSB-86.1-M91)[6]

3. Terminology

3.1 *Definitions*—For definitions of terms related to care labeling, refer to Terminology D 3136. For definitions of other textile terms used in this guide, refer to Terminology D 123.

3.1.1 *care instructions, n—in textiles*, a series of directions describing which care practices should refurbish a product without adverse effects, and warnings for those care practices expected to have a harmful effect.

3.1.2 *care label, n—in textiles*, a label or other affixed instuctions that report how a product should be refurbished.

3.1.2.1 *Discussion*—The Federal Trade Commission, in Rule 16 CFK 423, requires care instructions on most apparel and certain other textile items. In relation to these products, the FTC definition states: "Care Label means a permanent label or tag, containing regular care information and instruction, that is attached or affixed in some manner that will not become separated from the product and will remain legible during the useful life of the product."

3.1.3 *care symbol, n*—a pictorial symbol that gives directions for refurbishing a consumer textile product.

4. Significance and Use

4.1 This guide provides symbols and a system for their use by which care instructions for textile products can be conveyed in a simple, space-saving, and easily understood pictorial format that is not language dependent.

4.2 Care symbols are an important means for identifying the appropriate care procedure for home laundering, commercial laundering, professional drycleaning, and coin-operated drycleaning, of textile products.

4.3 Care labeling using symbols can be used by the purchaser to select textiles on the basis of the care method required without knowledge of the language.

4.4 In countries in which a word-based care labeling system is required, the care symbol system may be used as a supplemental system.

4.5 The word-based instructions for each symbol in this guide are harmonious with Terminology D 123, D 3136, the United States Federal Trade Commission Care Labeling Rule, 16 CFR 423 and industry practice. (See Fig. 1 and 2).

4.6 The care label symbol system is based on five basic care symbols representing five operations: washing, bleaching, drying, ironing, and drycleaning.

4.7 One color is used for all care symbols in this care labeling system.

NOTE 1—While this symbol system uses one color, it is harmonious with tri-color systems such as the Canadian system because the instructions are clear whether printed in one or three colors.

4.8 This guide does not specify the type of label material or fabric to use. However, appropriateness for consumer comfort is recommended.

5. Procedure

5.1 *Introduction*—This section defines the basic symbols

---

[1] This guide is under the jurisdiction of ASTM Committee D-13 on Textiles and is the direct responsibility of Subcommittee D13.62 on Textile Care Labeling.

Current edition approved April 10, 1996. Published June 1996. Originally published as D 5489 – 93. Last previous edition D 5489 – 96.

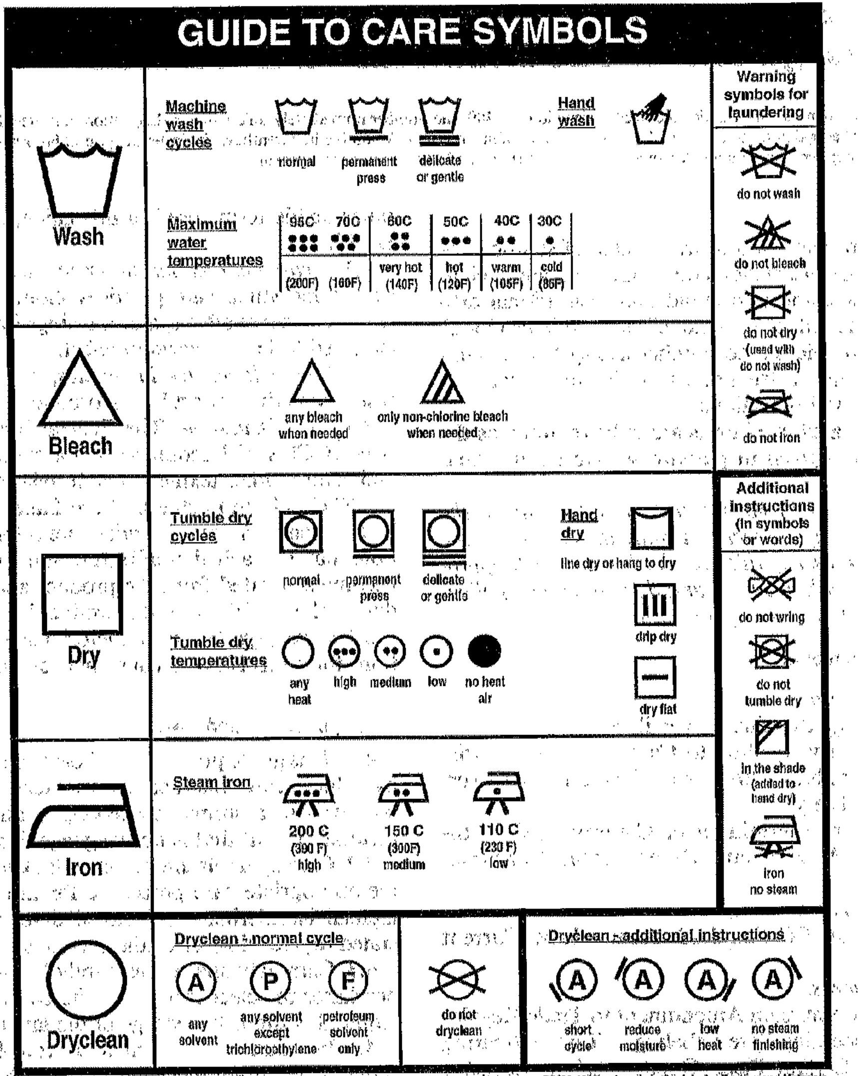
[2] *Annual Book of ASTM Standards*, Vol 07.01.

[3] *Annual Book of ASTM Standards*, Vol 07.02.

[4] *Annual AATCC Technical Manual*, available from the American Association of Textile Chemists and Colorists, P.O. Box 12215, Research Triangle Park, NC 27709.

[5] Available from U.S. Government Printing Office, North Capital and H Streets, NW, Washington, DC 20401.

[6] Available from CGSB, Sales Unit, Ottawa, Canada. (819) 956-0425 or (819) 956-0426.



Reprinted, with permission, from
1996 Annual Book of ASTM Standards

D5489-1996a. American Society for Testing and Materials
1916 Race Street, Philadelphia, PA 19103

NOTE—This figure illustrates the symbols to use for laundering and drycleaning instructions. As a minimum, laundering instructions shall include, in order, four symbols: washing, bleaching, drying, and ironing; and drycleaning instructions shall include one symbol. Additional symbols or words may be used to clarify the instructions.

FIG. 1 Commercial and Home Laundering and Drycleaning Symbols

and prohibitive symbols; the washing, bleaching, drying, ironing, and drycleaning processes; the required number and order of symbols; supplementary care information; and appropriate instructions and labels.

5.2 *Basic Symbols:*

5.2.1 There are five basic symbols: the washtub, triangle, square, iron, and circle.

5.2.2 The washtub represents the washing process, the triangle represents the bleaching process, the square represents the drying process; the iron represents the ironing or pressing process, and the circle represents the drycleaning process (Fig. 3).

5.3 *Prohibitive Symbols*—The prohibitive "X" symbol may be used only when evidence can be provided that the care procedure on which it is superimposed would adversely change the dimensions, hand, appearance, or performance of the textile. (Fig. 4).

5.4 *The Washing Process—The Washtub Symbol:*

5.4.1 The washtub with a water wave represents the washing process in a home laundering or commercial laundering setting.

5.4.2 Additional symbols inside the washtub indicate the suggested water temperature and hand-washing process.

5.4.3 Additional symbols below the tub indicate the permanent press cycle (one underline, minus sign, or bar) and delicate-gentle washing cycle (two underlines, minus signs, or bars).

5.4.4 The numerical or the dot system or both illustrated

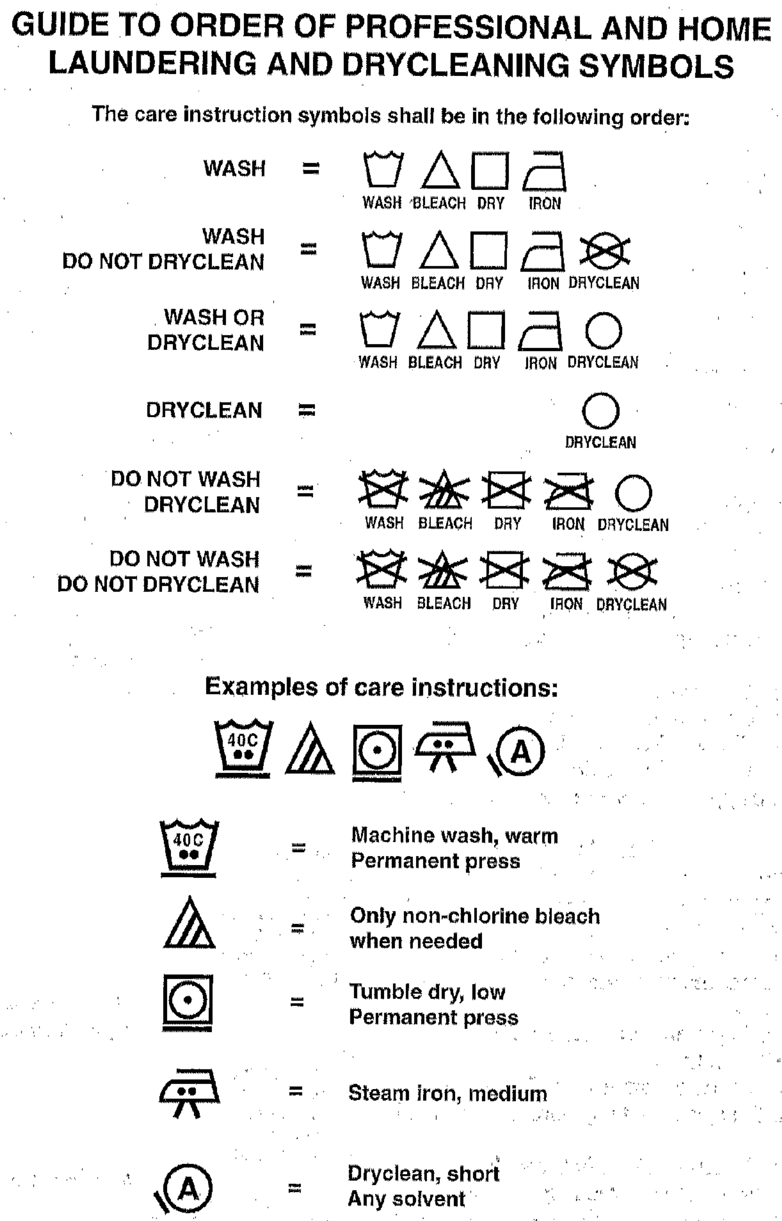


FIG. 2 Guide to Order of Professional and Home Laundering and Drycleaning Symbols

in Fig. 1 may be used to represent the maximum water temperature for machine and hand washing.

5.4.4.1 The six washing temperatures are 30°C (80°F), 40°C (105°F), 50°C (120°F), 60°C (140°F), 70°C (160°F), and 95°C (200°F) and shall be in Celsius when using the numerical water temperature system. The temperature in Farenheit may be included.

Note 2—The Fahrenheit temperatures, while not true conversions from Celsius to Fahrenheit, are within the range of tolerance and represent common consumer usage.

5.4.4.2 The symbols used to represent the maximum water temperature in the dot system are: six dots [95°C (200°F)], five dots [70°C (160°F)], four dots [60°C (140°F)], very hot, three dots [50°C (120°F)], hot, two dots [40°C

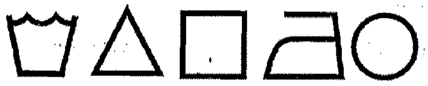


FIG. 3 Basic Symbols

FIG. 4 Prohibitive Symbols

(105°F)], warm, one dot [30°C (85°F)], cool/cold.

5.4.5 To represent the care instruction for a specific wash condition, use the appropriate symbol as illustrated in Fig. 1.

NOTE 3—Consumers may obtain washing machine temperatures that are frequently below the suggested temperature. The actual water temperature obtained when using the washing machine settings of hot, warm, and cold vary in North American by region, season, water heater settings, and regulations governing factory-set mixes. In general, North American washing machines do not have internal heaters.

5.5 *The Bleaching Process—The Triangle Symbol:*

5.5.1 The triangle represents the bleaching process.

5.5.2 The triangle and an additional symbol inside the triangle represent the type(s) of bleach to use.

5.5.3 To represent the care instruction for a specific bleaching condition, use the appropriate symbol as illustrated in Fig. 1.

5.6 *The Drying Process—The Square Symbol:*

5.6.1 The square represents the drying process.

5.6.2 Additional symbols inside the square represent the type of drying process to use, including tumble dry, line dry, drip dry, dry flat, and dry in shade.

5.6.3 Additional symbols below the tumble dry symbol indicate the permanent press cycle (one underline, one minus, or bar) and the delicate-gentle cycle (two underlines, minus signs, bars).

5.6.4 The dot(s) used to represent the dryer temperatures are: three dots (high), two dots (medium), one dot (low), no dots (any heat), and, a solid or filled-in circle (no heat/air).

5.6.5 To represent the care instruction for a specific drying condition, use the appropriate symbol as illustrated in Fig. 1.

5.7 *The Ironing Process—The Hand Iron Symbol:*

5.7.1 The hand iron represents both the hand ironing process and the pressing process on commercial equipment in laundering and cleaning plants.

5.7.2 Additional ironing symbols include dot symbols inside the iron to represent the temperature setting and the steam burst under the iron.

5.7.2.1 The three ironing temperatures are 200°C (392°F), 150°C (302°F), and 110°C (230°F).

5.7.3 To represent the care instruction for a specific ironing condition, use the appropriate symbol as illustrated in Fig. 1.

5.8 *The Drycleaning Process—The Circle Symbol:*

5.8.1 The circle represents the drycleaning process.

5.8.2 A letter enclosed in the drycleaning symbol indicates the type of solvent that is recommended.

5.8.3 Additional symbols with the drycleaning symbol give additional information concerning the drycleaning process.

5.8.4 To represent the care instruction for a specific drycleaning condition, use the appropriate symbol as illustrated in Fig. 1.

5.9 *Required Number and Order of Symbols:*

5.9.1 To represent the laundering process on a care label, a minimum of four care instruction symbols in the following order—washing, bleaching, drying, and ironing—shall be used. (See Fig. 2.)

5.9.1.1 The required symbol may be a prohibitive symbol ("X"), if necessary.

5.9.1.2 Additional warnings and information in symbols or words, as appropriate, shall be placed after or below the four laundering symbols or in the logical refurbishing sequence of the written instructions.

5.9.2 To represent the drycleaning process on a care label, the drycleaning symbol, as a minimum, shall be used. (See Fig. 2.)

5.9.2.1 As appropriate, additional warnings and information shall be placed around, after, or below the drycleaning symbol or in the logical refurbishing sequence of the written instructions.

NOTE 4—The ISO care symbol system requires four care symbols in the following order: washing, bleaching, ironing, and drycleaning. Tumble drying is an optional symbol, which, if used, appears after the four symbols.

TABLE 1 Additional Words to Use with Care Symbols

NOTE—This guide uses symbols to represent many textile refurbishing procedures. Additional words may be needed to clarify specific care procedures. This table of additional words to use with care symbols includes the remaining terms listed in the Federal Trade Commission Care Labeling Glossary of Standard Terms and additional terms in common usage that are not represented by symbols. These terms are illustrative only and are not meant to be an exhaustive list of all terms that might be appropriate or necessary. In general, whatever additional words are needed to state a care procedure that will result in the adequate refurbishment of the item should be used.

Federal Trade Commission Standard Terms	Terms in Common Usage
Preliminary and Laundering Instructions	
do not have commercially laundered	close zippers
small load	do not pretreat
separately	do not soak
with like colors	remove buttons
wash inside out	remove lining
	remove shoulder pads
	remove trim
	wash dark colors separately
warm rinse	wash once before wearing
cold rinse	wash separately
rinse thoroughly	wash with like colors
no spin or do not spin	do not use fabric softener
no wring or do not wring^A	remove promptly
no wring or twist^A	rinse twice
damp wipe only	use oversize washing machine
Bleaching (all terms represented by symbols)	
Drying, All Methods	
no heat^A	tumble dry, air^A
remove promptly	do not tumble dry
line dry in the shade^A	reshape and dry flat
line dry away from heat	block flat to dry
block to dry	
smooth by hand	
Ironing and Pressing	
iron wrong side only	do not iron decal
no steam or do not steam^A	iron reverse side only
steam only	iron right side only
iron damp	warm iron if needed
use press only	use press cloth
Wash or Dryclean (can be represented with symbols)	
Drycleaning, All Methods	
professionally dryclean	fur clean
short cycle^A	use clear solvent
minimum extraction	clear distilled solvent rinse
reduced or low moisture^A	
tumble warm	low heat^A
tumble cool	
cabinet dry warm	
cabinet dry cool	
steam only	
no steam or do not steam	no steam finishing
steam only	
use fluorocarbon solvent	

^{A} Care instruction may be reported in words or a symbol.

5.10 *Supplementary Care Information:*

5.10.1 Additional written care information in English (or the appropriate national language) may be necessary to convey special instructions not covered by the appropriate care symbol or may be legislated by the country of origin. See Fig. 1 and Table 1.

5.10.1.1 For example, the words "remove promptly" shall be added to an article for which this instruction would be appropriate.

5.10.2 The additional words shall appear on the care label in the logical refurbishing sequence.

5.10.3 The written information on a care symbol label shall be brief.

5.10.4 The symbol information and any accompanying detailed written instructions shall be consistent.

5.11 *Appropriate Instructions and Labels:*

5.11.1 It is the responsibility of the manufacturer, or importer to provide the correct information on the care label for refurbishment.

5.11.2 Determining and confirming care instructions requires setting performance specifications, testing, and evaluating the textile product.

5.11.2.1 To aid in determining and confirming appropriate instructions, see Guide D 3938 and published test methods and performance specifications are available in the current *Annual Book of ASTM Standards,* Vols 07.01 and 07.02, and the current Technical Manual of the American Association of Textile Chemists and Colorists (see 2.1 and 2.2).

5.11.3 In the United States, care labels must be attached permanently to apparel except when exempted by the U.S. Federal Trade Commission Regulation (see 2.3).

5.11.4 Permanent care labels shall remain attached and legible for the life of the textile product.

5.11.5 Either the care label or the detailed care instructions shall be visible at the point of purchase.

6. Keywords

6.1 bleaching; care instructions; care label; care symbol; consumer textile product; drycleaning; drying; ironing; permanent care label; pressing; washing

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 D5673: Standard Test Method for Elements in Water by Inductively Coupled Plasma

CFR Section(s): 40 CFR 444.12(b)(1)

Standards Body: American Society for Testing and Materials

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

Designation: D 5673 – 96

Standard Test Method for Elements in Water by Inductively Coupled Plasma—Mass Spectrometry[1]

This standard is issued under the fixed designation D 5673; 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 dissolved elements in ground water, surface water, and drinking water. It may also be used for the determination of total-recoverable elements in these waters as well as wastewater.[2]

1.2 This test method should be used by analysts experienced in the use of inductively coupled plasma—mass spectrometry (ICP-MS), the interpretation of spectral and matrix interferences and procedures for their correction.

1.3 It is the user's responsibility to ensure the validity of the test method for waters of untested matrices.

1.4 Table 1 lists elements for which the test method applies, with recommended masses and typical estimated instrumental detection limits using conventional pneumatic nebulization. Actual working detection limits are sample dependent and, as the sample matrix varies, these detection limits may also vary. In time, other elements may be added as more information becomes available and as required.

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

2. Referenced Documents

2.1 *ASTM Standards:*

D 1066 Practice for Sampling Steam[3]
D 1129 Terminology of Terms Relating to Water[3]
D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits[3]
D 1193 Specification for Reagent Water
D 3370 Practices for Sampling Water from Closed Conduits[3]

3. Terminology

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

3.2 *Description of Terms Specific to This Standard:*

3.2.1 *calibration blank*—a volume of water containing the same acid matrix as the calibration standards (see 11.1).

3.2.2 *calibration shock solution*—a solution prepared from the stock standard solution(s) to verify the instrument response with respect to analyte concentration.

TABLE 1 Recommended Analytical Mass and Estimated Instrument Detection Limits

Element	Recommended Analytical Mass	Estimated Instrument Detection Limit, µg/L[A]
Aluminum	27	0.05
Antimony	121	0.08
Arsenic	75	0.9
Barium	137	0.5
Beryllium	9	0.1
Cadmium	111	0.1
Chromium	52	0.07
Cobalt	59	0.03
Copper	63	0.03
Lead	206, 207, 208	0.08
Manganese	55	0.1
Molybdenum	98	0.1
Nickel	60	0.2
Selenium	82	5.0
Silver	107	0.05
Thallium	205	0.09
Thorium	232	0.03
Uranium	238	0.02
Vanadium	51	0.02
Zinc	66	0.2

[A] Instrument detection limits (3σ) estimated from seven replicate scans of the blank (1 % v/v HNO_3) and three replicate integrations of a multi-element standard.

3.2.3 *calibration standards*—a series of known standard solutions used by the analyst for calibration of the instrument (that is, preparation of the analytical curve) (see 11.).

3.2.4 *dissolved*—those elements that will pass through a 0.45-µm membrane filter.

3.2.5 *instrumental detection limit*—the concentration equivalent to a signal which is equal to three times the standard deviation of the blank signal at the selected analytical mass(es).

3.2.6 *internal standard*—pure analyte(s) added in known amount(s) to a solution. This is used to measure the relative instrument response to the other analytes that are components of the same solution. The internal standards must be analytes that are not a sample component.

3.2.7 *method detection limit*—the minimum concentration of an analyte that can be identified, measured and reported with 99 % confidence that the analyte concentration is greater than zero. This confidence level is determined from analysis of a sample in a given matrix containing the analyte(s).

3.2.8 *quality control reference solution*—a solution with the certified concentration(s) of the analytes, prepared by an independent laboratory, and used for a verification of the instrument's calibration.

3.2.9 *reagent blank*—a volume of water containing the

---

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

Current edition approved Feb. 10, 1996. Published April 1996.

[2] EPA Test Method: Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma—Mass Spectrometry, Method 200.8.

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

same matrix as the calibration standards, carried through the entire analytical procedure.

3.2.10 *total-recoverable*—a term relating to forms of each element that are determinable by the digestion method included in this procedure (see 12.2).

3.2.11 *tuning solution*—a solution that is used to determine acceptable instrument performance prior to calibration and sample analysis.

4. Summary of Test Method

4.1 This test method describes the multi-element determination of trace elements by inductively coupled plasma—mass spectrometry (ICP-MS). Sample material in solution is introduced by pneumatic nebulization into a radiofrequency plasma where energy transfer processes cause desolvation, atomization, and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer. The ions transmitted through the quadrupole are detected by a continuous dynode electron multiplier assembly and the ion information processed by a data handling system. Interferences relating to the technique must be recognized and corrected for (see Section 7 on interferences). Such corrections must include compensation for isobaric elemental interferences and interferences from polyatomic ions derived from the plasma gas, reagents, or sample matrix. Instrumental drift as well as suppressions or enhancements of instrument response caused by the sample matrix must be corrected for by the use of internal standardization.

5. Significance and Use

5.1 The test method is useful for the determination of element concentrations in many natural waters and wastewaters. It has the capability for the determination of up to 20 elements. High analysis sensitivity can be achieved for some elements that are difficult to determine by other techniques.

6. Interferences

6.1 Several types of interference effects may contribute to inaccuracies in the determination of trace elements. These interferences can be summarized as follows:

6.1.1 *Isobaric Elemental Interferences*—Isobaric elemental interferences are caused by isotopes of different elements which form singly or doubly charged ions of the same nominal mass-to-charge ratio and which cannot be resolved by the mass spectrometer in use. All elements determined by this test method have, at a minimum, one isotope free of isobaric elemental interference. Of the analytical isotopes recommended for use with this test method (see Table 2), only molybdenum-98 (ruthenium) and selenium-82 (krypton) have isobaric elemental interferences. If alternative analytical isotopes having higher natural abundance are selected in order to achieve greater sensitivity, an isobaric interference may occur. All data obtained under such conditions must be corrected by measuring the signal from another isotope of the interfering element and subtracting the appropriate signal ratio from the isotope of interest. A record of this correction process should be included with the report of the data. It should be noted that such corrections will only be as accurate as the accuracy of the isotope ratio used in the elemental equation for data calculations. Relevant isotope ratios and instrument bias factors should be established prior to the application of any corrections.

TABLE 2 Recommended Analytical Isotopes and Additional Masses That Are Recommended To Be Monitored

Isotope[A]	Element of Interest
27	Aluminum
121, 123	Antimony
75	Arsenic
135, 137	Barium
9	Beryllium
106, 108, 111, 114	Cadmium
52, 53	Chromium
59	Cobalt
63, 65	Copper
206, 207, 208	Lead
55	Manganese
95, 97, 98	Molybdenum
60, 62	Nickel
77, 82	Selenium
107, 109	Silver
203, 205	Thallium
232	Thorium
238	Uranium
51	Vanadium
66, 67, 68	Zinc
83	Krypton
99	Ruthenium
105	Palladium
118	Tin

[A] Isotopes recommended for analytical determination are underlined. These masses were recommended and are reflected in the precision and bias data. Alternate masses may be used but interferences must be documented.

6.1.2 *Abundance Sensitivity*—Abundance sensitivity is a property defining the degree to which the wings of a mass peak contribute to adjacent masses. The abundance sensitivity is affected by ion energy and quadrupole operating pressure. Wing overlap interferences may result when a small ion peak is being measured adjacent to a large one. The potential for these interferences should be recognized and the spectrometer resolution adjusted to minimize them.

6.1.3 *Isobaric Polyatomic Ion Interferences*—Isobaric polyatomic ion interferences are caused by ions consisting of more than one atom that have the same nominal mass-to-charge ratio as the isotope of interest, and which cannot be resolved by the mass spectrometer in use. These ions are commonly formed in the plasma or interface system from support gases or sample components. Most of the common interferences have been identified, and these are listed in Table 3 together with the method elements affected. Such interferences must be recognized, and when they cannot be avoided by the selection of an alternative analytical isotope, appropriate corrections must be made to the data. Equations for the correction of data should be established at the time of the analytical run sequence as the polyatomic ion interferences will be highly dependent on the sample matrix and chosen instrument conditions.

6.1.4 *Physical Interferences*—Physical interferences are associated with the physical processes that govern the transport of the sample into the plasma, sample conversion processes in the plasma, and the transmission of ions through the plasma—mass spectrometer interface. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the

TABLE 3 Common Molecular Ion Interferences

Molecular Ion	Mass	Element Interference[A]
	Background Molecular Ions	
NH^+	15	. . .
OH^+	17	. . .
OH_2^+	18	. . .
C_2^+	24	. . .
CN^+	26	. . .
CO^+	28	. . .
N_2^+	28	. . .
N_2H^+	29	. . .
NO^+	30	. . .
NOH^+	31	. . .
O_2^+	32	. . .
O_2H^+	33	. . .
$^{36}ArH^+$	37	. . .
$^{38}ArH^+$	39	. . .
$^{40}ArH^+$	41	. . .
CO_2^+	44	. . .
CO_2H^+	45	Sc
ArC^+, ArO^+	52	Cr
ArN^+	54	Cr
$ArNH^+$	55	Mn
ArO^+	56	. . .
$ArOH^+$	57	. . .
$^{40}Ar^{36}Ar^+$	76	Se
$^{40}Ar^{38}Ar^+$	78	Se
$^{40}Ar_2^+$	80	Se
	Matrix Molecular Ions	
Chloride		
$^{35}ClO^+$	51	V
$^{35}ClOH^+$	52	Cr
$^{37}ClO^+$	53	Cr
$^{37}ClOH^+$	54	Cr
$Ar^{35}Cl^+$	75	As
$Ar^{37}Cl^+$	77	Se
Sulphate		
$^{32}SO^+$	48	. . .
$^{32}SOH^+$	49	. . .
$^{34}SO^+$	50	V, Cr
$^{34}SOH^+$	51	V
SO_2^+, S_2^+	64	Zn
$Ar^{32}S^+$	72	. . .
$Ar^{34}S^+$	74	. . .
Phosphate		
PO^+	47	. . .
POH^+	48	. . .
PO_2^+	63	Cu
ArP^+	71	. . .
Group I, II Metals		
$ArNa^+$	63	Cu
ArK^+	79	. . .
$ArCa^+$	80	. . .
Matrix Oxides[B]		
TiO	62 to 66	Ni, Cu, Zn
ZrO	106 to 112	Ag, Cd
MoO	108 to 116	Cd

[A] Method elements or internal standards affected by molecular ions.

[B] Oxide interferences will normally be very small and will only impact the method elements when present at relatively high concentrations. Some examples of matrix oxides are listed of which the analyst should be aware. It is recommended that Ti and Zr isotopes be monitored if samples are likely to contain high levels of these elements. Mo is monitored as a method analyte.

nebulizer (for example, viscosity effects), at the point of aerosol formation and transport to the plasma (for example, surface tension), or during excitation and ionization processes within the plasma itself. High levels of dissolved solids in the sample may contribute deposits of material on the extraction, or skimmer cones, or both, reducing the effective diameter of the orifices and, therefore, ion transmission. Dissolved solids levels not exceeding 0.2 % (w/v) have been recommended to reduce such effects. Internal standardization may be effectively used to compensate for many physical interference effects. Internal standards should have similar analytical behavior to the elements being determined.

6.1.5 *Memory Interferences*—Memory interferences result when isotopes of elements in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the sampler and skimmer cones, and from the buildup of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank consisting of HNO_3 (1+49) in water between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element should be estimated prior to analysis. This may be achieved by aspirating a standard containing elements corresponding to ten times the upper end of the linear range for a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of ten of the method detection limit should be noted. Memory interferences may also be assessed within an analytical run by using a minimum of three replicate integrations for data acquisition. If the integrated signal values drop consecutively, the analyst should be alerted to the possibility of a memory effect, and should examine the analyte concentration in the previous sample to identify if this was high. If a memory interference is suspected, the sample should be re-analyzed after a long rinse period.

7. Apparatus

7.1 *Inductively Coupled Plasma-Mass Spectrometer*—Instrument capable of scanning the mass range 5 to 250 amu with a minimum resolution capability of 1 amu peak width at 5 % peak height. Instrument may be fitted with a conventional or extended dynamic range detection system. See manufacturers instruction manual for installation and operation.

8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that reagents shall conform to the specifications of the committee on analytical reagents of the American Chemical Society,[4] where such specifications are available. The high sensitivity of inductively coupled plasma—mass spectrometry may require reagents of higher purity. Stock standard solutions are prepared from high-purity metals, oxides, or non-hydroscopic reagent grade salts using Type I, II, or III reagent water and ultrapure acids. Other grades may be used provided it is first ascertained that the reagent is of sufficient

---

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

purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Type I, II, or III of Specification D 1193. It is the analyst's responsibility to insure that water is free of interferences.

8.3 *Argon*—High purity grade (99.99 %).

8.4 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl), ultrapure or equivalent.

8.5 *Hydrochloric Acid* (1+1)—Add one volume of hydrochloric acid (sp gr 1.19) to 1 volume of water.

8.6 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO_3), ultrapure or equivalent.

8.7 *Nitric Acid* (1+1)—Add one volume of nitric acid (sp gr 1.42) to 1 volume of water.

8.8 *Nitric Acid* (1+49)—Add one volume of nitric acid (sp gr 1.42) to 49 volumes of water.

8.9 *Nitric Acid* (1+99)—Add one volume of nitric acid (sp gr 1.42) to 99 volumes of water.

8.10 *Stock Solutions*—Preparation procedures for stock solutions of each element are listed in Table 4.

8.11 *Ammonium Hydroxide* (sp gr 0.902)—Concentrated ammonium hydroxide (NH_4OH), ultrapure or equivalent.

8.12 *Mixed Standard Solutions*—Prepare mixed standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks (see Note 1). Prior to preparing mixed standard solutions, each stock solution needs to be analyzed separately to determine possible interferences on the other analytes or the presence of impurities. Care needs to be taken when preparing the mixed standard solutions to ensure that the elements are compatible and stable.

TABLE 4 Preparation of Metal Stock Solutions[A]

Element or Compound	Weight, g	Solvent
Al	0.1000	10 mL of HCl (sp gr 1.19) + 2 mL of HNO_3 (sp gr 1.42)
Sb	0.1000	0.5 mL of HCl (sp gr 1.19) + 2 mL of HNO_3 (1+1)
As_2O_3	0.1320	1 mL of NH_4OH (sp gr 0.902) + 50 mL of H_2O
$BaCO_3$	0.1437	2 mL of HNO_3 (sp gr 1.42) + 10 mL of H_2O
$BeSO_4 \cdot 4H_2O$	1.9650	50 mL of H_2O, add 1 mL of HNO_3 (sp gr 1.42)
Bi_2O_3	0.1115	5 mL of HNO_3 (sp gr 1.42)
Cd	0.1000	5 mL of HNO_3 (1+1)
CrO_3	0.1923	1 mL of HNO_3 (sp 1.42) + 10 mL H_2O
Co	0.1000	5 mL of HNO_3 (1+1)
Cu	0.1000	5 mL of HNO_3 (1+1)
In	0.1000	10 mL of HNO_3 (1+1)
$PbNO_3$	0.1599	5 mL of HNO_3 (1+1)
MgO	0.1658	10 mL of HNO_3 (1+1)
Mn	0.1000	5 mL of HNO_3 (1+1)
MoO_3	0.1500	1 mL of NH_4OH (sp gr 0.902) + 10 mL of H_2O
Ni	0.1000	5 mL of HNO_3 (sp gr 1.42)
Sc_2O_3	0.1534	5 mL of HNO_3 (1+1)
SeO_2	0.1405	20 mL of H_2O
Ag	0.1000	5 mL of HNO_3 (1+1)
Tb_4O_7	0.1176	5 mL of HNO_3 (sp gr 1.42)
$TlNO_3$	0.1303	1 mL of HNO_3 (sp gr 1.42) + 10 mL of H_2O
$Th(NO_3)_4 \cdot 4H_2O$	0.2380	20 mL of H_2O
$UO_2(NO_3)_2 \cdot 6H_2O$	0.2110	20 mL of H_2O
V	0.1000	5 mL of HNO_2 (1+1)
Y_2O_3	0.1270	5 mL of HNO_3 (1+1)
Zn	0.1000	5 mL of HNO_3 (1+1)

[A] Metal stock solutions, 1.00 mL = 1000 µg of metal. Dissolve the listed weights of each metal or compound as specified in Table 4, then dilute to 100 mL with water. The metals may require heat to increase rate of dissolution. Commercially available standards may be used. Alternate salts or oxides may also be used.

NOTE 1—Mixed calibration standards will vary, depending on the number of elements being determined. Commercially prepared mixed calibration standards of appropriate quality may be used. An example of mixed calibration standards for 20 elements is as follows:

Mixed Standard Solution I		Mixed Standard Solution II
Aluminum	Manganese	Barium
Antimony	Molybdenum	Silver
Arsenic	Nickel	
Beryllium	Selenium	
Cadmium	Thallium	
Chromium	Thorium	
Cobalt	Uranium	
Copper	Vanadium	
Lead	Zinc	

Prepare multi-element mixed standard solutions I and II (1 mL = 10 µg) by pipeting 1.00 mL of each single element stock solution (see Table 4) onto a 100 mL volumetric flask. Add 50 mL of HNO_3 (1+99) and dilute to 100 mL with HNO_3 (1+99).

8.13 *Reagent Blank*—This solution must contain all the reagents and be the same volume as used in the processing of the samples. Carry reagent blank through the complete procedure. Reagent blank must contain the same acid concentration in the final solution as the sample solution used for analysis.

8.14 *Internal Standards*—Internal standards are recommended in all analyses to correct for instrument drift and physical interferences. A list of acceptable internal standards is provided in Table 5. For full mass range scans use a minimum of three internal standards with the use of five suggested. Add internal standards to blanks, samples and standards in a like manner. A concentration of 100 µg/L of each internal standard is recommended.

9. Hazards

9.1 The toxicity or carcinogenicity of each reagent used in this test method has not been precisely defined; however, each chemical should be treated as a potential health hazard. Adequate precautions should be taken to minimize exposure of personnel to chemicals used in this test method.

10. Sampling

10.1 Collect the samples in accordance with the applicable standards, Practice D 1066, Specification D 1192, or Practices D 3370.

10.2 Preserve the samples at the time of collection by immediately adding nitric acid (sp gr 1.42) to adjust the pH to 2. Normally, 2 mL of HNO_3 (sp gr 1.42) is required per

TABLE 5 Internal Standards and Limitations of Use

Internal Standard	Mass	Possible Limitation
Lithium	6	May be present in samples
Scandium[A]	45	Polyatomic ion interference
Yttrium[A]	89	May be present in samples
Rhodium	103	. . .
Indium[A]	115	Isobaric interference by Sn
Tarbium[A]	159	. . .
Holmium	165	. . .
Lutetium	175	. . .
Bismuth[A]	209	May be present in samples

[A] Internal standards recommended for use with this test method. It is also recommended when analyzing a new sample matrix that a scan for the presence of internal standards be performed.

litre of sample. If only dissolved elements are to be determined, filter the sample through a 0.45-µm membrane filter before acidification (see Note 2).

NOTE 2—Depending on the manufacturer, some filters have been found to be contaminated to various degrees with heavy metals. Care should be exercised in selecting a source of these filters. A good practice is to wash the filters first with HNO_3 (1+99) and then with 50 mL of the sample before filtering.

11. Calibration and Standardization

11.1 Calibrate the instrument for the elements chosen over a suitable concentration range by atomizing the calibration blank and mixed standard solutions and recording their concentrations and signal intensities. It is recommended that a minimum of three standards and a blank be used for calibration with one of the standards at three to five times the elements' MDL. It is recommended that the calibration blank and standards be matrix matched with the same acid concentration contained in the samples. Analyze appropriate reference solutions to validate the calibration of the instrument before proceeding to the sample analysis.

12. Procedure

12.1 To determine dissolved elements, add 1 mL of concentrated HNO_3 (sp gr 1.42) to 100 mL of filtered, acid-preserved sample. Proceed with 12.3.

12.2 When determining total-recoverable elements, use 100 mL of a well mixed, acid-preserved sample appropriate for the expected level of elements containing not more than 0.25 % (w/v) total solids.

12.2.1 Transfer the sample to a 125 mL (or larger) beaker or flask and add 2 mL of HNO_3 (1+1) and 1 mL HCl (1+1) and heat on a steam bath or hot plate until the volume has been reduced to near 25 mL, making certain the sample does not boil. Cool the sample, and if necessary, filter or let insoluble material settle to avoid clogging of the nebulizer. Adjust to original sample volume. To determine total-recoverable elements, proceed with 12.3. This method is suitable for the determination of silver in aqueous samples containing concentrations up to 0.1 mg/L. For the analysis of samples containing higher concentrations of silver, succeeding smaller volume, well mixed sample aliquots must be prepared until the analysis solution contains <0.1 mg/L silver.

12.3 Atomize each solution and record signal's intensity or calculated concentration for each mass of interest. Atomize a rinse blank consisting of HNO_3 (1+49) in water between samples.

12.4 Minimum quality control requirements for this method include: initial demonstration of method performance, monitoring of internal standard area counts in each sample (area of internal standard should be within 60–125 % of area in calibration blank), analysis of one reagent blank with each set of samples as continuing check on sample contamination, analysis of a quality control sample with each set of samples as a continuing check on method reference sample recovery, and analysis of calibration check standard every ten analyses as a continuing check on calibration curve (measured values should not exceed ±10 % of concentration).

12.4.1 Demonstrate initial, and continuing, method performance every six months by digesting seven spiked reagent water samples at two through five times estimated detection limit to determine method detection limits (MDL).

12.4.2 Determine detection limits annually or whenever a significant change in background or instrument response is expected.

$$MOL = (t) \times (s)$$

where:

t = students' t value for a 99 % confidence level and with $n-1$ degrees of freedom (t = 3.14 for seven replicates), and

s = standard deviation of the replicate analyses.

13. Calculation

13.1 Elemental equations recommended for sample data calculations are listed in Table 6.

13.2 Reagent blanks should be subtracted as appropriate (see 9.13) from the samples. This subtraction is particularly important for digested samples requiring large quantities of acids to complete the digestion (see Note 3).

TABLE 6 Recommended Elemental Equations for Data Calculation

Element	Elemental Equation[A]	Note
Al	$(1.000)\ (^{27}C)$	. . .
Sb	$(1.000)\ (^{121}C)$	. . .
As	$(1.000)\ (^{75}C) - (3.127)\ [(^{77}C) - (0.815)\ (^{82}C)]$	B
Ba	$(1.000)\ (^{137}C)$	. . .
Be	$(1.000)\ (^{9}C)$	. . .
Cd	$(1.000)\ (^{111}C) - (1.073)\ [(^{108}C) - (0.712)\ (^{106}C)]$	C
Cr	$(1.000)\ (^{52}C)$	D
Co	$(1.000)\ (^{59}C)$	. . .
Cu	$(1.000)\ (^{63}C)$	. . .
Pb	$(1.000)\ (^{206}C) + (1.000)\ (^{207}C) + (1.000)\ (^{208}C)$	E
Mn	$(1.000)\ (^{55}C)$	. . .
Mo	$(1.000)\ (^{98}C) - (0.146)\ (^{99}C)$	F
Ni	$(1.000)\ (^{60}C)$	. . .
Se	$(1.000)\ (^{82}C)$	G
Ag	$(1.000)\ (^{107}C)$	. . .
Tl	$(1.000)\ (^{205}C)$	. . .
Th	$(1.000)\ (^{232}C)$	. . .
U	$(1.000)\ (^{238}C)$	. . .
V	$(1.000)\ (^{51}C) - (3.127)\ [(^{53}C) - (0.113)\ (^{52}C)]$	H
Zn	$(1.000)\ (^{66}C)$	. . .
Kr	$(1.000)\ (^{83})$	. . .
Pd	$(1.000)\ (^{106})$	. . .
Ru	$(1.000)\ (^{99})$	. . .
Sn	$(1.000)\ (^{118})$	. . .
Bi	$(1.000)\ (^{209}C)$	I
In	$(1.000)\ (^{115}C) - (0.016)\ (^{118}C)$	J
Sc	$(1.0000)\ (^{45}C)$	K
Tb	$(1.000)\ (^{159}C)$	. . .
Y	$(1.000)\ (^{89}C)$	I

[A] C = calibration blank subtracted counts at specified mass.

[B] Correction for chloride interference with adjustment for Se77. ArCl 75/77 ratio may be determined from the reagent blank.

[C] Correction for MoO interference. An additional isobaric elemental correction should be made if palladium is present.

[D] In 0.4 % v/v HCl, the background from ClOH will normally be small. However the contribution may be estimated from the reagent blank.

[E] Allowance for isotopic variability of lead isotopes.

[F] Isobaric elemental correction for ruthenium.

[G] Some argon supplies contain krypton as an impurity. Selenium is corrected for Kr82 by background subtraction.

[H] Correction for chloride interference with adjustment for Cr53. ClO 51/53 ratio may be determined from the reagent blank.

[I] May be present in environmental samples.

[J] Isobaric elemental correction for tin.

[K] Polyatomic ion interference.

TABLE 7 Regression Equations for Bias and Precision, µg/L, Reagent Water

Element	Applicable Range	Bias	Overall Precision	Single Analyst Precision
Antimony	2.80 to 100	$X = 0.999C + 0.04$	$S_t = 0.013X + 0.61$	$S_o = 0.022X + 0.20$
Arsenic	8.00 to 200	$X = 1.013C + 0.50$	$S_t = 0.031X + 2.74$	$S_o = 0.007X + 2.95$
Barium	8.01 to 200	$X = 1.001C - 0.36$	$S_t = 0.039X + 0.31$	$S_o = 0.024X + 0.25$
Beryllium	2.80 to 100	$X = 1.056C + 0.32$	$S_t = 0.067X + 0.55$	$S_o = 0.038X + 0.11$
Cadmium	4.00 to 100	$X = 1.007C + 0.07$	$S_t = 0.041X + 0.19$	$S_o = 0.022X + 0.10$
Chromium	8.00 to 200	$X = 1.017C + 0.62$	$S_t = 0.066X + 0.48$	$S_o = 0.026X + 1.25$
Cobalt	0.80 to 101	$X = 0.977C + 0.01$	$S_t = 0.28X + 0.06$	$S_o = 0.027X + 0.02$
Copper	4.01 to 100	$X = 1.003C - 0.05$	$S_t = 0.037X + 0.64$	$S_o = 0.016X + 0.51$
Lead	4.00 to 100	$X = 1.043C - 0.31$	$S_t = 0.064X + 1.43$	$S_o = 3.42$
Manganese	8.00 to 200	$X = 0.983C + 0.02$	$S_t = 0.026X + 0.11$	$S_o = 0.027X + 0.06$
Molybdenum	2.80 to 100	$X = 1.012C + 0.20$	$S_t = 0.032X + 0.22$	$S_o = 0.021X + 0.09$
Nickel	4.00 to 100	$X = 1.000C + 0.12$	$S_t = 0.051X + 0.31$	$S_o = 0.017X + 0.40$
Selenium	32.00 to 200	$X = 1.036C - 0.06$	$S_t = 0.051X + 3.24$	$S_o = 0.061X - 0.64$
Silver	0.80 to 200	$X = 0.917C + 0.26$	$S_t = 0.196X + 0.09$	$S_o = 0.053X + 0.08$
Thallium	2.80 to 100	$X = 0.984C + 0.08$	$S_t = 0.035X + 0.09$	$S_o = 0.027X + 0.13$
Thorium	0.80 to 100	$X = 1.0913 + 0.08$	$S_t = 0.036X + 0.13$	$S_o = 0.025X + 0.07$
Uranium	0.80 to 100	$X = 1.026C - 0.02$	$S_t = 0.048X + 0.02$	$S_o = 0.027X + 0.05$
Zinc	8.00 to 200	$X = 1.042C + 0.87$	$S_t = 0.041X + 2.60$	$S_o = 0.030X + 1.42$

TABLE 8 Regression Equations for Bias and Precision, µg/L, Drinking Water

Element	Applicable Range	Bias	Overall Precision	Single Analyst Precision
Antimony	2.80 to 100	$X = 0.983C + 0.03$	$S_t = 0.049X + 0.19$	$S_o = 0.026X + 0.08$
Arsenic	8.00 to 200	$X = 0.993C + 0.57$	$S_t = 0.018X + 2.55$	$S_o = 0.031X + 1.65$
Barium	8.01 to 200	$X = 0.995C - 0.37$	$S_t = 0.045X + 0.97$	$S_o = 0.040X + 0.72$
Beryllium	2.80 to 100	$X = 1.055C + 0.20$	$S_t = 0.057X + 0.28$	$S_o = 0.016X + 0.25$
Cadmium	4.00 to 100	$X = 0.985C + 0.10$	$S_t = 0.031X + 0.65$	$S_o = 0.021X + 0.61$
Chromium	8.00 to 200	$X = 0.990C + 1.45$	$S_t = 0.015X + 2.19$	$S_o = 2.18$
Cobalt	0.80 to 101	$X = 0.964C + 0.06$	$S_t = 0.19X + 0.32$	$S_o = 0.014X + 0.30$
Copper	4.01 to 100	$X = 0.976C - 0.38$	$S_t = 0.063X + 0.86$	$S_o = 0.029X + 0.86$
Lead	4.00 to 100	$X = 1.032C - 0.30$	$S_t = 0.015X + 1.06$	$S_o = 0.011X + 1.13$
Molybdenum	2.80 to 100	$X = 1.013C + 0.07$	$S_t = 0.037X + 0.17$	$S_o = 0.035X + 0.20$
Nickel	4.00 to 100	$X = 0.953C - 0.19$	$S_t = 0.046X + 0.56$	$S_o = 0.023X + 0.91$
Selenium	32.00 to 200	$X = 1.022C + 0.14$	$S_t = 0.056X + 2.10$	$S_o = 0.040X + 2.15$
Thallium	2.80 to 100	$X = 1.010C + 0.01$	$S_t = 0.040X + 0.21$	$S_o = 0.039X + 0.02$
Uranium	0.80 to 100	$X = 1.026C - 0.04$	$S_t = 0.044X + 0.11$	$S_o = 0.022X + 0.07$
Vanadium	32.00 to 200	$X = 1.022C + 0.30$	$S_t = 0.023X + 1.45$	$S_o = 0.023X + 1.38$

NOTE 3—Reagent blank concentrations if the levels can influence the sample results.

13.3 If dilutions were required, apply the appropriate dilution factor to sample values.

13.4 Report results in the calibration concentration units.

14. Precision and Bias[5]

14.1 The precision and bias data for this test method are based on a joint interlaboratory method validation study conducted by the U.S. Environmental Protection Agency and the Association of Official Analytical Chemists.[6]

14.2 The test design of the study meets the requirements of Practice D 2777 for elements listed in this test method with the following exceptions. Thorium in drinking water and vanadium in ground and reagent water did not meet the requirements of 10.3 in Practice D 2777 and are deleted in the test method. In addition, the following elements did not meet the requirements of 10.5 of Practice D 2777 for the concentration levels (in µg/L) tested: Aluminum in reagent (8) and drinking water (12), antimony in ground water (2.0 and 100), manganese in ground (0.8 and 1.2) and drinking water (1.2), molybdenum in ground water (2.8), silver, in ground (0.8 and 2.2) and drinking water (0.8 and 1.2), and zinc in drinking water (8).

14.2.1 The regression equations are based on the results of 13 laboratories for 20 elements tested at six levels, they are outlined in Tables 7, 8, and 9 for reagent water, drinking water, and ground water, respectively.

14.2.2 Type I water was specified for this round robin.

14.2.3 These data may not apply to waters of other matrices; therefore, it is the responsibility of the analyst to ensure the validity of the test method in a particular matrix.

14.2.4 It is the user's responsibility to ensure the validity of precision and bias outside the joint interlaboratory method validation study ranges.

15. Keywords

15.1 elements; mass spectrometry; water

---

[5] Supporting data are available from ASTM Headquarters. Request RR:D19-1157.

[6] Longbottom, J. E., et al., "Determination of Trace Elements in Water by Inductively Coupled Plasma-Mass Spectrometry: Collaborative Study," *Journal of AOAC, International 77*, 1994, pp. 1004–1023.

TABLE 9 Regression Equations for Bias and Precision, µg/L, Ground Water

Element	Applicable Range	Bias	Overall Precision	Single Analyst Precision
Aluminum	8.00 to 200	$X = 0.946C + 2.20$	$S_t = 0.169X + 6.22$	$S_o = 0.172X + 0.75$
Arsenic	8.00 to 200	$X = 0.949C + 0.91$	$S_t = 0.048X + 4.52$	$S_o = 0.059X + 4.29$
Barium	8.01 to 200	$X = 1.055C - 0.21$	$S_t = 0.020X + 2.05$	$S_o = 0.014X + 2.08$
Beryllium	2.80 to 100	$X = 1.049C + 0.08$	$S_t = 0.084X + 0.16$	$S_o = 0.043X + 0.06$
Cadmium	4.00 to 100	$X = 0.944C + 0.11$	$S_t = 0.017X + 1.09$	$S_o = 0.029X + 0.01$
Chromium	8.00 to 200	$X = 1.026C + 0.89$	$S_t = 0.067X + 0.68$	$S_o = 0.068X - 0.37$
Cobalt	0.80 to 101	$X = 0.989C - 0.01$	$S_t = 0.057X + 0.09$	$S_o = 0.012X + 0.40$
Copper	4.01 to 100	$X = 0.977C - 0.01$	$S_t = 0.073X + 0.92$	$S_o = 0.077X + 0.35$
Lead	4.00 to 100	$X = 1.012C + 0.15$	$S_t = 0.048X + 1.27$	$S_o = 1.78$
Nickel	4.00 to 100	$X = 1.022C - 0.66$	$S_t = 0.091X + 2.03$	$S_o = 0.008X + 2.75$
Selenium	32.00 to 200	$X = 1.045C - 0.83$	$S_t = 0.037X + 2.97$	$S_o = 0.058X + 1.02$
Thallium	2.80 to 100	$X = 1.023C - 0.06$	$S_t = 0.056X + 0.04$	$S_o = 0.049X - 0.06$
Thorium	0.80 to 100	$X = 1.019C - 0.03$	$S_t = 0.041X + 0.13$	$S_o = 0.027X + 0.04$
Uranium	0.80 to 100	$X = 1.058C - 0.06$	$S_t = 0.039X + 0.17$	$S_o = 0.028X + 0.16$
Zinc	8.00 to 200	$X = 0.962C + 0.07$	$S_t = 0.093X + 0.92$	$S_o = 0.069X + 1.55$

APPENDIX

(Nonmandatory Information)

X1. PRECISION AND BIAS

X1.1 The following regression expressions in Table X1.1 are based on the measured values, X, S_t, and S_o that were derived from data of the joint interlaboratory method validation study conducted by the U.S. Environmental Protection Agency and the Association of Official Analytical Chemists,[6] some of which do not meet the requirements of 10.5 of Practice D 2777, as noted in 14.2 of this test method and were therefore are not included in Tables 7 through 9 in this test method.

TABLE X1.1 Regression Equations for Bias and Precision, µg/L

Element	Applicable Range	Bias	Overall Precision	Single Analyst Precision
		Reagent Water		
Aluminum	(8.00–200)	$X = 0.992C + 1.19$	$S_t = 0.056X + 2.59$	$S_o = 0.042X + 1.27$
		Drinking Water		
Aluminum	(8.00–200)	$X = 0.954C + 2.38$	$S_t = 7.70$	$S_o = 0.013X + 6.17$
Manganese	(8.00–200)	$X = 0.989C + 0.10$	$S_t = 0.047X + 0.29$	$S_o = 0.021X + 0.40$
Silver	(0.80–200)	$X = 0.888C + 0.09$	$S_t = 0.186X + 0.17$	$S_o = 0.164X + 0.18$
Zinc	(8.00–200)	$X = 0.943C + 2.54$	$S_t = 0.048X + 5.27$	$S_o = 0.004X + 5.66$
		Ground Water		
Antimony	(2.80–100)	$X = 1.003C + 0.01$	$S_t = 0.059X + 0.04$	$S_o = 0.058X + 0.02$
Manganese	(8.00–200)	$X = 0.954C - 0.16$	$S_t = 0.103X + 0.14$	$S_o = 0.025X + 0.09$
Molybdenum	(2.80–100)	$X = 1.032C - 0.09$	$S_t = 0.55X + 0.43$	$S_o = 0.042X + 0.27$
Silver	(0.80–200)	$X = 0.858C - 0.00$	$S_t = 0.169X + 0.14$	$S_o = 0.120X - 0.01$

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 D5865: Standard Test Method for Gross Calorific Value of Coal and Coke

CFR Section(s): 40 CFR 60.45(f)(5)(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 5865 – 98a

Standard Test Method for Gross Calorific Value of Coal and Coke[1]

This standard is issued under the fixed designation D 5865; 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 pertains to the determination of the gross calorific value of coal and coke by either an isoperibol or adiabatic bomb calorimeter.

1.2 The values stated in SI units are 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.* Specific hazard statements are given in 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 388 Classification of Coals by Rank[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 Method for Total Sulfur in the Analysis Sample of Coal and Coke[2]

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

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

D 5142 Test Methods for the Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures[2]

E 1 Specification for ASTM Thermometers[4]

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

E 178 Practice for Dealing with Outlying Observations[6]

3. Terminology

3.1 *Definitions:*

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

3.1.2 *calorimeter*—a device for measuring calorific value consisting of a bomb, its contents, a vessel for holding the bomb, temperature measuring devices, ignition leads, water, stirrer, and a jacket maintained at specified temperature conditions.

3.1.3 *adiabatic calorimeter*—a calorimeter which has a jacket temperature adjusted to follow the calorimeter temperature so as to maintain zero thermal head.

3.1.4 *isoperibol calorimeter*—a calorimeter which has a jacket of uniform and constant temperature.

3.1.5 *gross calorific value (gross heat of combustion at constant volume),* Q_v (gross)—the heat produced by complete combustion of a substance at constant volume with all water formed condensed to a liquid.

3.1.6 *heat of formation*—the change in heat content resulting from the formation of 1 mole of a substance from its elements at constant pressure.

3.1.7 *net calorific value (net heat of combustion at constant pressure),* Q_p (net)—the heat produced by combustion of a substance at a constant pressure of 0.1 MPa (1 atm), with any water formed remaining as vapor.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *corrected temperature rise*—the calorimeter temperature change caused by the process that occurs inside the bomb corrected for various effects.

3.2.2 *heat capacity*—the energy required to raise the temperature of the calorimeter one arbitrary unit.

NOTE 1—The heat capacity can also be referred to as the energy equivalent or water equivalent of the calorimeter.

4. Summary of Test Method

4.1 The heat capacity of the calorimeter is determined by burning a specified mass of benzoic acid in oxygen. A comparable amount of the analysis sample is burned under the same conditions in the calorimeter. The calorific value of the analysis sample is computed by multiplying the corrected temperature rise, adjusted for extraneous heat effects, by the

---

[1] This document 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 Nov. 10, 1999. Published April 1999. Originally published as D 5865 – 95. Last previous edition D 5865 – 98.

[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 14.04.

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

heat capacity and dividing by the mass of the sample.

5. Significance and Use

5.1 The gross calorific value can be used to compute the total calorific content of the quantity of coal or coke represented by the sample for payment purposes.

5.2 The gross calorific value can be used for computing the calorific value versus sulfur content to determine whether the coal meets regulatory requirements for industrial fuels.

5.3 The gross calorific value can be used to evaluate the effectiveness of beneficiation processes.

5.4 The gross calorific value can be required to classify coals according to Classification D 388.

6. Apparatus and Facilities

6.1 *Test Area*—An area free from drafts, shielded from direct sunlight and other radiation sources. Thermostatic control of room temperature and controlled relative humidity are desirable.

6.2 *Combustion Bomb*—Constructed of materials that are not affected by the combustion process or the products formed 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. The bomb shall be capable of withstanding a hydrostatic pressure test to 20 MPa (3000 psig) at room temperature without stressing any part beyond its specified elastic limit.

6.3 *Balance*—A laboratory balance capable of weighing the analysis sample to the nearest 0.0001 g. The balance shall be checked weekly, at a minimum, for accuracy.

6.4 *Calorimeter Vessel*—Made of metal with a tarnish-resistant coating, with all outer surfaces highly polished. Its size shall be such that the bomb is completely immersed in water during a determination. A stirrer shall be provided for uniform mixing of the water. The immersed portion of the stirrer shall be accessible to the outside through a coupler of low thermal conductivity. The stirrer speed shall remain constant to minimize any temperature variations due to stirring. Continuous stirring for 10 min shall not raise the calorimeter temperature more than 0.01°C when starting with identical temperatures in the calorimeter, test area and jacket. For calorimeters having a bucket it can be a separate component or integral component of the bomb. The vessel shall be of such construction that the environment of the calorimeter's entire outer boundaries can be maintained at a uniform temperature.

6.5 *Jacket*—A container with the inner perimeter maintained at constant temperature ±0.1°C (isoperibol) or at the same temperature ±0.1°C as the calorimeter vessel (adiabatic) during the test. To minimize convection, the sides, top and bottom of the calorimeter vessel shall not be more than 10 mm from the inner surface of the jacket. Mechanical supports for the calorimeter vessel shall be of low thermal conductivity.

6.6 *Thermometers*:

6.6.1 *Automated Calorimeters*—Platinum resistance or linear thermistor thermometers shall be capable of measuring to the nearest 0.0001°C. Thermometer calibration shall be traceable to a recognized certifying agency.

6.6.2 *Manual Calorimeters*:

6.6.2.1 *Platinum resistance* or *linear thermistor thermometers*, shall be capable of measuring to the nearest 0.0001°C. Thermometer calibration shall be traceable to a recognized certifying agency.

6.6.2.2 *Liquid-in-Glass Thermometers*—Conforming to the requirements for thermometers 56C, 116C, or 117C as prescribed in Specification E 1. Thermometers 56C shall be calibrated at intervals no larger than 2.0°C over the entire graduated scale. The maximum difference in correction between any two calibration points shall be no more than 0.02°C. Thermometers 116C and 117C shall be calibrated at intervals no larger than 0.5°C over the entire graduated scale. The maximum difference in correction between any two calibration points shall not be more than 0.02°C.

6.6.2.3 *Beckman Differential Thermometer*—(Glass enclosed scale, adjustable), having a range of approximately 6°C in 0.01°C subdivisions reading upward and conforming to the requirements for Thermometer 115C, as prescribed in Specification E 1. The thermometer shall be calibrated at intervals no larger than 1°C over the entire graduated scale. The maximum difference in the correction between any two calibration points shall be less than 0.02°C.

6.6.2.4 *Thermometer Accessories*—A magnifier is required for reading liquid-in-glass thermometers to one tenth of the smallest scale division. The magnifier shall have a lens and holder designed so as to minimize errors as a result of parallax.

6.7 *Sample Holder*—An open crucible of platinum, quartz, or base metal alloy. Before use in the calorimeter, heat treat base metal crucibles for a minimum of 4 h at 500°C to ensure the crucible surface is completely oxidized. Base metal alloy crucibles are acceptable, if after three preliminary firings, the weight does not change by more than 0.0001 g.

6.8 *Ignition Fuse*—Ignition fuse of 100-mm length and 0.16-mm (No. 34 B&S gage) diameter or smaller. Nickel-chromium alloy (Chromel C) alloy, cotton thread, or iron wire are acceptable. Platinum or palladium wire, 0.10-mm diameter (No. 38 B&S gage), can be used provided constant ignition energy is supplied. Use the same type and length (or mass) of ignition fuse for calorific value determinations as used for standardization.

6.9 *Ignition Circuit*—A 6- to 30-V alternating or direct current is required for ignition purposes. A step-down transformer connected to an alternating current circuit, capacitors, or batteries can be used. 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. An ammeter or pilot light can be used in the circuit to indicate when current is flowing.

6.10 *Controller*—For automated calorimeters, capable of charging the bomb; filling the calorimeter vessel; firing the ignition circuit; recording calorimeter temperatures before, during, and after the test; recording the balance weights; and carrying out all necessary corrections and calculations.

6.11 *Crucible Liner*—Quartz fiber or alundum for lining the crucible to promote complete combustion of samples that do not burn completely during the determination of the calorific value.

7. Reagents

7.1 *Reagent Water*—Conforming to conductivity requirements for Type II of Specification D 1193 for preparation of reagents and washing of the bomb interior.

7.2 *Purity of Reagents*—Use reagent grade chemicals conforming to the specification of the Committee on Analytical Reagents of the American Chemical Society in all tests.[7]

7.3 *Benzoic Acid—Standard (C_6H_5COOH)*—Pellets made from benzoic acid available from the National Institute of Standards and Technology (NIST) or benzoic acid calibrated against NIST standard material. The calorific value of benzoic acid, for use in the calibration calculations, shall be traceable to a recognized certificate value.

7.4 *Oxygen*—Manufactured from liquid air, guaranteed to be greater than 99.5 % pure, and free of combustible matter. Oxygen made by the electrolytic process contains small amounts of hydrogen rendering it unfit unless purified by passage over copper oxide at 500°C.

7.5 *Titration Indicator*—Methyl orange, methyl red, or methyl purple for indicating the end point when titrating the acid formed during combustion. The same indicator shall be used for both calibration and calorific value determinations.

7.6 *Standard Solution*—Sodium carbonate (Na_2CO_3) or other suitable standard solution. Dissolve 3.76 g of sodium carbonate, dried for 24 h at 105°C in water, and dilute to 1 L. One millilitre of this solution is equivalent to 4.2 J (1.0 calorie) in the acid titration.

8. Hazards

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

8.1.1 The mass of sample and any combustion aid as well as the pressure of the oxygen admitted to the bomb shall not exceed the bomb manufacturer's specifications.

8.1.2 Inspect the bomb parts carefully after each use. Replace cracked or significantly worn parts. Replace O-rings and valve seats in accordance with manufacturer's instruction. For more details, consult the manufacturer.

8.1.3 Equip the oxygen supply cylinder with an approved type of safety device, such as a relief valve, in addition to the needle valve and pressure gage used in regulating the oxygen feed to the bomb. Valves, gages, and gaskets shall meet industry safety codes. Suitable reducing valves and adapters for 3- to 4-MPa (300- to 500-psig) discharge pressure can be obtained from commercial sources of compressed gas equipment. Check the pressure gage annually for accuracy or after any accidental over pressures that reach maximum gage pressure.

8.1.4 During ignition of a sample, the operator shall not extend any portion of the body over the calorimeter.

8.1.5 Do not fire the bomb if the bomb has been dropped or turned over after loading.

8.1.6 Do not fire the bomb if there is evidence of gas leakage when the bomb is submerged in the calorimeter vessel.

8.1.7 For manually operated calorimeters, the ignition switch shall be depressed only long enough to fire the charge.

9. Sample

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

10. Determination of the Heat Capacity of the Calorimeter

10.1 *Sample*—Weigh 0.8 to 1.2 g of benzoic acid into a sample holder. Record sample weight to the nearest 0.0001 g.

10.2 *Preparation of Bomb*:

10.2.1 Rinse the bomb with water to wet internal seals and surface areas of the bomb or precondition the calorimeter according to the manufacturer's instructions. Add 1.0 mL of water to the bomb before assembly.

10.2.2 Connect a measured fuse in accordance with manufacturer's guidelines.

10.2.3 Assemble the bomb. Admit oxygen to the bomb to a consistent pressure of between 2 and 3 MPa (20 and 30 atm). The same pressure is used for each heat capacity run. Control oxygen flow to the bomb so as not to blow material from the sample holder. If the pressure exceeds the specified pressure, detach the filling connection and exhaust the bomb. Discard the sample.

10.3 *Preparation of Calorimeter*:

10.3.1 Fill the calorimeter vessel with water at a temperature not more than 2°C below room temperature and place the assembled bomb in the calorimeter. Check that no oxygen bubbles are leaking from the bomb. If there is evidence of leakage, remove and exhaust the bomb. Discard the sample.

10.3.2 The mass of water used for each test run shall be $M \pm 0.5$ g where M is a fixed mass of water. Devices used to supply the required mass of water on a volumetric basis shall be adjusted when necessary to compensate for change in the density of water with temperature.

10.3.3 With the calorimeter vessel positioned in the jacket start the stirrers.

10.4 *Temperature Observations Automated Calorimeters*:

10.4.1 *Stabilization*—The calorimeter vessel's temperature shall remain stable over a period of 30 s before firing. The stability shall be ±0.001°C for an adiabatic calorimeters and ±0.001°C/s or less for an isoperibol calorimeter.

10.4.2 *Extrapolation Method*—Fire the charge, record the temperature rise. The test can be terminated when the observed thermal curve matches a thermal curve which allows extrapolation to a final temperature with a maximum uncertainty of ±0.002°C.

10.4.3 *Full Development Method*—Fire the charge and record the temperature rise until the temperature has stabilized for a period of 30 s in accordance with the stability requirements specified in 10.4.1.

10.5 *Temperature Observations Manual Calorimeters*:

10.5.1 When using ASTM Thermometers 56C, estimate all

---

[7] *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.

readings to the nearest 0.002°C. When using ASTM Thermometers 115C, 116C, or 117C, estimate readings to 0.001°C and 25-Ω resistance thermometer readings to the nearest 0.0001 Ω. Tap or vibrate mercury thermometers just before reading to avoid errors caused by mercury sticking to the walls of the capillary.

10.5.2 Allow 5 min for the temperature of the calorimeter vessel to stabilize. Adjust the jacket temperature to match the calorimeter vessel temperature within 0.01°C and maintain for 3 min.

10.5.3 Fire the charge. Record the time as *a* and the temperature as t_a.

10.5.4 For adiabatic calorimeters adjust the jacket temperature to match that of the calorimeter vessel temperature during the period of the rise. Keep the two temperatures as equal as possible during the period of rapid rise. Adjust to within 0.01°C when approaching the final stabilization temperature. Record subsequent readings at intervals no greater than 1 min until three successive readings do not differ by more than ±0.001°C. Record the first reading after the rate of change has stabilized as the final temperature t_c and the time of this reading as *c*. For isoperibol calorimeters, when approaching the final stabilization temperature, record readings until three successive readings do not differ by more than 0.001°C per min. Record the first reading after the rate of change has stabilized as the final temperature as t_c and the time of this reading as *c*.

10.5.5 Open the calorimeter and remove the bomb. Release the pressure at a uniform rate such that the operation will not be less than 1 min. Open the bomb and examine the bomb interior. Discard the test if unburned sample or sooty deposits are found.

10.6 *Thermochemical Corrections (see* Appendix X1*):*

10.6.1 *Acid Correction (see* X1.1*)*—One may use either the titration (10.6.1.1) or calculated titration (10.6.1.2) procedure for coal and coke samples.

10.6.1.1 *Titration Method*—Wash the interior of the bomb with distilled water containing the titration indicator (see 7.5) until the washings are free of acid and combine with the rinse of the capsule. Titrate the washings with the standard solutions (see 7.6) using a titration indicator, or a pH or millivolt meter. The number of millilitres of standard Na_2CO_3 used in the titration shall be taken as *e*1.

10.6.1.2 *Calculated Titration Method*—Each calorimeter system shall be tested at several energy levels with benzoic acid pellets weighing 0.8, 1.0, and 1.2 g. This range corresponds to the optimum energy levels of 5000 through 8000 calories. Two runs shall be made at each weight. Plot millilitres of titrant (*y*) versus temperature rise, degree C (*x*), for each calibration and use linear regression to determine the formula for the line $y = m(x) + b$ (see Fig. 1). The resulting formula for a line is the equation for determining the calculated millilitres of titrant (*e*1). The calculated titrant = $m(x) + b$ where *m* and *b* have been determined by linear regression. The temperature rise (*x*) for each test shall be plotted on the graph to determine the calculated acid correction (*e*1) or determined from the equation $y = mx + b$.

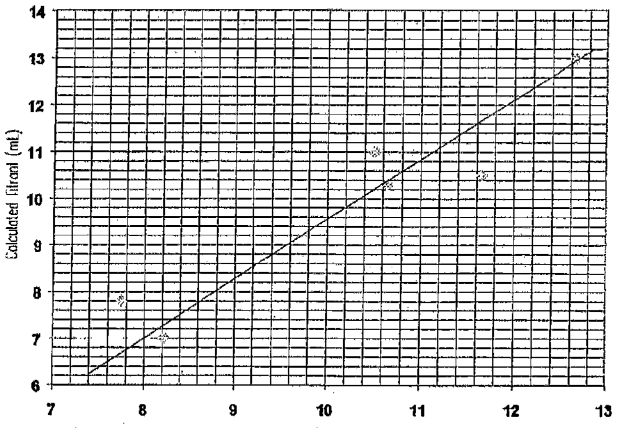


FIG. 1 Titration Versus Temperature Rise

Example:

Sample wt., g	Measured Titration (y)	Temperature Rise (x)
0.7643	7.8	7.7443
0.8104	7.0	8.2188
1.0392	11.0	10.5114
1.0506	10.3	10.6420
1.1539	10.5	11.6584
1.2562	13.0	12.6491

$$y = m(x) + b \qquad (1)$$

Using regression analysis, the above data yield the following data: slope = 1.0826, intercept = −1.1496, and the equation for the millilitres of titrant = $y = 1.0826x - 1.1496$.

With any given temperature rise (*x*), the value *y* (*e*1) may be determined.

NOTE 2—*m* above represents the slope of the line, whereas in other references in this method *m* represents mass.

NOTE 3—Regression analysis to determine the equation for the millilitres of titrant (*e*1) is to be done without forcing the data through zero.

10.6.2 *Fuse Correction (see* X1.3*)*—Determine the fuse correction using one of the two alternatives:

10.6.2.1 Measure the combined pieces of unburned ignition fuse and subtract from the original length to determine the fuse consumed in firing according to Eq 2.

$$e2 = K_l \times l \qquad (2)$$

where:

$e2$ = the correction for the heat of combustion of the firing fuse,
l = the length of fuse consumed during combustion,
K_l = 0.96 J/mm (0.23 cal/mm) for No. 34 B&S gage Chromel C,
K_l = 1.13 J/mm (0.27 cal/mm) for No. 34 B&S gage iron wire, and
K_l = 0.00 J/mm for platinum or palladium wire provided the ignition energy is constant.

or;

10.6.2.2 Weigh the combined pieces of unburned fuse and subtract from the original weight to determine the weight in milligrams of the fuse consumed in firing (m). Remove any ball of oxidized metal from the ends before weighing.

$$e2 = K_m \times m \tag{3}$$

where:

$e2$ = the correction for the heat of combustion of the firing fuse,
m = the weight in mg of fuse consumed during combustion,
K_m = 5.9 J/mg (1.4 cal/mg) for No. 34 B&S gage Chromel C,
K_m = 7.5 J/mg (1.8 cal/mg) for No. 34 B&S gage iron wire, and
K_m = 0.00 J/mg for platinum or palladium wire provided the ignition energy is constant.

When cotton thread is used, employ the correction in J recommended by the instrument manufacturer.

10.7 *Calculation of the Corrected Temperature Rise*—Compute the corrected temperature rise, t, as follows:

$$t = t_c - t_a + C_e + C_r + C_s \tag{4}$$

where:

t = corrected temperature rise, °C;
t_a = initial temperature reading at time of firing;
t_c = final temperature reading;
C_e = thermometer, emergent stem correction (see Eq A1.4);
C_r = radiation correction (see Eq A1.2); and
C_s = thermometer setting correction (see Eq A1.3).

10.7.1 The temperature rise in isoperibol calorimeters require a radiation correction.

10.7.2 Beckman differential thermometers require a setting correction and an emergent stem correction.

10.7.3 Solid-stem ASTM Thermometers 56C do not require emergent stem corrections if all tests are performed within the same 5.5°C interval. If the operating temperature range is beyond this limit, a differential emergent stem correction shall be applied.

10.8 *Calculation of the Heat Capacity*—Calculate the heat capacity (E) of the calorimeter using the following equation:

$$E = [(H_c \times m) + e1 + e2]/t \tag{5}$$

where:

E = the calorimeter heat capacity, J/°C;
H_c = heat of combustion of benzoic acid, as stated in the certificate, J/g;
m = mass of benzoic acid, g;
$e1$ = acid correction from 10.6.1 from either the titration method (10.6.1.1) or the calculated titration (10.6.1.2);
$e2$ = fuse correction from 10.6.2, J; and
t = corrected temperature rise from 10.7,°C.

10.8.1 Using the procedures described in 10.1-10.8 complete a total of ten acceptable test runs. An individual test shall be rejected only if there is evidence of incomplete combustion.

10.8.2 The relative standard deviation of the heat capacity of ten acceptable test runs shall be 0.15 % or less of the average energy equivalent. If after considering the possibility of outliers using criterion established in Practice E 178, this limit is not met, one should review operation of the calorimeter for any assignable cause which should be corrected before repeating the series. Table 1 summarizes a series of heat capacity runs. This table would be applicable regardless of the unit of measure for the heat capacity.

11. Heat Capacity Checks

11.1 The heat capacity value shall be checked a minimum of once a month, after changing any part of the calorimeter, or after changing the oxygen supply. Two procedures are available for heat capacity check: Standard Method and Rolling Average Method.

NOTE 4—Although it is only required to check the heat capacity once a month, this may be inadequate. A more frequent check of heat capacity values is recommended for laboratories making a large number of tests on a daily basis. The frequency of the heat capacity check should be determined to minimize the number of tests that would be affected by an undetected shift in the heat capacity values.

11.2 *Standard Method*:

11.2.1 A single new heat capacity test value shall not differ from the existing heat capacity value by more than ±0.17 %. If this requirement is met, the existing heat capacity value is acceptable. For example: existing heat capacity value is 2402 cal/°C. 2402 cal/°C × 0.0017 = 4.1 cal/°C. If single test value is within 4.1 cal/°C of the 2402 cal/°C value, then the existing heat capacity value is still acceptable.

11.2.2 If the requirements given in 11.2.1 are not met, an additional heat capacity test shall be run. The difference between the two new heat capacity values shall not exceed 0.21 % of the existing heat capacity value. The average of the two new heat capacity values shall not differ from the existing heat capacity value by more than ±0.13 %. If this requirement is met, the existing heat capacity value is acceptable.

11.2.3 If the requirements given in 11.2.2 are not met, two more heat capacity tests shall be run. The range of the four new test values shall not exceed 0.33 % of the existing heat capacity value. The average of the four new heat capacity values shall not differ from the existing heat capacity value by more than ±0.08 %. If this requirement is met, the existing heat capacity value is acceptable.

11.2.4 If the requirements given in 11.2.3 are not met, a fifth and sixth heat capacity test shall be run. The range of the six new test values shall not exceed 0.42 % of the existing heat capacity value. The average of the six new heat capacity values

TABLE 1 Heat Capacity Runs

NOTE—Variance = s^2 = {Sum Column C − [(Sum Column B)^2/10]}/9 = 89.51.
Standard Deviation = s = $\sqrt{s^2}$ = 9.46.
Relative Standard Deviation = (s/Average) × 100 = 0.09 %.

Run Number	Column A Heat Capacity, J/°C	Column B Difference From Average	Column C (Column B)^2
1	10 257.7	+4.2	17.6
2	10 249.3	−4.2	17.6
3	10 270.2	+16.7	278.9
4	10 253.5	0.0	0
5	10 245.1	−8.4	70.6
6	10 249.3	−4.2	17.6
7	10 240.9	−12.6	158.8
8	10 266.0	+12.5	156.3
9	10 257.7	+4.2	17.6
10	10 245.1	−8.4	70.6
SUM		−0.2	805.6
AVERAGE	E = 10 253.5		

shall not differ from the existing heat capacity value by more than ±0.08 %. If these requirements are met, do not change the existing heat capacity value.

11.2.5 If the requirements given in 11.2.4 are not met, four more heat capacity tests shall be run. The range of the ten new test values shall not exceed 0.50 % of the existing heat capacity value. The average of the ten new heat capacity values shall not differ from the existing heat capacity value by more than ±0.04 %. If this requirement is met, the existing heat capacity value is acceptable.

11.2.6 If requirements given in 11.2.5 are not met, the average value from the ten new test values shall be used to determine a new heat capacity value provided the relative standard deviation of the ten values does not exceed 0.15 %.

11.2.7 The summary of the numerical requirements at each step in checking the heat capacity is given in Table 2.

11.3 *Rolling Average Method*:

11.3.1 A single new heat capacity value shall not differ from the existing heat capacity value by more than ±0.17 %.

11.3.2 Values that serve to confirm existing heat capacity values will be included with the original 10 calibration tests until a total of 20 tests are made. These tests will comprise a database for calculating the mean heat capacity value provided the relative standard deviation of the 20 values does not exceed 0.15 %. Any new calibration check beyond the 20 tests will replace the oldest value in the heat capacity database of 20 tests. A maximum relative standard deviation of 0.15 % shall be maintained for the heat capacity database of 20 tests.

11.3.3 When using a rolling average, the heat capacity data must be continually evaluated for four indications of out-of-control conditions: first, seven consecutive results are higher than the mean; second, seven consecutive results are lower than the mean; third, seven consecutive results are continually increasing; and fourth, seven consecutive results are continually decreasing.

11.3.4 Out-of-control trends indicate that the calorimeter operation is suspect and causes should be identified. Whether or not causes are identified, the calorimeter should be recalibrated according to the procedure in Section 10.

12. Procedure for Coal and Coke Samples

12.1 Weigh 0.8 to 1.2 g of sample into a sample holder. Record the weight to the nearest 0.0001 g (see 12.6.3).

12.2 Follow the procedures as described in 10.2-10.5 for determination of heat capacity. The starting temperature for determinations shall be within ±0.5°C of that used in the determination of the heat capacity.

TABLE 2 Numerical Requirements

Number of Check Runs	Maximum Range $((E_{nmax} - E_{nmin})/E_e) \times 100$	Maximum Difference $((E_{nav} - E_e)/E_e) \times 100$
1	...	±0.17
2	0.21	±0.13
4	0.33	±0.08
6	0.42	±0.08
10	0.50	±0.04

E_e is the existing heat capacity value.
E_{nmin} is the minimum reading in group of heat capacity check runs.
E_{nmax} is the maximum reading in a group of heat capacity check runs.
E_{nav} is the average of the group of heat capacity check runs.

12.3 Carry out a moisture determination in accordance with Test Method D 3173 or Test Methods D 5142 on a separate portion of the analysis sample preferably on the same day but not more than 24 h apart from the calorific value determination so that reliable corrections to other bases can be made.

12.4 Conduct the sulfur analysis in accordance with Test Methods D 3177 or D 4239. From the weight % sulfur, calculate the sulfur corrections (see X1.2):

$$e3 = 55.2\ J/g \times S \times m\ (13.18\ cal/g \times S \times m) \qquad (6)$$

where:
$e3$ = a correction for the difference between the heat of formation of H_2SO_4 from SO_2 with respect to the formation of HNO_3, J;
S = wt % sulfur in the sample; and
m = mass of sample from 12.1, g.

12.4.1 When titration method is used (see 10.6.1.1), the sulfur correction is

$$e3 = 55.18\ J/g \times S \times m \text{ or } (13.18\ cal/g \times S \times m) \qquad (7)$$

12.4.2 When the calculated titration method is used (see 10.6.1.2), the sulfur correction is

$$e3 = 94.51\ J/g \times S \times m \text{ or } (22.57\ cal/g \times S \times m) \qquad (8)$$

12.5 For eight mesh samples, analyze coals susceptible to oxidation within 24 h of preparation.

12.6 Coal or coke that do not burn completely can be treated as follows:

12.6.1 Use a crucible liner of the type recommended in 6.11.

12.6.2 Use a combustion aid such as benzoic acid, ethylene glycol, mineral oil or a gelatin capsule. A minimum of 0.4 g of combustion aid shall be used. Record the weight to the nearest 0.0001 g. Calculate the correction for use of a combustion aid using the following:

$$e4 = Ha \times ma \qquad (9)$$

where:
$e4$ = correction for use of a combustion aid,
Ha = heat of combustion of the combustion aid J/g (cal/g), and
ma = mass of combustion aid, g.

12.6.3 Vary the mass of the sample to obtain good ignition and so that the total heat generated is the same as the heat generated during calibration.

13. Calculations

13.1 *Gross Calorific Value*—Calculate the gross calorific value Q_{vad} (gross) using the following equation:

$$Q_{vad}\ (\text{gross}) = [(tE_e) - e1 - e2 - e3 - e4]/m \qquad (10)$$

where:
Q_{vad} (gross) = gross calorific value at constant volume as determined, J/g (cal/g);
E_e = the heat capacity of the calorimeter, J/°C (cal/°C);
t = corrected temperature rise according to 10.7, °C;
$e1$ = acid correction according to 10.6.1, J;
$e2$ = fuse correction according to 10.6.2, J;

$e3$ = sulfur correction determined according to 12.4, J;
$e4$ = combustion aid correction determined according to 12.7, J; and
m = mass of the sample, g.

13.1.1 See Appendix X1.2.3 for an example calculation.

13.2 *Net Calorific Value*—Calculate the net calorific value Q_p (net) as follows:

$$Q_p \text{ (net)} = Q_{var} \text{ (gross)} - 215.5 \text{ J/g} \times H_{ar} \tag{11}$$

or:

$$(Q_p \text{ (net)}_{ar} = Q_{var} \text{ (gross)} - 92.67 \text{ Btu/lb} \times H_{ar}) \tag{12}$$

where:

Q_p (net) = net calorific value, at constant pressure;
Q_{var} (gross) = gross calorific value, at constant volume, as-received basis; and
H_{ar} = total hydrogen, %, as-received basis, where hydrogen includes hydrogen in the sample moisture.

Example:

Calorific value as determined Q_{vad} (gross) = 31 420 J/g
Moisture, as determined M_{ad} = 2.13 wt %
Moisture, as received M_{ar} = 8.00 wt %
Hydrogen, as determined H_{ad} = 5.00 wt %

Q_{var} (gross) = Q_{vad} (gross) × $[(100 - M_{ar})/(100 - M_{ad})]$ = 31 420 J/g × [(100 − 8.00)/(100 − 2.13)] = 29 535 J/g

$H_{ar} = [(H_{ad} - 0.1119 \times M_{ad}) \times \{(100 - M_{ar})/(100 - M_{ad})\}] + 0.1119\, M_{ar} = [(5.00 - 0.1119 \times 2.13) \times \{(100 - 8.00)/(100 - 2.13)\}] + 0.1119 \times 8.0 = 5.37$

Q_p (net) = 29 535 J/g − (215.5 × 5.37) = 29 535 J/g − 1153 J/g = 28 388 J/g

14. Report

14.1 Report the calorific value as Q_{vad} (gross) along with the moisture of the sample as determined M_{ad} from 12.3.

14.2 The results of the calorific value can be reported in any of a number of bases differing in the manner the moisture is treated. Procedures for converting the value obtained on an analysis sample to other bases are described in Practice D 3180.

15. Precision and Bias

15.1 *Manual Calorimeters*:

15.1.1 *Repeatability*—The difference in absolute value between two test results calculated to a dry basis (Practice D 3180) performed on two separate test portions of the same analysis sample of 250-μm (No. 60) coal in the same laboratory, by the same operator, using the same equipment with the same heat capacity value shall not exceed the repeatability interval *I(r)* of 115 J/g (50 Btu/lb) more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the repeatability interval, there is reason to question one or both of the test results.

15.1.2 *Reproducibility*—The difference in absolute value between test results calculated to a dry basis (Practice D 3180) performed in different laboratories on representative analysis samples of 250-μm (No. 60) coal shall not exceed the reproducibility interval *I(r)* of 250 J/g (100 Btu/lb) more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the reproducibility interval there is reason to question one or both of the test results.

15.1.3 *Bias*—Bias in the determination of the gross calorific value is eliminated provided samples are treated identically to the benzoic acid used in the determination of the calorimeter heat capacity.

15.2 *Automated Calorimeters*:

15.2.1 *Repeatability*—The repeatability has not been determined.

15.2.2 *Reproducibility*—The reproducibility has not been determined.

15.2.3 *Bias*—Bias in the determination of the gross calorific value is eliminated provided samples are treated identically to the benzoic acid used in the determination of the calorimeter heat capacity.

16. Keywords

16.1 adiabatic calorimeter; bomb calorimeters; calorific value; calorimeter; coal; coke; isoperibol bomb calorimeter

ANNEX

(Mandatory Information)

A1. THERMOMETRIC CORRECTIONS

A1.1 *Thermometer Corrections*—The following corrections shall be made:

A1.1.1 *Calibration Correction*, shall be made in accordance with the calibration certificate furnished by the calibration authority.

A1.1.2 *Radiation Corrections*—Radiation corrections are required to calculate heat loss or gain to the isoperibol 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 shall be used consistently in the determination of

---

[8] Dickinson, H. C., *Bulletin*, U.S. Bureau of Standards, Vol. 11, 1951, p. 189.

[9] Pfaundler, L., *Annalen der Physik* (Leipzig), ANPYA, Vol. 129, 1966, p. 102.

[10] "Methods of Analyzing & Testing Coal and Coke" U.S. Bureau of Mines *Bulletin* 638, XMBUA, 1967, pp. 16–17.

heat capacity and sample measurements.

A1.1.2.1 *Dickinson Formula*:

$$C_r = -r1 \times (b - a) - r2 \times (c - b) \quad \text{(A1.1)}$$

where:

C_r = radiation correction;
$r1$ = rate of rise in temperature per minute in the preliminary period;
$r2$ = rate of rise of temperature per minute in the final period (if temperature is falling, $r2$ is negative;
ta = firing temperature;
tc = final temperature, being the first temperature after which the rate of change is constant;
a = time at temperature ta, min;
b = time at temperature $ta + 0.60\ (tc - ta)$, min; and
c = time at temperature tc, min.

A1.1.2.2 Regnault-Pfaundler Formula:

$$C_r = nr1 + kS \quad \text{(A1.2)}$$

where:

C_r = radiation correction,
n = number of minutes in the combustion period,

$$k = (r1 - r2) / (t'' - t'), \quad \text{(A1.3)}$$

$$S = tn - 1 + (1/2)(ti + tf)nt' \quad \text{(A1.4)}$$

t' = average temperature during the preliminary period,
t'' = average temperature during the final period,

$r1$, $r2$ see A1.1.2.1,

$t1, t2, \ldots tn$ = successive temperature recorded during the combustion period, at 1-min intervals, and

$$tn - 1 = \text{sum of } t1, t2, t3 \ldots tn - 1 \quad \text{(A1.5)}$$

A1.1.2.3 *Bureau of Mines Method*—A table of radiation corrections can be established so that only the initial and final readings are required to determine the calorific value of a fuel. This can be done by carrying out a series of tests using 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, $c - a$, 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 A1.1.2.1), or the Regnault-Pfaundler method (see A1.1.2.2). These corrections are constant for a given temperature rise. From the 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.

A1.1.3 *Setting Correction*

This is necessary for the Beckman 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:

$$Ce = K(tf - ti)(tf + ti - L - T) \quad \text{(A1.6)}$$

where:

Ce = emergent stem correction,
K = 0.000 16 for thermometers calibrated in °C,
L = scale reading to which the thermometer was immersed,
T = mean temperature of emergent stem,
ti = initial temperature reading, and
tf = final temperature reading.

Example:

A thermometer was immersed to 16°C; its initial reading, *ti*, was 24.127°C; its final reading, *tf*, was 27.876; the mean temperature of the emergent stem, *T*, was 26°C.

$$Ce = 0.000\,16 \times (28 - 24) \times (28 + 24 - 16 - 26) = 0.0064°\text{C} \quad \text{(A1.7)}$$

A1.1.4.2 *Thermometers Calibrated and Used in Partial Immersion, But at a Different Temperature Than the Calibrated Temperature:*

$$Ce = K(tf - ti)(tc - to) \quad \text{(A1.8)}$$

where:

Ce = emergent stem correction,
K = 0.000 16 for thermometers calibrated in °C,
ti = initial temperature reading,
tf = final temperature reading,
to = observed stem temperature, and
tc = stem temperature at which the thermometer was calibrated.

Example:

A thermometer has an initial reading, *ti*, 27°C; a final reading, *tf*, 30°C; the observed stem temperature, *to*, 28°C; and the calibration temperature, *tc*, 22°C.

$$Ce = 0.000\,16 \times (30 - 27) \times (28 - 22) = 0.003°\text{C} \quad \text{(A1.9)}$$

APPENDIX

(Nonmandatory Information)

X1. THERMOCHEMICAL CORRECTIONS

X1.1 *Energy of Formation of Nitric Acid (HNO_3):*

X1.1.1 A correction, *e*1, (10.6.1) is applied for the formation of nitric acid.

X1.1.2 (1) HNO_3 is formed in the calorimeter by the following reaction:

$$1/2\ N_2\,(g) + 5/4\,O_2\,(g) + 1/2\,H_2O\,(l) = HNO_3\,(\text{in } 500 \text{ mol } H_2O) \qquad (X1.1)$$

X1.1.3 (2) the energy of formation of HNO_3 in approximately 500 mol of water under bomb conditions is minus 59.0 kJ/mol (14.09 Kcal/mole).[11]

X1.1.4 Normal convention assigns a negative value for a heat of formation that is exothermic. By definition, heat released from combustion processes are expressed as positive values. Hence, the negative factors developed for nitric and sulfuric acid corrections are expressed as positive values in the calculations.

X1.1.5 A convenient concentration of Na_2CO_3 is 3.76-g Na_2CO_3/L which gives *e*1 = *V* where *V* is the volume of Na_2CO_3 in millilitres. When H_2SO_4 is produced during the combustion of coal or coke, a part of the correction for H_2SO_4 is present in the *e*1 correction. The remainder is in the *e*3 correction (see X1.2).

X1.2 *Energy of Formation of Sulfuric Acid (H_2SO_4)*—By definition (see Terminology D 121), the gross calorific value is obtained when the product of the combustion of sulfur in the sample is $SO_2(g)$. However, in actual bomb combustion processes, all the sulfur is found as H_2SO_4 in the bomb washings.

X1.2.1 A correction *e* 3 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 from SO_2. This energy is taken as −303.0 kJ/mol.[12]

X1.2.2 When the bomb washings are titrated, a correction of 2 × 59.0 kJ/mole of sulfur is applied in the *e*1 correction so that the additional correction that is necessary is the difference in the heats of formation for nitric and sulfuric acid and this correction is − 303.0 − (−2 times 59.0) = −185 kJ/mol, or = −58 J/g (13.8 cal/g) of sulfur times the weight of sample in grams times percent sulfur in sample.

X1.2.3 If a 1-g sample 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 under the conditions of the bomb process is −303 kJ/mole.

$$SO_2\,(g) + 1/2\,O_2\,(g) + H_2O\,(l) = H_2SO_4\,(\text{in } 15 \text{ mol of } H_2O) \qquad (X1.2)$$

X1.2.4 The values above are based on a sample containing approximately 5 % sulfur and approximately 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]

X1.2.5 For different sample weights or sulfur content, or both, the resultant normality of acid formed can be different, and therefore, the normality of titrant must be adjusted accordingly. Basing the calculation upon a sample of comparatively large sulfur content reduces the possible overall errors, because, for small percentages of sulfur, the correction is smaller.

X1.3 *Fuse Correction*—The energy required to melt a platinum or palladium wire is constant for each experiment if the same amount of platinum or palladium 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.

X1.4 *Reporting Results in Other Units:*

X1.4.1 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 the table below:

1 Btu = 1055.06 J
1 calorie = 4.1868 J
1 J/g = 0.430 Btu/lb
1 J/g = 0.239 cal/g
1 cal/g = 1.8 Btu/lb

X1.5 *Sample Calculations:*

X1.5.1 *Heat Capacity*:

$E = [(Hc \times m) + e1 + e2]/t$

$Hc = 26\,435$ J/g,

$m = 1.0047$ g,

$e1 = 43$-J acid correction,

$e2 = 55$-J fuse correction,

$t = 2.6006$°C,

$E = [(26\,435 \text{ J/g} \times 1.0047 \text{ g}) + 43 \text{ J} + 55 \text{ J}]/2.6006°\text{C}$, and

$E = 10\,250.4$ J/°C.

X1.6 *Heat of Combustion:*

Q_{vad} (gross) = $[(tE) - e1 - e2 - e3 - e4]/m$;

$E_e = 10\,250.4$ J/°C;

$t = 2.417$°C;

$e1 = 77$-J acid correction;

$e2 = 52$-J fuse correction;

$e3 = 58 \times 1.24\ \% \times 0.7423$ g, sulfur correction;

$e4 = 46\,025$ J/g $\times$ 0.2043 g, combustion aid correction;

$m = 0.7423$ g, mass of sample;

---

[11] Mott, R. A., and Parker, C., "Studies in Bomb Calorimetry IV—Corrections," Fuel, FUELB, Vol. 34, 1955, p. 303–316.

[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, Fuel B*, Vol. 37, 1958, p. 371.

Q_{vad} = [(10 250.4 J/°C × 2.417°C) − 77 J − 52 J − 53 J − 9403 J]/0.7423 g; and

Q_{vad} = 20 464 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 D611: Standard Test Method for Aniline Point and Mixed Aniline Point of Petroleum Products and Hydrocarbon Solvents

CFR Section(s): 21 CFR 177.1520(b)

Standards Body: American Society for Testing and Materials

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

Designation: D 611 – 82 (Reapproved 1998)

An American National Standard

Designation: 2/98

Standard Test Methods for Aniline Point and Mixed Aniline Point of Petroleum Products and Hydrocarbon Solvents[1]

This standard is issued under the fixed designation D 611; 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.

These test methods were adopted as a joint ASTM-IP standard in 1964.

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

1. Scope

1.1 These test methods cover the determination of the aniline point of petroleum products and hydrocarbon solvents. Method A is suitable for transparent samples with an initial boiling point above room temperature and where the aniline point is below the bubble point and above the solidification point of the aniline-sample mixture. Method B, a thin-film method, is suitable for samples too dark for testing by Method A. Methods C and D are for samples that may vaporize appreciably at the aniline point. Method D is particularly suitable where only small quantities of sample are available. Method E describes a procedure using an automatic apparatus suitable for the range covered by Methods A and B.

1.2 These test methods also cover the determination of the mixed aniline point of petroleum products and hydrocarbon solvents having aniline points below the temperature at which aniline will crystallize from the aniline-sample mixture.

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.* Specific precautionary statements are given in Sections 7.1 and 7.3.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1015 Test Method for Freezing Points of High-Purity Hydrocarbons[2]

D 1217 Test Method for Density and Relative Density (Specific Gravity) of Liquids by Bingham Pycnometer[2]

D 1218 Test Method for Refractive Index and Refractive Dispersion of Hydrocarbon Liquids[2]

D 1500 Test Method for ASTM Color of Petroleum Products (ASTM Color Scale)[2]

D 2700 Test Method for Knock Characteristics of Motor and Aviation Fuels by the Motor Method[3]

E 1 Specification for ASTM Thermometers[4]

3. Terminology

3.1 *Definitions:*

3.1.1 *aniline point*—the minimum equilibrium solution temperature for equal volumes of aniline and sample.

3.1.2 *mixed aniline point*—the minimum equilibrium solution temperature of a mixture of two volumes of aniline, one volume of sample, and one volume of *n*-heptane of specified purity.

4. Summary of Test Methods

4.1 Specified volumes of aniline and sample, or aniline and sample plus *n*-heptane, are placed in a tube and mixed mechanically. The mixture is heated at a controlled rate until the two phases become miscible. The mixture is then cooled at a controlled rate and the temperature at which two phases separate is recorded as the aniline point or mixed aniline point.

5. Significance and Use

5.1 The aniline point (or mixed aniline point) is useful as an aid in the characterization of pure hydrocarbons and in the analysis of hydrocarbon mixtures. Aromatic hydrocarbons exhibit the lowest, and paraffins the highest values. Cycloparaffins and olefins exhibit values that lie between those for paraffins and aromatics. In homologous series the aniline points increase with increasing molecular weight. Although it occasionally is used in combination with other physical properties in correlative methods for hydrocarbon analysis, the aniline point is most often used to provide an estimate of the aromatic hydrocarbon content of mixtures.

---

[1] These test methods are under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricantsand are the direct responsibility of D02.04on Hydrocarbon Analysis.

Current edition approved Aug. 27, 1982. Published January 1983. Originally published as D 611 – 41 T. Last previous edition D 611 – 77.

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

[3] *Annual Book of ASTM Standards*, Vol 05.04.

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

6. Apparatus

6.1 For details of the aniline point apparatus required for each method see:

Annex A1 for Method A
Annex A2 for Method B
Annex A3 for Method C
Annex A4 for Method D
Annex A5 for Method E

Note 1—Alternative apparatus may be used, such as the U-tube method for dark oils, provided it has been shown to give results of the same precision and accuracy as those described in the Annexes.

6.2 *Heating and Cooling Bath*—A suitable air bath, a nonvolatile, transparent liquid bath, or an infrared lamp (250 to 375 W), provided with means for controlling the rate of heating.

Note 2—Water should not be used as either a heating or cooling medium since aniline is hygroscopic and moist aniline will give erroneous test results. For example, the aniline point of the *n*-heptane reagent as measured with aniline containing 0.1 volume % water is approximately 0.5°C (0.9°F) higher than that measured with dry aniline. If the aniline point is below the dew point of the atmosphere, pass a slow stream of dry inert gas into the aniline point tube to blanket the aniline-sample mixture.

6.3 *Thermometers*, having the following ranges and conforming to the requirements of the designated ASTM or IP specification:

Range	ASTM (Specification E 1)	IP
−38 to + 42°C (−36.5 to + 107.5°F)	33C, 33F	20C
25 to 105°C (77 to 221°F)	34C, 34F	21C
90 to 170°C (194 to 338°F)	35C, 35F	59C

6.4 *Pipets*, with capacities of 10 ± 0.04 mL, 5 ± 0.02 mL, the latter equipped with a long, fine tip. Provide a rubber suction bulb for use with pipets when measuring aniline.

6.5 *Balance*—A laboratory balance sensitive to 0.01 g, suitable for weighing the tube and sample when the sample cannot be pipetted conveniently.

6.6 *Safety Goggles*.

6.7 *Plastic Gloves*, impervious to aniline.

7. Reagents

7.1 *Aniline* (**Warning**—See Note 3.) Dry chemically pure aniline over potassium hydroxide pellets, decant, and distill fresh on the day of use, discarding the first and last 10 %. Aniline thus prepared when tested with *n*-heptane according to Section 9 shall give an aniline point of 69.3 ± 0.2°C (156.7 ± 0.4°F) as determined from the average of two independent tests having a difference of not more than 0.1°C (0.2°F).

Note 3—**Warning:** Aniline should not be pipetted directly by mouth because of its extreme toxicity. Aniline is also toxic by absorption through the skin even in *very small quantities*, and should be handled with great caution.

Note 4—For routine purposes the distillation process is not mandatory provided the aniline meets the requirements of the test with *n*-heptane.

Note 5—The aniline point of aniline and *n*-heptane determined with automatic apparatus (Method E) shall be 69.3 ± 0.2°C (156.7°F ± 0.4°F) when corrected in accordance with the equation in Section A5.2.1

Note 6—As an alternative to distilling the aniline on the day of use, the aniline may be distilled as described in 7.1, collecting the distillate in ampoules, sealing the ampoules under vacuum or dry nitrogen, and storing in a cool dark place for future use. In either case, rigid precaution must be taken to avoid contamination from atmospheric moisture (Note 2). It is believed that under these conditions the aniline will remain unchanged for a period exceeding 6 months.

7.2 *Calcium Sulfate*, anhydrous.

7.3 *n-Heptane* (**Warning**—See Note 7), conforming to the requirements listed in Table 1.[5]

Note 7—**Warning:** Flammable. Harmful if inhaled. See Annex A6.1.

8. Sample

8.1 Dry the sample by shaking vigorously for 3 to 5 min with about 10 volume % of a suitable drying agent such as anhydrous calcium sulfate or anhydrous sodium sulfate. Reduce the viscosity of viscous samples by warming to a temperature below that which would cause the loss of light ends or the dehydration of the drying agent. Remove any suspended drying agent by use of a centrifuge or by filtration. Heat samples containing separated wax until they are homogeneous and keep heated during filtration or centrifugation to ensure against separation of wax. When suspended water is visibly present and the sample material is known to dissolve less than 0.03 mass % of water, the use of a centrifuge for the removal of suspended water is an acceptable procedure.

9. Procedure for Aniline Point

9.1 The following methods, to be used as applicable, are covered as follows:

9.1.1 *Method A*, described in detail in Annex A1, is applicable to clear samples or to samples not darker than No. 6.5 ASTM color, as determined by Test Method D 1500, having initial boiling points well above the expected aniline point.

9.1.2 *Method B*, described in detail in Annex A2, is applicable to light-colored samples, moderately dark samples, and to very dark samples. It is suitable for samples that are too dark to be tested by Method A.

9.1.3 *Method C*, described in detail in Annex A3, is applicable to clear samples or to samples not darker than No. 6.5 ASTM color, as determined by Test Method D 1500, having initial boiling points sufficiently low as to give incorrect aniline point readings by Method A, for example, aviation gasoline.

9.1.4 *Method D*, described in detail in Annex A4, is applicable to the same type of sample as Method C. It is particularly useful when only limited quantities of sample are available.

TABLE 1 Requirements for *n*-Heptane

		ASTM Method
ASTM Motor Octane Number	0.0 ± 0.2	D 2700
Density at 20°C, g/mL	0.68380 ± 0.00015	D 1217
Refractive index, $n_D^{20°C}$	1.38770 ± 0.00015	D 1218
Freezing point, °C	−90.710 min	D 1015
Distillation, 50 % recovered at 1.013 bar (760 mm Hg), °C	98.427 ± 0.025	A
Differential, 80 % recovered minus 20 % recovered, °C	0.020 max	

A For equipment and method used, see *Journal of Research*, National Institute of Standards and Technology, Vol 44, No. 3, 1950, pp. 309 and 310 (*RP2079*).

---

[5] These requirements for *n*-heptane are identical, except for tetraethyl lead, with those prescribed in the *1987 Annual Book of ASTM Standards*, Vol 05.04.

9.1.5 *Method E* is applicable when using automatic apparatus in accordance with the instructions in Annex A5.

10. Procedure for Mixed Aniline Point

10.1 This procedure is applicable to samples having aniline points below the temperature at which aniline crystallizes from the mixture. Pipet 10 mL of aniline (**Warning:** See Note 3), 5 mL of sample, and 5 mL of *n*-heptane into a clean, dry apparatus. Determine the aniline point of the mixture by Method A or B as described in Annex A1 or Annex A2.

11. Report

11.1 If the range of three successive observations of the aniline point temperature is not greater than 0.1°C (0.2°F) for light-colored samples or 0.2°C (0.4°F) for dark samples, report the average temperature of these observations, corrected for thermometer calibration errors, to the nearest 0.05°C (0.1°F) as the aniline point.

11.2 If such a range is not obtained after five observations, repeat the test using fresh quantities of aniline and sample in a clean, dry apparatus, and if consecutive temperature observations show a progressive change, or if the range of observations is greater than the repeatability given in 12.1, report the method as being inapplicable.

12. Precision and Bias

12.1 The precision of these test methods as obtained by statistical examination of interlaboratory test results is as follows:

12.1.1 *Repeatability*—The difference between successive test results (two average temperatures obtained in a series of observations as described in Section 11 obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

	Repeatability	
Aniline point of:		
Clear, light-colored samples	0.16°C	(0.3°F)
Moderately dark to very dark samples	0.3°C	(0.6°F)[A]
Mixed aniline point of:		
Clear, light-colored samples	0.16°C	(0.3°F)[A]
Moderately dark to very dark samples	0.3°C	(0.6°F)[A]

[A] Not determined from recent cooperative tests; however, the ratios with those given in the 1953 version are believed to apply.

12.1.2 *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:

	Reproducibility
Aniline point of:	
Clear, light-colored samples	0.5°C (0.9°F)
Moderately dark to very dark samples	1.0°C (1.8°F)[A]
Mixed aniline point of:	
Clear, light-colored samples	0.7°C (1.3°F)[A]
Moderately dark to very dark samples	1.0°C (1.8°F)[A]

[A] Not determined from recent cooperative tests; however, the ratios with those given in the 1953 version are believed to apply.

12.2 *Bias*—A statement of bias is now being developed by the subcommittee.

12.3 The precision of this test was not obtained in accordance with Committee D-2 Research Report RR:D02-1007, "Manual on Determining Precision Data for ASTM Methods on Petroleum Products and Lubricants."

13. Keywords

13.1 aniline point; aromatics; mixed aniline point

ANNEXES

(Mandatory Information)

A1. METHOD A

A1.1 Apparatus

A1.1.1 The apparatus shown in Fig. A1.1 shall consist of the following:

A1.1.1.1 *Test Tube*, approximately 25 mm in diameter and 150 mm in length, made of heat-resistant glass.

A1.1.1.2 *Jacket*, approximately 37 to 42 mm in diameter and 175 mm in length, made of heat-resistant glass.

A1.1.1.3 *Stirrer*, manually operated, metal, approximately 2 mm in diameter (14 B&S gage) metal wire as shown in Fig. A1.1. A concentric ring shall be at the bottom, having a diameter of approximately 19 mm. The length of the stirrer to a right-angle bend shall be approximately 200 mm. The right-angle bend shall be approximately 55 mm long. A glass sleeve approximately 65 mm in length of 3-mm inside diameter shall be used as a guide for the stirrer. Any suitable mechanical device for operating the stirrer as specified is an approved alternative for the manual operation.

A1.2 Procedure

A1.2.1 Clean and dry the apparatus. Pipet 10 mL of aniline (**Warning**— see 7.1) and 10 mL of the dried sample (8.1) into the test tube fitted with stirrer and thermometer. If the material is too viscous for pipetting, weigh to the nearest 0.01 g a quantity of the sample corresponding to 10 mL at room temperature. Center the thermometer in the test tube so that the immersion mark is at the liquid level, making sure that the thermometer bulb does not touch the side of the tube. Center the test tube in the jacket tube. Stir the mixture rapidly using a 50-mm (2-in.) stroke, avoiding the introduction of air bubbles.

A1.2.2 If the aniline-sample mixture is not miscible at room temperature, apply heat directly to the jacket tube so that the temperature rises at a rate of 1 to 3°C (2 to 5°F)/min by

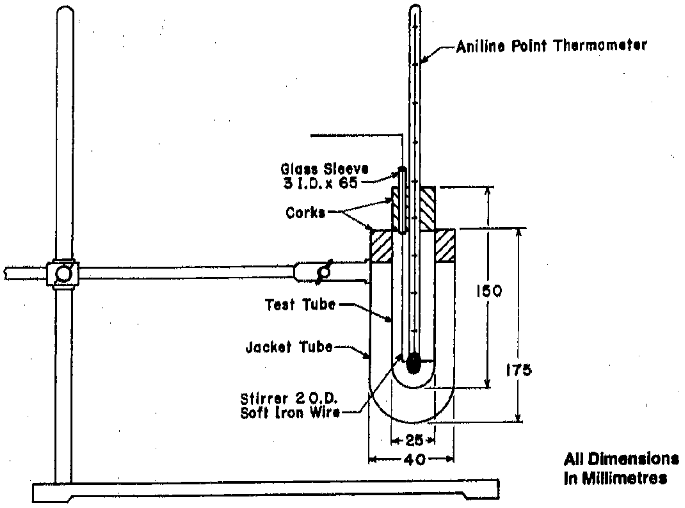


FIG. A1.1 Aniline Point Apparatus (Method A)

removing or reducing the heat source until complete miscibility is obtained. Continue stirring and allow the mixture to cool at a rate of 0.5 to 1.0°C (1.0 to 1.8°F)/min. Continue cooling to a temperature of 1 to 2°C (2.0 to 3.5°F) below the first appearance of turbidity, and record as the aniline point the temperature at which the mixture suddenly becomes cloudy throughout (Note A1.1). This temperature, and not the temperature of separation of small amounts of material, is the minimum equilibrium solution temperature.

NOTE A1.1—The true aniline point is characterized by a turbidity that is so cloudy as to obscure the thermometer bulb in reflected light.

A1.2.3 If the aniline-sample mixture is completely miscible at room temperature, substitute a non-aqueous cooling bath for the heating source, allow to cool at the rate specified in A1.2.2 and determine the aniline point as described.

A1.2.4 Repeat the observation of aniline point temperature by heating and cooling repeatedly until a report as directed in Section 11 can be made.

A2. METHOD B

A2.1 Apparatus

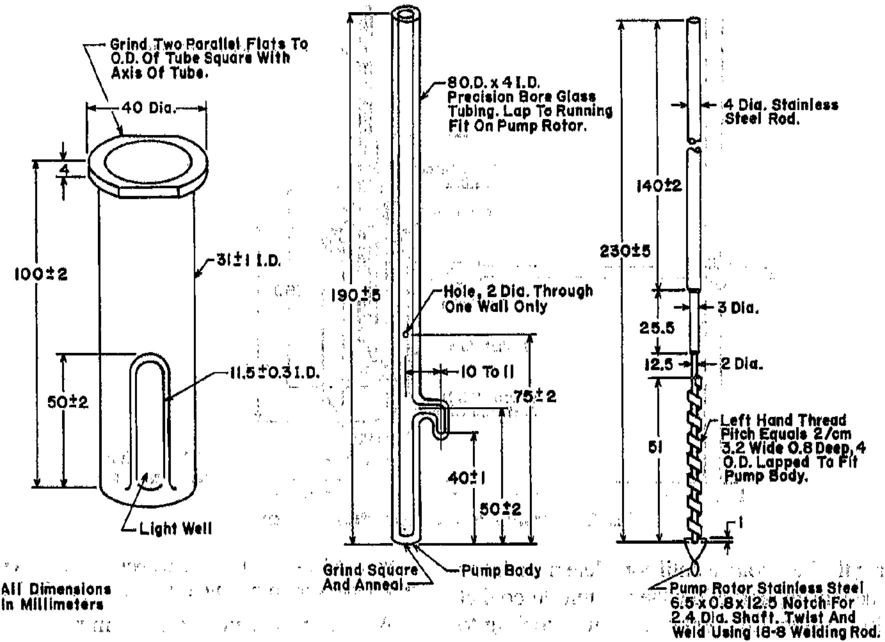
A2.1.1 *Thin-Film Apparatus*, made of heat-resistant glass and stainless steel, conforming to the dimensions given in Fig. A2.1. A suggested assembly is shown in Fig. A2.2.

A2.2 Procedure

A2.2.1 Clean and dry the apparatus. Pipet 10 mL of aniline (**Warning**— see Note 3) and 10 mL of the dried sample (8.1) into the tube fitted with pump-stirrer and thermometer. If the material is too viscous for pipetting, weigh to the nearest 0.01 g a quantity of sample corresponding to 10 mL at room temperature. Place the thermometer in the tube so that the contraction chamber is below the liquid level and so that the mercury bulb does not touch the side of the tube. Assemble the apparatus as shown in Fig. A2.2.

A2.2.2 Adjust the speed of the pump to produce a continuous stream of the oil-aniline mixture in the form of a thin film flowing over the light well. With extremely dark oils, operate the pump slowly and lower it so that the delivery tube nearly touches the top of the light well, so as to obtain a continuous film thin enough to permit observation of the aniline point. Adjust the voltage on the lamp until just enough light is given for the filament to be visible through the film. Raise the temperature of the mixture at a rate of 1 to 2°C (2.0 to 3.5°F)/min until the aniline point has just been passed, as denoted by a definite, sudden brightening of the lamp filament, and by the disappearance of the more or less opalescent condition of the film (Note A2.1). Discontinue heating and adjust the lamp voltage so that the filament appears clear and distinct but not uncomfortably bright to the eye. Adjust the temperature of the bath so that the sample-aniline mixture cools at a rate of 0.5 to 1.0°C (1.0 to 1.8°F)/min and note the appearance of the film and light filament. Record as the aniline point the temperature at which a second phase appears as evidenced by the reappearance of the opalescent condition of the film (usually causing a halo to appear around the lamp filament) or by a sudden dimming of the lamp filament, or both. At temperatures above the aniline point the edges of the light filament appear clear and distinct. At the aniline point temperature a halo or haze forms around the filament, replacing the distinct lines of the filament edge with lines that appear cloudy or hazy in appearance. Further darkening of the cloud over the filament occurs at lower temperature, but is not to be confused with the aniline point.

NOTE A2.1—For those making the test for the first time, the following procedure may be helpful: Make preliminary operational adjustments and tests using a colorless sample-aniline mixture, and observing changes taking place in the body of the liquid and film. Make rough tests with dark oils to become familiar with the appearance of the film and light source as the mixture passes from the clear state above the aniline point, to the



DETAIL OF TUBE DETAIL OF PUMP BODY AND ROTOR

FIG. A2.1 Details of Aniline Point Thin-Film Apparatus (Method B)

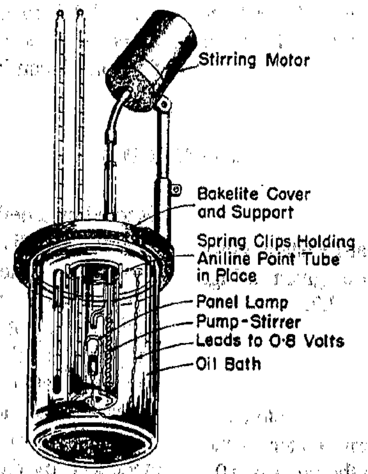


FIG. A2.2 Assembly of Thin-Film Apparatus (Method B)

translucent state below. If the sample is such that there is difficulty in observing the exact point of the phase change, make experiments with the sample, using various intensities of light and paying particular attention to the appearance of the light in the immediate vicinity of the lamp filament.

A2.2.3 Repeat the observation of aniline point temperature by heating and cooling repeatedly until a report as directed in Section 11 can be made.

A3. METHOD C

A3.1 Apparatus

A3.1.1 *Aniline-Point Tube*, of heat-resistant glass, of the shape and dimensions shown in Fig. A3.1, and fitted internally with a thin-walled glass thermometer tube, sealed at the lower end. The latter tube accommodates a tight-fitting cork stopper carrying the thermometer, the bulb of which rests on a cork ring or disk placed at the bottom of the tube; the tube contains sufficient light transformer oil to cover the bulb of the thermometer. The inner tube is held in the top of the aniline-point tube by a tightly fitting stopper, and a clamp is provided to hold the stopper in position to prevent loss of vapor from the sample.

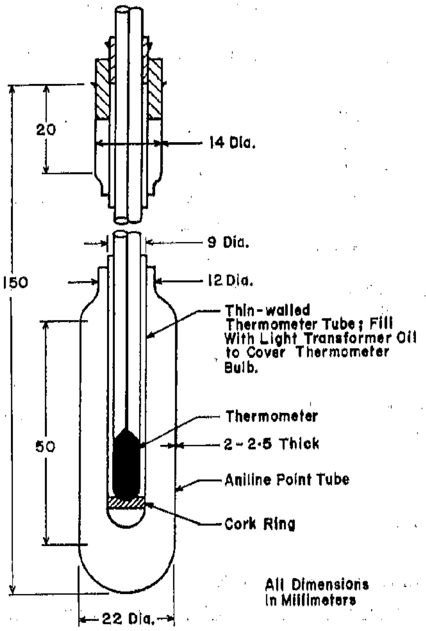


FIG. A3.1 Apparatus for Volatile Samples (Method C)

NOTE A3.1—Any other suitable arrangement, such as a screwed plastic gland carrying the thermometer, that will prevent the loss of vapor from the apparatus, may be used. In such cases it may be possible to omit the thermometer tube and immerse the thermometer bulb in the aniline-sample mixture.

A3.1.2 *Guard*, of stout metal gauze and surrounding the aniline point tube. It should preferably be combined with the clamp for holding the thermometer tube in place.

A3.2 Procedure

A3.2.1 Clean and dry the apparatus. Pipet 5 mL of aniline (Note A3.2 Precaution see Note 3) and 5 mL of the dried sample (8.1), both cooled to a temperature at which the sample may be measured without loss of vapor. Close the tube by means of the stopper and fit the thermometer tube centrally so that the bottom is 5 mm from the bottom of the aniline point tube. Clamp the stopper in position and attach the guard.

NOTE A3.2—**Precaution:** Put on goggles of safety glass and plastic gloves impervious to aniline.

A3.2.2 Follow the procedure described in A1.2.2 and A1.2.3 but mix the sample and aniline by shaking the tube. If the rate of change of temperature is greater than 1°C (2°F)/min when the aniline point is being approached, place the tube in a jacket that has previously been warmed or cooled to an appropriate temperature.

A3.2.3 Repeat the observation of aniline point by heating and cooling repeatedly until a report as directed in Section 11 can be made.

A4. METHOD D

A4.1 Apparatus

A4.1.1 *Bulb*, 1.5 to 2.0-mL capacity, blown from heat-resistant glass tubing, 5 mm in external diameter and 3 mm in internal diameter.

A4.1.2 *Guard*, as for Method C.

A4.2 Procedure

A4.2.1 Dry the bulb thoroughly in an oven at 105 ± 5°C, allow it to cool to room temperature, and charge it by means of the pipets with 0.5 mL of aniline (**Warning**— see Note 3) and 0.5 mL of the dried sample (8.1). Cool the mixture thoroughly and rapidly draw out and seal the open end of the bulb at about 10 mm from the center of the bulb.

NOTE A4.1—**Precaution:** Put on goggles of safety glass and plastic gloves impervious to aniline.

A4.2.2 Attach the bulb to the thermometer by rubber bands so that the bulb is adjacent to the thermometer bulb. Attach the mesh guard and follow the procedure described in A1.2.2 and A1.2.3 but mix the sample and aniline by shaking.

A4.2.3 Repeat the observation of aniline point temperature by heating and cooling repeatedly until a report as directed in Section 11 can be made.

A5. METHOD E

A5.1 Apparatus

A5.1.1 *Automatic Aniline Point Apparatus*, commercially available, using a modified thin film technique and direct heating of the sample-aniline mixture with electrical immersion heater. Detection of change of sample turbidity at the aniline point is by response of a photoelectric cell to collimated light directed through the thin film of sample.

A5.2 Procedure

A5.2.1 Determine the automatic aniline point in accordance with instructions provided with the apparatus. Correct the aniline point as follows:

$$\text{Corrected aniline point} = (X_a - A)/B \quad \text{(A5.1)}$$

where:

X_a = automatic aniline point, and

A and B = constants determined for each apparatus as described in A5.2.2

NOTE A5.1—It has been established by cooperative tests that observed aniline points determined by some automatic apparatus are lower than the determinations by Methods A and B. The difference is greater for automatic apparatus when relatively high sample-cooling rates are used, and increases as the aniline point increases.

A5.2.2 Determine the aniline point by either Method A or Method B and also using the automatic apparatus for three or more samples with aniline points in each of the ranges 43 to 49°C (110 to 120°F), 60 to 66°C (140 to 150°F), and 77 to 82°C (170 to 180°F). Calculate the constants *A* and *B* by the least squares method by simultaneous solution of the following equations:

$$\Sigma(X_a) = NA + B\Sigma(X_c) \quad \text{(A5.2)}$$

$$\Sigma(X_aX_c) = A\Sigma(X_c) + B\Sigma(X_c^2)$$

where:

$\Sigma(X_a)$ = sum of all aniline point data by automatic apparatus,

$\Sigma(X_c)$ = sum of all aniline point data by either Method A or B,

$\Sigma(X_c^2)$ = sum of the squares of all aniline point data by either Method A or B,

$\Sigma(X_aX_c)$ = sum of the products of aniline points determined by either Method A or B and by using the automatic apparatus for each sample, and

N = number of samples.

NOTE A5.2—Cooperative data were obtained from five laboratories for five samples with aniline points in the range from 34 to 87°C (93 to 188°F). Constants *A* and *B* were calculated for the composite data as 0.79 and 0.991 respectively. Although a minimum number of nine samples is specified in this method, constants *A* and *B* in the preceding equation may be obtained with a slightly greater precision if data for a larger number of samples are used.

A6. PRECAUTIONARY STATEMENT

A6.1 *n*-Heptane

Warning—Flammable. Harmful if inhaled.
Keep away from heat, sparks, and open flame.
Keep container closed.
Use with adequate ventilation.
Avoid prolonged breathing of vapor or spray mist.
Avoid prolonged or repeated skin contact.

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:

CFR Section(s):

Standards Body:

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

Designation: D 6216 – 98

An American National Standard

Standard Practice for Opacity Monitor Manufacturers to Certify Conformance with Design and Performance Specifications[1]

This standard is issued under the fixed designation D 6216; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice covers the procedure for certifying continuous opacity monitors. It includes design and performance specifications, test procedures, and quality assurance requirements to ensure that continuous opacity monitors meet minimum design and calibration requirements, necessary in part, for accurate opacity monitoring measurements in regulatory environmental opacity monitoring applications subject to 10 % or higher opacity standards.

1.2 This practice applies specifically to the original manufacturer, or to those involved in the repair, remanufacture, or resale of opacity monitors.

1.3 Test procedures that specifically apply to the various equipment configurations of component equipment that comprise either a transmissometer, an opacity monitor, or complete opacity monitoring system are detailed in this practice.

1.4 The specifications and test procedures contained in this practice exceed that of the United States Environmental Protection Agency (USEPA). For each opacity monitor or monitoring system that the manufacturer demonstrates conformance to this practice, the manufacturer may issue a certificate that states that that opacity monitor or monitoring system conforms with all of the applicable design and performance requirements of 40 CFR 60, Appendix B, Performance Specification 1 except those for which tests are required after installation.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres[2]

2.2 *U.S. Environmental Protection Agency Document:*[3]

40 CFR 60 Appendix B, Performance Specification 1

2.3 *Other Documents:*

ISO/DIS 9004 Quality Management and Quality System Elements-Guidelines[4]

ANSI/NCSL Z 540-1-1994 Calibration Laboratories and Measuring Equipment - General Requirements[4]

NIST 260-116 - Filter calibration procedures[5]

3. Terminology

3.1 For terminology relevant to this practice, see Terminology D 1356.

3.2 *Definitions of Terms Specific to This Standard:*

Analyzer Equipment

3.2.1 *opacity, n*—measurement of the degree to which particulate emissions reduce (due to absorption, reflection, and scattering) the intensity of transmitted photopic light and obscure the view of an object through ambient air, an effluent gas stream, or an optical medium, of a given pathlength.

3.2.1.1 *Discussion*—Opacity (Op), expressed as a percent, is related to transmitted light, (T) through the equation:

$$Op = (1 - T)(100). \quad (1)$$

3.2.2 *opacity monitor, n*—an instrument that continuously determines the opacity of emissions released to the atmosphere.

3.2.2.1 *Discussion*—An opacity monitor includes a transmissometer that determines the *in-situ* opacity, a means to correct opacity measurements to equivalent single-pass opacity values that would be observed at the pathlength of the emission outlet, and all other interface and peripheral equipment necessary for continuous operation.

3.2.2.2 *Discussion*—An opacity monitor may include the following: (*1*) sample interface equipment such as filters and purge air blowers to protect the instrument and minimize contamination of exposed optical surfaces, (*2*) shutters or other devices to provide protection during power outages or failure of the sample interface, and (*3*) a remote control unit to facilitate monitoring the output of the instrument, initiation of zero and upscale calibration checks, or control of other capacity monitor functions.

3.2.3 *opacity monitor model, n*—a specific transmissometer or opacity monitor configuration identified by the specific measurement system design, including: (*1*) the use of specific light source, detector(s), lenses, mirrors, and other optical components, (*2*) the physical arrangement of optical and other

---

[1] This practice is under the jurisdiction of ASTM Committee D-22 on Sampling and Analysis of Atmospheres and is the direct responsibility of Subcommittee D22.03 on Ambient Atmospheres and Source Emissions.

Current edition approved Feb. 10, 1998. Published April 1998.

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

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

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

[5] Available from National Institute of Standards and Technology, Gaithersburg, MD 20899.

principal components, (*3*) the specific electronics configuration and signal processing approach, (*4*) the specific calibration check mechanisms and drift/dust compensation devices and approaches, and (*5*) the specific software version and data processing algorithms, as implemented in a particular manufacturing process, at a particular facility and subject to an identifiable quality assurance system.

3.2.3.1 *Discussion*—Changing the retro-reflector material or the size of the retro-reflector aperture is not considered to be a model change unless it changes the basic attributes of the optical system.

3.2.4 *opacity monitoring system, n*—the entire set of equipment necessary to monitor continuously the in-stack opacity, average the emission measurement data, and permanently record monitoring results.

3.2.4.1 *Discussion*—An opacity monitoring system includes at least one opacity monitor with all of its associated interface and peripheral equipment and the specific data recording system (including software) employed by the end user. An opacity monitoring system may include multiple opacity monitors and a common data acquisition and recording system.

3.2.5 *optical density (OD), n*—a logarithmic measure of the amount of incident light attenuated.

3.2.5.1 *Discussion*—OD is related to transmittance and opacity as follows:

$$OD = \log_{10}(1/T) = -\log_{10}(T) = -\log_{10}(1-Op), \quad (2)$$

where Op is expressed as a fraction.

3.2.6 *transmittance, n*—the fraction of incident light within a specified optical region that passes through an optical medium.

3.2.7 *transmissometer, n*—an instrument that passes light through a particulate-laden effluent stream and measures *in situ* the optical transmittance of that light within a specified wavelength region.

3.2.7.1 *Discussion*—Single-pass transmissometers consist of a light source and detector components mounted on opposite ends of the measurement path. Double-pass instruments consist of a transceiver (including both light source and detector components) and a reflector mounted on opposite ends of the measurement path.

3.2.7.2 *Discussion*—For the purposes of this practice, the transmissometer includes the following mechanisms (1) means to verify the optical alignment of the components and (2) simulated zero and upscale calibration devices to check calibration drifts when the instrument is installed on a stack or duct.

3.2.7.3 *Discussion*—Transmissometers are sometimes referred to as *opacity analyzers* when they are configured to measure opacity.

Analyzer Zero Adjustments and Devices

3.2.8 *dust compensation, n*—a method or procedure for systematically adjusting the output of a transmissometer to account for reduction in transmitted light reaching the detector (apparent increase in opacity) that is specifically due to the accumulation of dust (that is, particulate matter) on the exposed optical surfaces of the transmissometer.

3.2.8.1 *Discussion*—The dust compensation is determined relative to the previous occasion when the exposed optics were cleaned and the dust compensation was reset to zero. The determination of dust accumulation on surfaces exposed to the effluent must be limited to only those surfaces through which the light beam passes under normal opacity measurement and the simulated zero device or equivalent mechanism necessary for the dust compensation measurement.

3.2.8.2 *Discussion*—The dust accumulation for all of the optical surfaces included in the dust compensation method must actually be measured. Unlike zero drift, which may be either positive or negative, dust compensation can only reduce the apparent opacity. A dust compensation procedure can correct for specific bias and provide measurement results equivalent to the *clean window* condition.

3.2.8.3 *Discussion*—The opacity monitor must provide a means to display the level of dust compensation. Regulatory requirements may impose a limit on the amount of dust compensation that can be applied and require that an alarm be activated when the limit is reached.

3.2.9 *external zero device, n*—an external device for checking the zero alignment of the transmissometer by simulating the zero opacity condition for a specific installed opacity monitor.

3.2.10 *simulated zero device, n*—an automated mechanism within the transmissometer that produces a simulated clear path condition or low level opacity condition.

3.2.10.1 *Discussion*—The simulated zero device is used to check zero drift daily or more frequently and whenever necessary (for example, after corrective actions or repairs) to assess opacity monitor performance while the instrument is installed on the stack or duct.

3.2.10.2 *Discussion*—The proper response to the simulated zero device is established under clear path conditions while the transmissometer is optically aligned at the installation pathlength and accurately calibrated. The simulated zero device is then the surrogate, clear path calibration value, while the opacity monitor is in service.

3.2.10.3 *Discussion*—Simulated zero checks do not necessarily assess the optical alignment, the reflector status (for double-pass systems), or the dust contamination level on all optical surfaces. (See also 6.9.1.)

3.2.11 *zero alignment, n*—the process of establishing the quantitative relationship between the simulated zero device and the actual clear path opacity responses of a transmissometer.

3.2.12 *zero compensation, n*—an automatic adjustment of the transmissometer to achieve the correct response to the simulated zero device.

3.2.12.1 *Discussion*—The zero compensation adjustment is fundamental to the transmissometer design and may be inherent to its operation (for example, continuous adjustment based on comparison to reference values/conditions, use of automatic control mechanisms, rapid comparisons with simulated zero and upscale calibration drift check values, and so forth) or it may occur each time a calibration check cycle (zero and upscale calibration drift check) is performed by applying either analog or digital adjustments within the transmissometer.

3.2.12.2 *Discussion*—For opacity monitors that do not distinguish between zero compensation and dust compensation, the accumulated zero compensation may be designated as the dust compensation. Regulatory requirements may impose a limit on the amount of dust compensation that can be applied and require that an alarm be activated when the limit is reached.

3.2.13 *zero drift, n*—the difference between the opacity monitor response to the simulated zero device and its nominal value (reported as percent opacity) after a period of normal continuous operation during which no maintenance, repairs, or external adjustments to the opacity monitor took place.

3.2.13.1 *Discussion*—Zero drift may occur due to changes in the light source, changes in the detector, variations due to internal scattering, changes in electronic components, or varying environmental conditions such as temperature, voltage or other external factors. Depending on the design of the transmissometer, particulate matter (that is, dust) deposited on optical surfaces may contribute to zero drift. Zero drift may be positive or negative.

Calibrations and Adjustments

3.2.14 *attenuator, n*—a glass or grid filter that reduces the transmittance of light.

3.2.15 *calibration drift, n*—the difference between the opacity monitor response to the upscale calibration device and its nominal value after a period of normal continuous operation during which no maintenance, repairs, or external adjustments to the opacity monitor took place.

3.2.15.1 *Discussion*—Calibration drift may be determined after determining and correcting for zero drift. For opacity monitors that include automatic zero compensation or dust compensation features, calibration drift may be determined after zero drift or dust compensation, or both, are applied.

3.2.16 *calibration error, n*—the sum of the absolute value of the mean difference and confidence coefficient for the opacity values indicated by an optically aligned opacity monitor (laboratory test) or opacity monitoring system (field test) as compared to the known values of three calibration attenuators under clear path conditions.

3.2.16.1 *Discussion*—The calibration error indicates the fundamental calibration status of the opacity.

3.2.17 *external adjustment, n*—either (*1*) a physical adjustment to a component of the opacity monitoring system that affects its response or its performance, or (*2*) an adjustment applied by the data acquisition system (for example, mathematical adjustment to compensate for drift) which is external to the transmissometer and control unit, if applicable.

3.2.17.1 *Discussion*—External adjustments are made at the election of the end user but may be subject to various regulatory requirements.

3.2.18 *intrinsic adjustment, n*—an automatic and essential feature of an opacity monitor that provides for the internal control of specific components or adjustment of the opacity monitor response in a manner consistent with the manufacturer's design of the instrument and its intended operation.

3.2.18.1 *Discussion*—Examples of intrinsic adjustments include automatic gain control used to maintain signal amplitudes constant with respect to some reference value, or the technique of ratioing the measurement and reference beams in dual beam systems. Intrinsic adjustments are either non-elective or are configured according to factory recommended procedures; they are not subject to change from time to time at the discretion of the end user.

3.2.19 *upscale calibration device, n*—an automated mechanism (employing a filter or reduced reflectance device) within the transmissometer that produces an upscale opacity value.

3.2.19.1 *Discussion*—The upscale calibration device is used to check the upscale drift of the measurement system. It may be used in conjunction with the simulated zero device (for example, filter superimposed on simulated zero reflector) or a parallel fashion (for example, zero and upscale (reduced reflectance) devices applied to the light beam sequentially). (See also 6.9.2.)

Opacity Monitor Location Characteristics

3.2.20 *installation pathlength, n*—the installation flange-to-flange separation distance between the transceiver and reflector for a double-pass transmissometer or between the transmitter and receiver for a single-pass transmissometer.

3.2.21 *monitoring pathlength, n*—the effective single pass depth of effluent between the receiver and the transmitter of a single-pass transmissometer, or between the transceiver and reflector of a double-pass transmissometer at the installation location.

3.2.22 *emission outlet pathlength, n*—the physical pathlength (single pass depth of effluent) at the location where emissions are released to the atmosphere.

3.2.22.1 *Discussion*—For circular stacks, the emission outlet pathlength is the internal diameter at the stack exit. For non-circular outlets, the emission outlet pathlength is the hydraulic diameter. For rectangular stacks:

$$D = (2LW)/(L + W), \tag{3}$$

where L is the length of the outlet and W is the width of the stack exit.

3.2.23 *pathlength correction factor (PLCF), n*—the ratio of the emission outlet pathlength to the monitoring pathlength.

3.2.23.1 *Discussion*—The PLCF is used to calculate the equivalent single pass opacity that would be observed at the stack exit.

3.2.23.2 *Discussion*—A number of similar terms are found in the literature, manufacturer operating manuals, and in common usage. OPLR (optical pathlength ratio) and STR (stack taper ratio) are common. The OPLR is equal to one half of the pathlength correction. Refer to the instrument manufacturer for the proper factor.

Opacity Monitor Optical Characteristics

3.2.24 *angle of projection (AOP), n*—the total angle that contains all of the visible (photopic) radiation projected from the light source of the transmissometer at a level greater than 2.5 % of its peak illuminance.

3.2.25 *angle of view (AOV), n*—the total angle that contains all of the visible (photopic) radiation detected by the photodetector assembly of the transmissometer at a level greater than 2.5 % of the peak detector response.

3.2.26 *instrument response time, n*—the time required for the electrical output of an opacity monitor to achieve 95 % of a step change in the path opacity.

3.2.27 *mean spectral response, n*—the mean response wavelength of the wavelength distribution for the effective spectral response curve of the transmissometer.

3.2.28 *optical alignment indicator, n*—a device or means to determine objectively the optical alignment status of opacity monitor components.

3.2.29 *peak spectral response, n*—the wavelength of maximum sensitivity of the transmissometer.

3.2.30 *photopic, n*—a region of the electromagnetic spectrum defined by the response of the light-adapted human eye as characterized in the "Source C, Human Eye Response" contained in 40CFR60, Appendix B, Performance Specification 1.

4. Summary of Practice

4.1 A comprehensive series of specifications and test procedures that opacity monitor manufacturers must use to certify opacity monitoring equipment (that is, that the equipment meets minimum design and performance requirements) prior to shipment to the end user is provided. The design and performance specifications are summarized in Table 1.

4.2 Design specifications and test procedures for (*1*) peak and mean spectral responses, (*2*) angle of view and angle of projection, (*3*) insensitivity to supply voltage variations, (*4*) thermal stability, (*5*) insensitivity to ambient light, and (*6*) an optional procedure for opacity monitors with external zero devices that states or other regulatory agencies might require are included. The manufacturer periodically selects and tests for conformance with these design specifications an instrument that is representative of a group of instruments) produced during a specified period or lot. Non-conformance with the design specifications requires corrective action and retesting. Each remanufactured opacity monitor must be tested to demonstrate conformance with the design specifications. The test frequency, transmissometer installation pathlength (that is, set-up distance) and pathlength correction factor for each design specification test are summarized in Table 2.

4.3 This practice includes manufacturer's performance specifications and test procedures for (*1*) instrument response time, (*2*) calibration error, (*3*) optical alignment sight performance - homogeneity of light beam and detector. It also includes a performance check of the spectral response of the instrument. Conformance with these performance specifications is determined by testing each opacity monitor prior to shipment to the end user. (The validity of the results of the calibration error test depends upon the accuracy of the installation pathlength measurements, which is provided by the end user.) The test frequency, transmissometer installation pathlength (that is, set-up distance) and pathlength correction factor for each performance specification test are summarized in Table 3.

4.4 This practice establishes appropriate guidelines for QA programs for manufacturers of continuous opacity monitors, including corrective actions when non-conformance with specifications is detected.

5. Significance and Use

5.1 Continuous opacity monitors are required to be installed at many stationary sources of air pollution by federal, state, and local air pollution control agency regulations. EPA regulations regarding the design and performance of opacity monitoring systems for sources subject to "Standards of Performance for New Stationary Sources" are found in 40 CFR 60, Subpart A General Provisions, §60.13 Monitoring Provisions, Appendix B, Performance Specification 1, and in applicable source-specific subparts. Many states have adopted these or very similar requirements for opacity monitoring systems.

TABLE 1 Summary of Manufacturer's Specifications and Requirements

Specification	Requirement
Spectral response	peak and mean spectral response between 500 and 600 nm: less than 10% of peak response below 400 nm and above 700 nm
Angle of view, angle of projection	≤4° for all radiation above 2.5 % of peak
Insensitivity to supply voltage variations	±1.0 % opacity max. change over specified range of supply voltage variation, or ±10 % variation from the nominal supply voltage
Thermal stability	±2.0 % opacity change per 40°F change over specified operational range
Insensitivity to ambient light	±2.0 % opacity max. change from sunrise to sunset with at least one 1-h average solar radiation level of ≥ 900 W/m^2
External audit filter access	required
External zero device repeatability - Optional	±1.0 % opacity
Automated calibration checks	check of all active analyzer internal optics with power or curvature, all active electronic circuitry including the light source and photodetector assembly, and electric or electro-mechanical systems used during normal measurement operation
Simulated zero check device	simulated condition during which the energy reaching the detector is between 90 and 190 % of the energy reaching the detector under actual clear path conditions
Upscale calibration check device	check of the measurement system where the energy level reaching the detector is between the energy levels corresponding to 10 % opacity and the highest level filter used to determine calibration error
Status indicators	manufacturer to identify and specify
Pathlength correction factor security	manufacturer to specify one of three options
Measurement output resolution	0.5 % opacity over measurement range from -5 % to 50 % opacity, or higher value
Measurement and recording frequency	sampling and analyzing at least every 10 s: calculate averages from at least 6 measurements per minute
Instrument response time	≤10 s to 95 % of final value
Calibration error	≤3 % opacity for the sum of the absolute value of mean difference and 95 % confidence coefficient for each of three test filters
Optical alignment indicator - (uniformity of light beam and detector)	clear indication of misalignment at or before the point where opacity changes ±2 % due to misalignment as system is misaligned both linearly and rotationally in horizontal and vertical planes
Calibration device repeatability	≤1.5 % opacity

TABLE 2 Manufacturer's Design Specifications – Test Frequency, Set-Up Distance, and Pathlength Correction Factor

Manufacturer's Design Specification	Test Frequency	Set-Up Distance	Pathlength Correction Factor
Spectral Response	annually, and following failure of spectral response performance check[A]	1 to 3 m when measured (not applicable when spectral response is calculated)	NA
Angle of view, angle of projection	monthly, or 1 in 20 units (whichever is more frequent)	3 m	NA
Insensitivity to supply voltage variations	monthly, or 1 in 20 units (whichever is more frequent)	3 m	1.0
Thermal stability	annually[B]	3 m (external jig for tests)	1.0
Insensitivity to ambient light	annually[B]	3 m	1.0
External zero device repeatability - optional	annually[B]	3 m	1.0
Additional design specifications[C]	as applicable		

[A] The spectral response is determined annually for each model and whenever there is a change in the design, manufacturing process, or component that might affect performance. Reevaluation of the spectral response is necessary when an instrument fails to meet the spectral response performance check.

[B] Annually, and whenever there is a change in the design, manufacturing process, or component that might affect performance.

[C] The manufacturer shall certify that the opacity monitor design meets the applicable requirements for (*a*) external audit filter access, (*b*) external zero device (if applicable), (*c*) simulated zero and upscale calibration devices, (*d*) status indicators, (*e*) pathlength correction factor security, (*f*) measurement output resolution, and (*g*) measurement recording frequency.

TABLE 3 Manufacturer's Performance Specification – Test Applicability, Set-Up Distance and Pathlength Correction Factor

Manufacturer's Performance Specification	Test Applicability	Set-Up Distance	Pathlength Correction Factor
Instrument response time	each instrument	per actual installation	per actual installation
Calibration error	each instrument	per actual installation[A]	per actual installation[A]
Acceptable tolerance comparing test to actual conditions		±10 % reset clear path zero values for subsequent monitoring[B]	±10 %, use actual value for all subsequent monitoring[B]
Optical alignment indicator - (uniformity of light beam and detector)	each instrument	per actual installation	per actual installation
Spectral response performance check	each instrument	per actual installation	per actual installation
Calibration device repeatability	each instrument	per actual installation	per actual installation

[A] Default test values are provided for use where the installation pathlength and pathlength correction factor can not be determined.

[B] When actual measurements are within ±10 % tolerance, a field performance audit can be performed rather than a field calibration error test at the time of installation.

5.2 Regulated industrial facilities are required to report continuous opacity monitoring data to control agencies on a periodic basis. The control agencies use the data as an indirect measure of particulate emission levels and as an indicator of the adequacy of process and control equipment operation and maintenance practices.

5.3 EPA Performance Specification 1 provides minimum specifications for opacity monitors and requires source owners or operators of regulated facilities to demonstrate that their installed systems meet certain design and performance specifications. Performance Specification 1 allows, as an alternative to testing each instrument, manufacturers to demonstrate conformance with certain design specifications by selecting and testing representative instruments.

5.4 Previous experience has demonstrated that EPA Performance Specification 1 does not address all of the important design and performance parameters for opacity monitoring systems. The additional design and performance specifications included in this practice are needed to eliminate many of the performance problems that have been encountered. This practice also provides purchasers and vendors flexibility, by designing the test procedures for basic transmissometer components or opacity monitors, or in certain cases, complete opacity monitoring systems. However, the specifications and test procedures are also sufficiently detailed to support the manufacturer's certification and to facilitate independent third party evaluations (if desired) of the procedures.

5.5 Purchasers of opacity monitoring equipment meeting all of the requirements of this practice are assured that the opacity monitoring equipment meets all of the design requirements of EPA Performance Specification 1, and additional design specifications that eliminate many of the operational problems that have been encountered in the field. Purchasers can rely on the manufacturer's published operating range specifications for ambient temperature and supply voltage. These purchasers are also assured that the specific instrument has been tested at the point of manufacture and demonstrated to meet the manufacturer's performance specifications for instrument response time, calibration error (based on pathlength measurements provided by the end user), optical alignment, and the spectral response performance check requirement. Conformance with the requirements of this practice ensures conformance with all of the requirements of 40CFR60, Appendix B, Performance Specification 1 except those requirements for which tests are required after installation.

5.6 The original manufacturer, or those involved in the repair, remanufacture, or resale of opacity monitors can use this practice to demonstrate that the equipment components or opacity monitoring systems provided meet appropriate design and performance specifications.

5.7 The applicable test procedures and specifications of this practice are selected to address the equipment and activities that are within the control of the manufacturer; they do not mandate testing of the opacity system data recording equipment or reporting.

5.8 This practice also may serve as the basis for third party independent audits of the certification procedures used by manufacturers of opacity monitoring equipment.

6. Procedure—Design Specification Verification

6.1 *Test Opacity Monitor Selection, Test Frequency, and Summary of Tests*:

6.1.1 Perform the design specification verification procedures in this section for each representative model or configuration involving substantially different optics, electronics, or software before being shipped to the end user.

6.1.2 At a minimum, select one opacity monitor from each month's production, or one opacity monitor from each group of twenty opacity monitors, whichever is more frequent. Test this opacity monitor for (*1*) angle of view, (*2*) angle of projection, and (*3*) insensitivity to supply voltage variations. If any design specification is unacceptable, institute corrective action according to the established quality assurance program and remedy the cause of unacceptability for all opacity monitors produced during the month or group of twenty. In addition, test all of the opacity monitors in the group and verify conformance with the design specifications before shipment to the end users.

NOTE 1—The selected opacity monitor may be the first opacity monitor produced each month, or the first opacity monitor in each group of twenty, provided that it is representative of the entire group.

6.1.3 At a minimum, test one opacity monitor each year for (*1*) spectral response, (*2*) thermal stability, and (*3*) insensitivity to ambient light. If any design specification is unacceptable, institute corrective action according to the established quality assurance program and remedy the cause of unacceptability for all affected opacity monitors. In addition, retest another representative opacity monitor after corrective action has been implemented to verify that the problem has been resolved.

6.1.4 Certify that the opacity monitor design meets the applicable requirements (see 6.7-6.13) for (*1*) external audit filter access, (*2*) external zero device (if applicable), (*3*) simulated zero and upscale calibration devices, (*4*) status indicators, (*5*) pathlength correction factor security, (*6*) measurement output resolution, and (*7*) measurement recording frequency. Maintain documentation of tests and data necessary to support certification.

6.2 *Spectral Response*:

NOTE 2—The purpose of the spectral response specifications is to ensure that the transmissometer measures the transmittance of light within the photopic range. The spectral response requirements ensure some level of consistency among opacity monitors because the determination of transmittance for effluent streams depends on the particle size, wavelength, and other parameters. The spectral response requirements also eliminate potential interfering effects due to absorption by various gaseous constituents except NO_2 which can be an interferent if present in abnormally high concentrations or over long pathlengths, or both. The spectral response requirements apply to the entire transmissometer. Any combination of components may be used in the transmissometer so long as the response of the entire transmissometer satisfies the applicable requirements.

6.2.1 *Test Frequency*— See 6.1.3. In addition, conduct this test (*1*) anytime a change in the manufacturing process occurs or a change in a component that may affect the spectral response of the transmissometer occurs or (*2*) on each opacity monitor that fails the spectral response performance check in 7.10.

6.2.2 *Specification*— The peak and mean spectral responses must occur between 500 nm and 600 nm. The response at any wavelength below 400 nm and above 700 nm must be less than 10 % of the peak spectral response. Calculate the mean spectral response as the arithmetic mean value of the wavelength distribution for the effective spectral response curve of the transmissometer.

6.2.3 *Spectral Response Design Specification Verification Procedure*—Determine the spectral response of the transmissometer by either of the procedures in 6.2.4 (Option 1) or 6.2.5 (Option 2), then calculate the mean response wavelength from the normalized spectral response curve according to 6.2.6. Option 1 is to measure the spectral response using a variable slit monochromator. Option 2 is to determine the spectral response from manufacturer-supplied data for the active optical components of the measurement system.

6.2.4 *Option 1, Monochromator*—Use the following procedure:

6.2.4.1 Verify the performance of the monochromator using a NIST traceable photopic band pass filter or light source, or both.

6.2.4.2 Set-up, optically align, and calibrate the transmissometer for operation on a pathlength of 1 to 3 m.

6.2.4.3 Connect an appropriate data recorder to the transmissometer and adjust the gain to an acceptable measurement level.

6.2.4.4 Place the monochromator in the optical path with the slit edge at an appropriate distance from the permanently mounted focusing lenses.

6.2.4.5 Use the monochromator with a range from 350 nm to 750 nm or greater resolution. Record the response of the transmissometer at each wavelength in units of optical density or voltage.

6.2.4.6 Cover the reflector for double-pass transmissometers, or turn off the light source for single-pass transmissometers, and repeat the test to compensate measurement values for dark current at each wavelength.

6.2.4.7 Determine the spectral response from the opacity monitor double pass response and the monochromator calibration.

6.2.4.8 Graph the raw spectral response of the transmissometer over the test range.

6.2.4.9 Normalize the raw response curve to unity by dividing the response at 10 nm intervals by the peak response.

6.2.5 *Option 2, Calculation from Manufacturer Supplied Data*—Obtain data from component suppliers that describes the spectral characteristics of the light source, detector, filters, and all other optical components that are part of the instrument design and affect the spectral response of the transmissometer. Ensure that such information is accurately determined using reliable means and that the information is representative of the specific components used in current production of the transmissometer under evaluation. Update the information at least every year or when new components are used, or both. Keep the information and records necessary to demonstrate its applicability to the current spectral response determination on file. Using the component manufacturer-supplied data, calculate the effective spectral response for the transmissometer as follows:

6.2.5.1 Obtain the spectral emission curve for the source. The data must be applicable for the same voltages or currents, or both, as that used to power the source in the instrument.

6.2.5.2 Obtain the spectral sensitivity curve for the detector that is being used in the system.

6.2.5.3 Obtain spectral transmittance curves for all filters and other active optical components that affect the spectral response.

6.2.5.4 Perform a point-wise multiplication of the data obtained in 6.2.5.1-6.2.5.3, at 10 nm intervals, over the range

350 to 750 nm, to yield the raw response curve for the system.

6.2.5.5 Normalize the raw response curve to unity by dividing the response at 10 nm intervals by the peak response.

6.2.6 Using the results from Option 1 or 2, as applicable, determine conformance to the specifications in 6.2.2. Then calculate the mean response wavelength (response-weighted average wavelength) by (*1*) multiplying the response at 10 nm intervals by the wavelength, (*2*) summing all the products, and (*3*) dividing by the sum of all 10 nm interval responses. Verify that this result is greater than 500 nm but less than 600 nm.

6.2.7 *Monitor-Specific Performance Check Limits*—Establish the monitor-specific performance check limits for use in conducting the Spectral Response Performance Check (7.10) as follows:

NOTE 3—The equivalent single-pass opacity from 6.2.7.2 and the single-pass opacity results corresponding to the applicable shifts from 6.2.7.3 bound the acceptable limits for the spectral response performance check.

6.2.7.1 Obtain a photopic transmission filter that has (*1*) a peak transmission ≥70 %, (*2*) maximum transmission between 550 nm and 560 nm, (*3*) half-maximum transmission between 500 nm and 520 nm, (*4*) half-maximum transmission between 600 nm and 620 nm, (*5*) transmission <10 % at any wavelength less than 450 nm or greater than 650 nm, and (*6*) a traceable calibration. Calibrate and verify the transmittance of the photopic filter as a function of wavelength initially and at least annually.

6.2.7.2 Calculate the expected single-pass opacity (assuming PLCF = 1) that would result from inserting the photopic transmission filter into the clear-stack path of the transmissometer by (*1*) performing a point-wise multiplication of the photopic transmission filter curve with the normalized transmissometer response curve (obtained from 6.2.4.9 or 6.2.5.5), (*2*) summing the products, (*3*) dividing by the sum of the 10 nm responses to form the single-pass transmission, and (*4*) calculating the equivalent single-pass opacity.

6.2.7.3 Repeat the calculations in 6.2.7.2, except use (*1*) the normalized transmissometer curve shifted by +20 nm or the amount which would cause the peak or mean spectral response to shift to the limiting value of 600 nm, whichever shift is less, and (*2*) the normalized transmissometer curve shifted by −20 nm or the amount which would cause the peak or mean spectral response to shift to the limiting value of 500 nm, whichever shift is less.

6.2.7.4 Repeat the calculations with any design changes involving the source, detector(s), or light transmitting optics. Although failure of the spectral response performance check in 7.10 does not necessarily mean that the transmissometer response is no longer within the photopic range, it is a sufficient basis to warrant additional investigation, including reevaluation of the spectral response and performance check limits, explanation, and documentation of the problem.

6.3 *Angle of View and Angle of Projection*:

NOTE 4—The purpose of the angle of view (AOV) and angle of projection (AOP) design specifications is to minimize the effects of light scattering in the measurement path when determining transmittance or opacity.

6.3.1 *Test Frequency*— See 6.1.2. Manufacturers that demonstrate and document using good engineering practice that a specific design results in an AOP of less than 0.5° are not required to perform the following AOP or AOV tests.

6.3.2 *Specification*— The total AOP and the total AOV must each be no greater than 4°. Transmissometers with an AOP of less than 0.5° are exempt from the AOV or AOP specification.

6.3.3 *AOV and AOP Design Specification Verification Procedure*—Conduct the AOV and AOP tests using the procedures given in 6.3.4-6.3.13.

6.3.4 *Transmissometer Configuration*—Conduct the AOV and AOP tests with the complete transmissometer assembly, including all parts of the measurement system that may impact the results. Provide a justification of (*1*) exactly what is included and excluded from the AOV and AOP tests and (*2*) any test procedure modifications necessary to accommodate particular designs, such as those that may be required for dual beam designs that are chopped and synchronously detected. Include the justifications with documentation of the results.

6.3.5 *Set-Up*—Focus and configure the transmissometer for a flange-to-flange installation separation distance of 3 m.

6.3.6 *Test Fixture*— Set up the AOV test fixture that incorporates (*1*) a movable light source along arcs of 3 m radius relative to the first optical surface encountered by the light beam entering the detector housing assembly, in both the horizontal and vertical directions relative to the normal installation orientation, and (*2*) recording measurements at 2.5 cm increments along the arc. Similarly, set up the AOP test fixture that incorporates (*1*) a movable photodetector along an arc of 3 m radius relative to the final optical surface encountered by the light beam exiting the transmitter housing assembly, in both the horizontal and vertical directions relative to the normal installation orientation, and (*2*) recording measurements at 2.5 cm increments along the arc.

NOTE 5—It is helpful to mount on test stands the detector and transmitter housings for single-pass transmissometers, or the transceiver for double-pass transmissometers.

6.3.7 *Alternative Test Fixture*—For the AOV test, at a distance of 3 m from a stationary light source, mount the detector housing on a turntable that can be rotated (both horizontally and vertically) in increments of 0.5° [28.6 min], corresponding to measurements displaced 2.5 cm along the arc, to a maximum angle of 5° (corresponding to a distance of 26 cm along the arc) on either side of the alignment centerline. Similarly, for the AOP test, mount transmitter housing on the turntable at a distance of 3 m relative to a stationary photodetector.

NOTE 6—If the turntable is capable of rotating only in either the horizontal or vertical direction, the detector or transmitter housing may be mounted on its side or bottom (as appropriate) to simulate the other direction.

6.3.8 *Light Source*— For the AOV test, use a small non-directional light source (less than 3 cm wide relative to the direction of movement) that (*1*) includes the visible wavelengths emitted by the light source installed in the transmissometer, (*2*) provides sufficient illuminance to conduct the test but doe snot saturate the detector, (*3*) does not include lenses or focusing devices, and (*4*) does not include non-directional characteristics, that is, the intensity in the 20° sector facing the detector assembly varies by less than ±10 %.

NOTE 7—A light source that does not meet the non-directional criteria may still be used for the AOV test, if a specific procedure is followed. This procedure is given in 6.3.9.

6.3.9 *Alternative Light Source*—For the AOV test, if the light source does not meet the non-directional criteria, rotate the light source in the vertical and horizontal planes about its normal optical axis as it is pointed at the entrance aperture of the instrument under test in order to obtain the maximum response from the instrument under test at each position in the test procedure.

6.3.10 *AOV Test Procedure*—Test the entire detector assembly (that is, transceiver for double-pass transmissometers or receiver/detector for a single-pass transmissometer). If applicable, include the mounting flanges normally supplied with the opacity monitor. Use an appropriate data recorder to record continuously the detector response during the test.

NOTE 8—Alternative AOV test procedures are necessary for certain designs. For example, a transmissometer with an optical chopper/modulator responds only to light modulated at a certain frequency. An external chopper/modulator used in conjunction with the test light source must match both the phase and duty cycle for accurate results. If this cannot be done, the manufacturer may either (*1*) provide additional electronics to drive another similar external source in parallel wit the internal source or (*2*) modify the detector electronics so that its response may be used to accurately evaluate the AOV of the test transmissometer. The manufacturer must take appropriate measures to ensure (*1*) that the background, or ambient light, and detector offsets do not significantly reduce the accuracy of the AOV measurements, (*2*) that the field of view restricting hardware normally included with the instrument are not modified in any way, and (*3*) that good engineering practice is followed in the design of the test configuration to ensure an accurate measurement of AOV.

6.3.10.1 Align the test light source at the center position and observe the detector assembly response. Optimize the test light source and optical chopper/modulator (if applicable) to maximize the detector assembly response. If the detector response is not within the normal operating range (that is, 25 to 200 % of the energy value equivalent to a clear path transmittance measurement for the transmissometer), adjust the test apparatus (for example, light source power supply) to achieve a detector response in the acceptable range.

6.3.10.2 Position the test light source on the horizontal arc 26 cm from the detector centerline (5°) and record the detector response. Move the light source along the arc at intervals not larger than 2.5 cm (or rotate the turntable in increments not larger than 0.5°) and record the detector response for each measurement location. Continue to make measurements through the aligned position and on until a position 26 cm (5°) on the opposite side of the arc from the starting position is reached. Record the response for each measurement location and over the full test range; continue recording data for all positions up to 26 cm (5°) even if no response is observed at an angle of ≤26 cm (5°) from the centerline.

6.3.10.3 Repeat the AOV test on an arc in the vertical direction relative to the normal orientation of the detector housing.

6.3.10.4 For both the horizontal and vertical directions, calculate the relative response of the detector as a function of viewing angle (response at each measurement location as a percentage of the peak response). Determine the maximum viewing angle for the horizontal and vertical directions yielding a response greater than 2.5 % of the peak response. Determine conformance to the specification in 6.3.2. Report these angles as the angle of view. Report the relative angle of view curves in both the horizontal and vertical directions. Document and explain any modifications to the test procedures as described in 6.3.11.

6.3.11 *AOP Test Procedure*—Perform this test for the entire light source assembly (that is, transceiver for double-pass transmissometers or transmitter for single-pass transmissometers). The test may also include the mounting flanges normally supplied with the opacity monitor. Conduct the AOP test using the procedures in either 6.3.12 or 6.3.13.

6.3.12 *Option 1*—Use a photodetector (*1*) that is less than 3 cm wide relative to the direction of movement, (*2*) that is preferably of the same type and has the same spectral response as the photodetector in the transmissometer, (*3*) that is capable of detecting 1 % of the peak response, and (*4*) that does not saturate at the peak illuminance (that is, when aligned at the center position of the light beam. Use an appropriate data recorder to record continuously the photodetector response during the test.

6.3.12.1 Perform this test in a dark room. If the external photodetector output is measured in a dc-coupled circuit, measure the ambient light level in the room (must be <0.5 % of the peak light intensity to accurately define the point at which 2.5 % peak intensity occurs). If the external photodetector is measured in an ac-coupled configuration, demonstrate that (*1*) ambient light level in the room, when added to the test light beam, does not cause the detector to saturate, and (*2*) turning on and off the ambient lights does not change the detected signal output. Include documentation for these demonstrations in the report.

6.3.12.2 Position the photodetector on the horizontal arc 26 cm from the projected beam centerline (5°) and record the response. Move the photodetector along the arc at ≤2.5-cm intervals (or rotate the turntable in ≤0.5° increments) until a position 26 cm (5°) on the opposite side of the arc is reached. Record the response for each measurement location and over the full test range; continue recording data for all positions up to 26 cm (5°) even if no response is observed at an angle of ≤26 cm (5°) from the centerline.

6.3.12.3 Repeat the AOP test on an arc in the vertical direction relative to the normal orientation of the detector housing.

6.3.12.4 For both the horizontal and vertical directions, calculate the relative response of the photodetector as a function of projection angle (response at each measurement location as a percentage of the peak response). Determine the maximum projection angle for the horizontal and vertical directions yielding a response greater than 2.5 % of the peak response. Determine conformance to the specification in 6.3.2. Report these angles as the angle of projection. Report the relative angle of projection curves in both the horizontal and vertical directions.

6.3.13 *Option 2*—Use this test procedure for only transmissometer designs that have previously met the AOP specification using Option 1 procedure during the preceding 12 months. Ensure that the light beam is focused at the actual flange-to-flange separation distance of the transmissometer.

6.3.13.1 Perform this test in a darkened room. Project the light beam onto a target located at a distance of 3 m from the transceiver/transmitter. Focus the light beam on the target.

6.3.13.2 Measure the beam dimensions (for example, diameter) on the target in both the horizontal and vertical directions. Calculate the maximum total angle of projection (that is, total subtended angle) based on the separation distance and beam dimensions. Compare this result to the previously measured AOP result obtained using Option 1. If the AOP results obtained by Option 1 and Option 2 do not agree within ±0.3°, repeat the test using Option 1.

6.3.13.3 Report the greater AOV result of Option 1 or Option 2 as the AOV for the test instrument.

6.4 *Insensitivity to Supply Voltage Variations*:

NOTE 9—The purpose of this design specification is to ensure that the accuracy of opacity monitoring data is not affected by supply voltage variations over ±10 % from nominal or the range specified by the manufacturer, whichever is greater. This specification does not address rapid voltage fluctuations (that is, peaks, glitches, or other transient conditions), emf susceptibility or frequency variations in the power supply.

6.4.1 *Test Frequency*— See 6.1.2.

6.4.2 *Specification*— The opacity monitor output (measurement and calibration check responses, both with and without compensation, if applicable) must not deviate more than ±1.0 % single pass opacity for variations in the supply voltage over ±10 % from nominal or the range specified by the manufacturer, whichever is greater.

6.4.3 *Design Specification Verification Procedure*:

6.4.3.1 Determine the acceptable supply voltage range from the manufacturer's published specifications for the model of opacity monitor to be tested. Use a variable voltage regulator and a digital voltmeter to monitor the rms supply voltage to within ±0.5 %. Measure the supply voltage over ±10 % from nominal, or the range specified by the manufacturer, whichever is greater.

6.4.3.2 Set-up and align the opacity monitor (transceiver and reflector for double-pass opacity monitors, or transmitter and receiver for single-pass opacity monitors) at a measurement pathlength of 3 m. Use a pathlength correction factor of 1.0. Calibrate the instrument using external attenuators at the nominal operating voltage. Insert an external attenuator with a nominal value between 10 and 20 % single-pass opacity into the measurement path and record the response. Initiate a calibration check cycle and record the low level and upscale responses.

6.4.3.3 Do not initiate any calibration check cycle during this test procedure except as specifically required. Decrease the supply voltage in increments of 2 % of the nominal value and record the one-minute or more frequent measurement response to the attenuator at each voltage (after the instrument response has stabilized) until the minimum value is reached. Initiate a calibration check cycle at the minimum supply voltage and record the low level and upscale responses. Reset the supply voltage to the nominal value and then increase the supply voltage in increments of 2 % of the nominal value and record the measurement response to the attenuator at each voltage (after the instrument response has stabilized) until the maximum value is reached. Initiate a calibration check cycle at the maximum supply voltage and record the low level and upscale responses, both with and without compensation, if applicable.

6.4.3.4 Determine conformance to specifications in 6.4.2.

6.5 *Thermal Stability*:

NOTE 10—The purpose of this design specification is to ensure that the accuracy of opacity monitoring data is not affected by ambient temperature variations over the range specified by the manufacturer.

6.5.1 *Test Frequency*— See 6.1.3. Repeat this test anytime there is a major change in the manufacturing process or change in a major component that could affect thermal stability.

6.5.2 *Specification*— The opacity monitor output output (measurement and calibration check responses, both with and without compensation, if applicable) must not deviate more than ±2.0 % single pass opacity for every 22.2°C (40°F) change in ambient temperature over the range specified by the manufacturer.

6.5.3 *Design Specification Verification Procedure*:

6.5.3.1 Determine the acceptable ambient temperature range from the manufacturer's published specifications for the model of opacity monitor to be tested. Use a climate chamber capable of operation over the specified range. If the climate chamber cannot achieve the full range (for example, cannot reach minimum temperatures), clearly state the temperature range over which the opacity monitor was tested and provide additional documentation of performance beyond this range to justify operating at lower temperatures.

6.5.3.2 Set-up and align the opacity monitor (transceiver and reflector for double-pass opacity monitors, or transmitter and receiver for single-pass opacity monitors) at a measurement pathlength of 3 m. Use a pathlength correction factor of 1.0. If the opacity monitor design introduces purge air through the housing that contains optical components of the transceiver, transmitter, or detector, operate the purge air system during this test. If the purge air does not contact internal optics and electronics, the air purge system need not be operative during the test.

NOTE 11—For double-pass systems with reflectors that can be shown to be insensitive to temperature, this test may be performed using a zero reference similar to an external zero jig, but one that is designed specifically to evaluate the temperature stability of the instrument for this test. This device must be designed to be temperature invariant so that the test evaluates the stability of the instrument, not the stability of the zero reference. Another acceptable approach is to construct a test chamber where the reflector is mounted outside the chamber at a constant temperature. The control unit, if applicable, need not be installed in the climate chamber if it is to be installed in a controlled environment by the end user.

6.5.3.3 Establish proper calibration of the instrument using external attenuators at a moderate temperature that is, 21.1 ± 2.8°C (70 ± 5°F). Insert an external attenuator with a single-pass value between 10 and 20 % opacity into the measurement path and record the response. Initiate a calibration check cycle and record the low level and upscale responses.

NOTE 12—Grid filters are recommended for these tests to eliminate temperature dependency of the attenuator value.

6.5.3.4 Do not initiate any calibration check cycle during this test procedure except as specifically stated. Continuously record the temperature and measurement response to the attenuator during this entire test. Decrease the temperature in the climate chamber at a rate not to exceed 11.1°C (20°F) per hour until the minimum temperature is reached. Note data recorded during brief periods when condensation occurs on optical surfaces due to temperature changes. Allow the opacity monitor to remain at the minimum temperature for at least one hour and then initiate a calibration check cycle and record the low level and upscale responses with and without compensation, if applicable. Return the opacity monitor to the initial temperature and allow sufficient time for it to equilibrate and for any condensed moisture on exposed optical surfaces to evaporate. Increase the temperature in the climate chamber at a rate not to exceed 11.1°C (20°F) per hour until the maximum temperature is reached. Allow the opacity monitor to remain at the maximum temperature for at lest one hour and then initiate a calibration check cycle and record the low level and upscale responses.

NOTE 13—The notations when condensation occurs are for explanatory purposes only.

6.5.3.5 Determine conformance to specifications in 6.5.2.

6.6 *Insensitivity to Ambient Light*:

NOTE 14—The purpose of this design specification is to ensure that opacity monitoring data are not affected by ambient light.

6.6.1 *Test Frequency*— See 6.1.3. Repeat this test anytime there is a major change in the manufacturing process or change in a major component that could affect the opacity monitor sensitivity to ambient light.

6.6.2 *Specification*— The opacity monitor output (measurement and calibration check responses, both with and without compensation, if applicable) must not deviate more than ±2.0 % single pass opacity when exposed to ambient sunlight over the course of a day.

6.6.3 *Design Specification Verification Procedure*:

6.6.3.1 Perform this test (*1*) at a time of maximum insolation, on a clear day where light scattering from atmospheric haze, clouds, or particulate matter are at a minimum, (*2*) when at least one 1-h solar radiation average is ≥900 W/m ^{2}, and (*3*) for a specific opacity monitor that has successfully completed the spectral response, thermal stability tests, and other design specification verification procedures.

6.6.3.2 Set-up the opacity monitor outside, with the light path in a horizontal position, and where it will be directly exposed to sunlight for the entire day. Use mounting flanges of normal length, and attach the flanges to mounting plates that extend at least 0.305 m (12 in.) above, below, and to both sides of the mounting flanges. Paint the interior surfaces of the mounting flanges and the facing surfaces of the mounting plates white. Optically align the opacity monitor (transceiver and reflector for double-pass opacity monitors, or transmitter and receiver for single-pass opacity monitors) at a measurement pathlength of 3 m on an approximate east-west axis aligned with the transit of the sun. Use a pathlength correction factor of 1.0. Calibrate the instrument using external attenuators prior to the test. Insert an external attenuator with a single-pass value between 10 and 20 % opacity into the measurement path and record the response. Initiate a calibration check cycle and record the low level and upscale responses.

6.6.3.3 Use a cosine corrected total solar radiation monitor that (*1*) is capable of detecting light from 400 to 1100 nm, (*2*) has been calibrated under natural daylight conditions to within ±5 % against industry standards, (*3*) has a sensitivity of at least 90 μA/100 W/m ^{2}, and (*4*) has a linearity with a maximum deviation of less than 1 % up to 3000 W/m^2. Place the solar radiation monitor on top of the transceiver for double-pass opacity monitors, or detector for single-pass opacity monitors. If weather covers are supplied with all opacity monitors, install the solar radiation monitor on top of the weather cover. Measure the total solar radiation according to the manufacturer's instructions.

6.6.3.4 Continuously record the opacity monitor response to the attenuator and the output of the solar radiation monitor for a period from two hours before sunrise to two hours after sunset. Record the ambient temperature during this period. Do not conduct calibration check cycles during this test more frequently than once per 24-h period or the longest interval recommended in the manufacturer's published specifications. Document and report the frequency of conducting calibration check cycles during the insensitivity to ambient light test.

6.6.3.5 If necessary, correct the measurement data for changes in instrument response due to ambient temperature variation by running a separate test with the same instrument shielded from the sunlight. Determine the maximum percent deviation in the measurement response for any six minute period during the test.

6.6.3.6 Determine conformance with the specifications 6.6.2.

6.7 *External Audit Filter Access*:

NOTE 15—The opacity monitor design must accommodate independent assessments of the measurement system response to commercially available external (that is, not intrinsic to the instrument) audit filters. These calibration attenuators may be placed within the mounting flange, air purge plenum, or other location after the projected light beam passes through the last optical surface of the transceiver or transmitter. They may also be placed in a similar location at the other end of the measurement path prior to the light beam reaching the first optical surface of the reflector or receiver. The external audit filter access design must ensure (*a*) the filters are used in conjunction with a zero condition based on the same energy level, or within 5 % of the energy reaching the detector under actual clear path conditions, (*b*) the entire beam received by the detector will pass through the attenuator, and (*c*) the attenuator is inserted in a manner that minimizes interference from the reflected light.

6.7.1 Insert the external audit filter into the system.

6.7.2 Determine whether the entire beam received by the detector passes through the attenuator and that interference from reflected light is minimal.

6.7.3 Determine whether the zero condition corresponds to the same energy level reaching the detector as when actual clear path conditions exist

6.8 *External Zero Device—Optional*:

NOTE 16—The opacity monitor design may include an external, removable device for checking the zero alignment of the transmissometer. Such a device may provide an independent means of simulating the zero opacity condition for a specific installed opacity monitor over an extended period of time and can be used by the operator to periodically verify the accuracy of the internal simulated zero device. The external zero device must be designed: (*1*) to simulate the zero opacity condition based on the same energy level reaching the detector as when actual clear path conditions exist; (*2*) to produce the same response each time it is installed on the transmissometer; and (*3*) to minimize the chance that inadvertent adjustments will affect the zero level response produced by the device. The opacity monitor operator is responsible for the proper storage and are of the external zero device and for reverifying the proper calibration of the device during all clear path zero alignment tests.

NOTE 17—The purpose of this design specification is to ensure that the external zero device design and mounting procedure will produce the same response each time that the device is installed on the transmissometer.

6.8.1 *Test Frequency*— If the optional external zero device is supplied with any opacity monitors of the subject model, select and perform this test for one representative external zero device manufactured each year for the opacity monitor model certified by this practice.

6.8.2 *Specification*— The opacity monitor output must not deviate more than ±1.0 % single pass opacity for repeated installations of the external zero device on a transmissometer.

6.8.3 *Design Specification Verification Procedure*—Perform this test using an opacity monitor that has successfully completed the tests to demonstrate insensitivity to ambient light (6.6) and which is set up and properly calibrated for a measurement pathlength of 3 meters. Install the external zero device and make any necessary adjustment to it so that it produces the proper zero opacity response from the test transmissometer. Remove the external zero device and return the test transmissometer to operation and verify that the opacity monitor output indicates 0.0 ± 0.5 % opacity. Without making any adjustments to the external zero device or the test opacity monitor, install and remove the external zero device five times. Record the zero response of the test opacity monitor to the external zero device and to the clear path condition after it is returned to operation after each installation.

6.8.4 Determine conformance with the design specification in 6.8.3.

6.9 *Calibration Check Devices*:

NOTE 18—Opacity monitors covered by this practice must include automated mechanisms to provide calibration checks of the installed opacity monitor.

6.9.1 *Simulated Zero Device*—Establish the proper response to the simulated zero device under clear path conditions while the transmissometer is optically aligned at the installation pathlength and accurately calibrated. Certify that the simulated zero device conforms to the following:

6.9.1.1 The simulated zero device produces a simulated clear path condition or low level opacity condition, where the energy reaching the detector is between 90 and 190 % of the energy reaching the detector under actual clear path conditions. Corrections for energy levels other than 100 % are permitted provided that they do not interfere with the instrument's ability to measure opacity accurately.

6.9.1.2 The simulated zero device provides a check of all active analyzer internal optics with power or curvature, all active electronic circuitry including the light source and photodetector assembly, and electric or electro-mechanical systems, and hardware and/or software used during normal measurement operation.

NOTE 19—The simulated zero device allows the zero drift to be determined while the instrument is installed on the stack or duct. Simulated zero checks, however, do not necessarily assess the optical alignment, status of the reflector (for double-pass systems), or the level of dust contamination of all optical surfaces.

6.9.2 *Upscale Calibration Device*—Certify that the device conforms to the following:

6.9.2.1 The upscale calibration device measures the upscale calibration drift under the same optical, electronic, software, and mechanical components as are included in the simulated zero check.

6.9.2.2 The upscale calibration device checks the pathlength corrected measurement system response where the energy level reaching the detector is between the energy levels corresponding to 10 % opacity and the highest level filter used to determine calibration error.

6.9.2.3 The upscale calibration check response is not altered by electronic hardware or software modification during the calibration cycle and is representative of the gains and offsets applied to normal effluent opacity measurements.

NOTE 20—The upscale calibration device may employ a neutral density filter or reduced reflectance device to produce an upscale drift check of the measurement system. The upscale calibration device may be used in conjunction with the simulated zero device (for example, neutral density filter superimposed on simulated zero reflector) or in a parallel fashion (for example, zero and upscale [reduced reflectance] devices applied to the light beam sequentially).

6.10 *Status Indicators*:

NOTE 21—Opacity monitors must include alarms or fault condition warnings to facilitate proper operation and maintenance of the opacity monitor. Such alarms or fault condition warnings may include lamp/source failure, purge air blower failure, excessive zero or calibration drift, excessive zero or dust compensation, and so forth.

6.10.1 Specify the conditions under which the alarms or fault condition warnings are activated.

6.10.2 Verify the conditions of activations in 6.10.1 on an annual basis.

6.10.3 Certify the that the system's visual indications, or audible alarms, as well as electrical outputs can be recorded as part of the opacity data record and automatically indicate when either of the following conditions are detected:

6.10.3.1 A failure of a sub-system or component which can be reasonably expected to invalidate the opacity measurement, or

6.10.3.2 A degradation of a subsystem or component which requires maintenance to preclude resulting failure.

6.11 *Pathlength Correction Factor (PLCF) Security*:

NOTE 22—The opacity monitoring system must display and record all measured opacity values (including effluent opacity measurements, zero and upscale calibration checks, and zero or dust compensation values) corrected to the emission outlet pathlength.

6.11.1 Certify that the system has been designed and constructed so that the value of the pathlength correction factor

6.11.1.1 Cannot be changed by the end user, or

6.11.1.2 Is recorded during each calibration check cycle, or

6.11.1.3 The system must provides an alarm when the value is changed from the certified value.

6.11.2 Document the option(s) that are selected and write corresponding instructions. Provide them to the end user to minimize the likelihood that the PLCF will be changed inadvertently.

6.12 *Measurement Output Resolution*:

6.12.1 Certify that the opacity monitor output, including visual measurement displays, analog outputs, or digital outputs, or combinations thereof, have a resolution ≤0.5 % opacity over the measurement range from −4.0 % opacity to 50 % opacity or higher value.

NOTE 23—The 0.5 % opacity resolution is required for determining calibration error or achieving conformance with applicable regulatory requirements.

6.13 *Measurement and Recording Frequency*:

6.13.1 Certify that each opacity monitor is designed and constructed to do the following:

6.13.1.1 To complete a minimum of one cycle of sampling and analyzing for each successive 10-s period.

6.13.1.2 To calculate average opacity values from 6 or more data points equally spaced over each 1-min period included in the average (for example, 6 measurements per 1-min average or 36 measurements per 6-min average),

6.13.1.3 To record values for each averaging period.

NOTE 24—Most regulations require recording of six-min average opacity values, however, some regulatory agencies require calculation of one-minute or other less than 6-min average values.

7. Procedure—Manufacturer's Performance Specifications

7.1 *Required Performance Tests*—Test each instrument prior to shipment to ensure that the opacity monitor meets manufacturer's performance specifications for instrument response time, calibration error, and optical alignment sight performance. Conduct a performance check of the spectral response for each instrument.

NOTE 25—These tests are performed for the specific transmissometer components (transceiver and reflector for double-pass opacity monitors or transmitter and receiver for single-pass opacity monitors), the specific control unit (if included in the installation), and any other measurement system components that are supplied by the manufacturer. The data recording system that will be employed by the end user is not required to be evaluated by these tests. Additional field tests are necessary to evaluate the complete opacity monitoring system after it is installed at the end user's facility. The field test procedures may be simplified when certain conditions are met in the conduct of the manufacturer's performance specification tests.

7.2 *Representative Test Conditions*:

7.2.1 Conduct the manufacturer's performance specification tests under conditions that are representative of the specific intended installation, whenever possible. Obtain from the end user accurate information about the installation pathlength (that is, flange-to-flange separation distance), monitoring pathlength, emission outlet pathlength, and the applicable opacity standard. Use the applicable opacity standard, monitoring pathlength, and emission outlet pathlength to select appropriate attenuators for the calibration error test and to establish the pathlength correction factor for the opacity monitor being tested. Set-up and test the transmissometer components at the same installation pathlength and the same pathlength correction factor as that of the field installation.

NOTE 26—When these conditions are met, the equivalent *clear path* setting for an external zero device can be established in conjunction with the manufacturer's calibration error test. This device can then be used in subsequent field calibration error tests to verify performance of the opacity monitor. If both the actual installation pathlength and the pathlength correction factors are within ±10 % of the values used for the manufacturer's calibration error test, the manufacturer's calibration error test results are valid and representative for the installation.

7.2.2 If actual pathlength values differ by >2 %, but ≤10 % relative to that used for the manufacturer's calibration error test, repeat the zero alignment (for installation pathlength errors) or reset the pathlength correction factor (for pathlength correction errors) prior to subsequent opacity monitoring.

NOTE 27—A field performance audit may be substituted for the field calibration error test when the above criteria are satisfied.

7.2.3 If the actual installation pathlength and pathlength correction factors exceed ±10 % of the values used for the manufacturer's calibration error test, repeat the calibration error test.

7.3 *Default Test Conditions*—If the installation pathlength, monitoring pathlength, and emission outlet pathlength cannot be determined by the manufacturer (for example, opacity monitor is intended for future resale, opacity monitor will serve as backup for multiple installations, construction of facility is not complete and so forth), test the opacity monitor at an installation pathlength of 5 m and use a pathlength correction factor of 1.0. If an opacity monitor is designed for a range of measurement pathlengths that does not include 5 m, test the opacity monitor at the middle of the range specified by the manufacturer (see example in Note 28). If the applicable opacity standard cannot be determined, assume a standard of 20 % opacity for the selection of attenuators used for the calibration error test.

NOTE 28—Example: If an opacity monitor is designed for measurement pathlengths from 6 to 12 m, use a pathlength of 9 m.

7.4 *Test Set-Up*—Conduct the performance tests of the opacity monitor in a clean environment in an area protected from manufacturing or other activities that create dust, mist, fumes, smoke, or any other ambient condition that will interfere with establishing a clear path opacity condition.

7.4.1 Set-up the transmissometer components on test stands that will facilitate adjustments to, and maintenance of, the optical alignment throughout the test procedure.

7.4.2 Use the appropriate installation pathlength as determined from 7.2, if possible, or 7.3, if necessary.

7.4.3 Adjust the focus of the transmissometer for the installation pathlength, if applicable.

7.4.4 Optically align the transmissometer components according to the written procedures of the manufacturer.

7.4.5 Verify that the alignment sight indicates proper alignment.

7.4.6 Enter the proper pathlength correction factor (if applicable) for the opacity monitor.

7.4.7 Establish proper calibration of the measurement system according to the manufacturer's written procedures.

7.4.8 Connect the opacity monitor to an appropriate data recorder for documenting the performance test results. At a minimum, use a data recorder that

7.4.8.1 Is capable of resolving 0.25 % opacity,

7.4.8.2 Has been accurately calibrated and verified according to the manufacturer's QA procedures, and

7.4.8.3 Has a sufficiently fast response to measure the instrument response time.

7.5 *Selection of Calibration Attenuators*—Using the applicable pathlength correction factor and opacity standard values from 7.2 (if possible) or 7.3 (if necessary), select calibration attenuators that will provide an opacity monitor response corrected to single-pass opacity values for the emission outlet pathlength in accordance with the following:

Applicable Standard	10 to 19 % opacity	≥20 % opacity
Low level:	5 to 10 %	10 to 20 %
Mid level:	10 to 20 %	20 to 30 %
High level:	20 to 40 %	30 to 60 %

NOTE 29—The manufacturer may elect to use additional calibration attenuators in the calibration error test. The use of additional calibration attenuators may be advantageous in demonstrating the linear range of the measurement system. Alternate calibration attenuator values may be used where required by applicable regulatory requirements (for example, state or local regulations, permit requirements, and so forth).

7.6 *Attenuator Calibrations*—Calibrate the attenuators used for the manufacturer's calibration at the frequency and according to the procedures specified in 40 CFR 60, Appendix B, Performance Specification 1, 7.1.3. For transmissometers operating over narrow bandwidths, determine the attenuator calibration values for the actual operating wavelengths of the transmissometer.

7.7 *Instrument Response Time*:

NOTE 30—The purpose of the instrument response time test is to demonstrate that the instantaneous output of the opacity monitor is capable of tracking rapid changes in effluent opacity, using the instantaneous output or signal input used to generate averages. It includes the transmissometer components and the control unit if one is included for the particular installation. The instrument response time test does not include the opacity monitoring system permanent data recorder. (A separate field test should be conducted to verify the ability of the system to properly average or integrate and record 6-min opacity values.)

7.7.1 *Specification*— The instrument response time must be less than or equal to 10 s.

7.7.2 *Instrument Response Time Test Procedure* —Using a high-level calibration attenuator, alternately insert the filter five times and remove it from the transmissometer light path.

7.7.2.1 For each filter insertion and removal, determine the amount of time required for the opacity monitor to display 95 % of the step change in opacity on the data recorder used for the test. For upscale response time, determine the time it takes to reach 95 % of the final, steady upscale reading. For downscale response time, determine the time it takes for the display reading to fall to 5 % of the initial upscale opacity reading.

7.7.2.2 Calculate the mean of the five upscale response time measurements and the mean of the five downscale response time measurements. Report each of the scale and downscale response time determinations and the mean upscale and downscale response times.

7.7.3 Determine conformance with the specification in 7.7.1. If the response time is not acceptable, take corrective action and repeat the test.

7.8 *Calibration Error*:

NOTE 31—The calibration error test is performed to demonstrate that the opacity monitor is properly calibrated and can provide accurate and precise measurements.

7.8.1 *Specification*— The calibration error must be ≤3 % opacity as calculated ad the sum of the absolute value of the mean difference and confidence coefficient for each of three test attenuators.

7.8.2 *Calibration Error Test Procedure*:

7.8.2.1 Zero the instrument. Insert the calibration attenuators (low-, mid- and high-level) into the light path between the transceiver and reflector (or transmitter and receiver).

7.8.2.2 While inserting the attenuator, ensure that the entire beam received by the detector passes through the attenuator and insert the attenuator in a manner that minimizes interference from the reflected light.

NOTE 32—See also Note 15. The placement and removal of the attenuator must be such that measurement of opacity is performed over a sufficient period to obtain a stable response from the opacity monitor.

7.8.2.3 Make a total of five non-consecutive readings for each filter. Record the opacity monitoring system output readings in single-pass percent opacity.

7.8.2.4 Subtract the single-pass calibration attenuator values corrected to the stack exit conditions from the opacity monitor responses. Calculate the arithmetic mean difference, standard deviation, and confidence coefficient of the five measurements value. Calculate the calibration error as the sum of the absolute value of the mean difference and the 95 % confidence coefficient for each of the three test attenuators. Report the calibration error test results for each of the three attenuators.

$$\bar{x} = \frac{1}{n} \sum_{i=1}^{n} x_i \qquad (4)$$

where:

x = arithmetic mean,
x_i = individual measurements, and
n = number of data points.

$$S_d = \sqrt{\frac{\sum_{i=l}^{n} x_i^2 - \frac{(\sum_{i=l}^{n} x_i)^2}{n}}{n-1}} \qquad (5)$$

where:

s_d = standard deviation.

$$CC = t_{0.975} \frac{S_d}{\sqrt{n}} \qquad (6)$$

where:

$t_{0.975}$ = t-value ($t_{0.975} = 2.776$ for $n = 5$), and
CC = confidence coefficient

7.8.2.5 Determine conformance with the specification in 7.8.1. If the calibration error test results are not acceptable, take corrective action, recalibrate the opacity monitor according to the manufacturer's written instructions, and repeat the calibration error test.

7.9 *Optical Alignment Indicator – (Uniformity of Light Beam and Detector)*:

NOTE 33—Each transmissometer must provide a means for visually determining that the instrument is optically aligned. The purpose of this specification is to ensure that the alignment device is capable of clearly indicating when the transmissometer components are misaligned. The performance test procedure will also detect opacity monitors where the accuracy of opacity measurements is adversely affected by the use of the light beams having non-uniform intensity, or the use of non-uniform detectors, or inefficient or poor quality retro-reflector material.

7.9.1 *Specification*— The alignment sight must clearly indicate that the unit is misaligned when an error of ±2 % single-pass opacity occurs due to shifts in the optical alignment of the transmissometer components. For opacity monitor designs that include automatic beam steering (that is beam position sensing and an active means for adjusting alignment so that centered alignment is maintained even with slowly changing misalignment conditions), an alarm must be activated when the alignment is varied beyond the manufacturer's specified range of angular tolerance is unable to maintain alignment.

NOTE 34—Modifications of the alignment indicator test procedures for systems with beam steering are included in 7.9.7.

7.9.2 *Alignment Indicator Performance Test Procedure*—Conduct the alignment indicator test according to the procedures in 7.9.3-7.9.7.

NOTE 35—The test procedure can be modified to accommodate moving of either component of the transmissometer to achieve equivalent geometric misalignment as described in 7.9.3-7.9.6. Alignments tests may be performed in the horizontal or vertical planes of the instrument and the instrument components may be turned on their side to accommodate the tests.

7.9.3 *Set-up*:

7.9.3.1 Set up the transmissometer on test stands that allow adjustments for the rotational and translational misalignment tests.

7.9.3.2 Optically align the transceiver and reflector (double-pass opacity monitor) or transmitter and receiver (single-pass opacity monitor) according to the manufacturer's written instructions. Verify that all alignment indicator devices show proper alignment.

7.9.3.3 Conduct the alignment indicator performance test with a clear path condition. Alternatively, insert an external attenuator that produces a response ≤10 % single-pass opacity into the measurement path turn it approximately 3° from normal to the light path to eliminate surface reflection, and record the indicated opacity.

7.9.4 *Case 1: Single and Double Pass Opacity Monitors*:

7.9.4.1 Slowly tilt the transceiver (double-pass opacity monitor) or transmitter (single-pass opacity monitor) upward in the vertical plane (for example, adjust the appropriate alignment bolts or mounting mechanism) relative to the reflector (double-pass opacity monitor) or receiver (single-pass opacity monitor) until an error of ±2 % opacity is first indicated on the data recorder. Verify that the alignment indicator shows misalignment.

7.9.4.2 Illustrate and record the alignment indicator and the degree of misalignment shown.

7.9.4.3 Return the system to its aligned condition.

7.9.4.4 Repeat the entire procedure by tilting the transceiver in the opposite (downward) direction.

7.9.4.5 Repeat the rotational misalignment check of the transceiver or transmitter in the horizontal plane (both to the left and right) and again illustrate and record the visual depiction of the alignment for each step of the procedure.

7.9.5 *Case 2, Single-Pass Opacity Monitors Only*

7.9.5.1 Slowly tilt the receiver in the vertical plane (for example, adjust the appropriate alignment bolts or mounting mechanism) until an error of ±2 % opacity is first indicated on the data recorder, Verify that the alignment indicator shows misalignment.

7.9.5.2 Illustrate and record the alignment indicator and the degree of misalignment shown.

7.9.5.3 Return the system to its aligned condition and again draw the alignment indicator.

7.9.5.4 Repeat the entire procedure by tilting the receiver in the opposite direction.

7.9.5.5 Repeat the rotational misalignment check of the receiver in the horizontal plane (both to the left and right) and again illustrate and record the visual depiction of the alignment for each step of the procedure.

7.9.6 *Case 3: Single and Double Pass Opacity Monitors*:

7.9.6.1 Achieve lateral misalignment of the transceiver or transmitter relative to the reflector or receiver by slowly moving either assembly linearly to the left until a positive or negative error of ±2 % opacity is first indicated on the data recorder. Verify that the alignment indicator shows lateral misalignment of the transceiver or transmitter relative to reflector or receiver.

7.9.6.2 Illustrate and record the alignment indicator and the degree of misalignment shown.

7.9.6.3 Return the system to its aligned condition and again draw the alignment indicator.

7.9.6.4 Repeat the entire procedure by moving the same component to the right.

7.9.6.5 Repeat the test in the vertical plane (both above and below the aligned position) and again illustrate and record the visual depiction of the alignment for each step of the procedure.

7.9.7 *Assessment*—Determine conformance with the specification in 7.9.1.

NOTE 36—The performance of the alignment indicator is acceptable if: (*1*) for each case of rotational or translational misalignment, misalignment is clearly shown when an error of ±2 % single-pass opacity first occurs in each direction, and (*2*) proper alignment status is consistently indicated when the opacity monitor is optically aligned. A clear indication of misalignment is one that is objectively apparent relative to reference marks or conditions; an alignment device that requires a subjective judgement of the degree of misalignment is not acceptable.

7.9.8 *Automatic Beam Steering*:

7.9.8.1 If the design includes automatic beam steering, investigate each case of rotational and translational misalignment. Vary the alignment over the manufacturer's specified range of angular tolerance for which the alignment is maintained and for which the opacity is maintained within ±2 % single pass opacity.

7.9.8.2 During each misalignment test, record the angular misalignment where the alarm is activated.

7.9.8.3 Determine conformance with the specification in 7.9.2.

NOTE 37—Acceptable performance is indicated if (*1*) the alarm is activated or misalignment is clearly show at, or before, the angular tolerance specified by the manufacturer is reached, and (*2*) for translational misalignment, an alarm is activated or misalignment is clearly shown at, or before, an error of ±2 % single-pass opacity first occurs in each direction.

7.10 *Special Response Performance Check*:

NOTE 38—This performance check provides a simple method to ensure that the special response of each instrument satisfies the spectral response design specifications of 6.2. The performance check uses a photopic transmission filter placed in the measurement beam and comparison with a range of expected responses determined from Monitor-Specific Performance Check Limits (6.2.7).

7.10.1 *Specification*— The transmissometer response to the photopic transmission filter used to establish performance check limits, after correction of the response to account for the applicable pathlength correction factor, must be within ±2 % opacity of the range defined by the maximum and minimum responses (determined in 6.2.7 in units of percent opacity.

7.10.2 *Spectral Response Performance Check Procedure*:

7.10.2.1 Insert the photopic transmission filter used to establish the performance check limits into the opacity monitor measurement beam after the calibration error test has been completed. Record the opacity monitor response to the photopic filter in units of percent opacity.

7.10.2.2 Correct the opacity monitor response to the equivalent value corresponding to a pathlength correction factor of 1.

7.10.2.3 Compare the corrected response to the acceptable limits and determine conformance with the specification in 7.10.1.

7.10.2.4 If an unacceptable result is obtained, do not assume that the spectral response design requirements are met. Investigate the causes for an unacceptable result. Unless a clear explanation of the problem is apparent, repeat Spectral Response Design Specifications Verification Procedure (6.2.3) and recalibrate the photopic filter.

7.11 *Calibration Device Value and Repeatability*:

NOTE 39—The purpose of this specification is to verify that the upscale calibration device response is repeatable and provides results consistent with the use of external filters. This specification may also be applied to additional internal calibration check devices (values), if provided in the instrument.

7.11.1 *Specification*— The 95 % confidence coefficient for repeated measurements of the upscale calibration device must be less than 1.5 % opacity. The upscale calibration device must be assigned a value relative to the calibration error test results for the specific opacity monitor.

7.11.2 *Calibration Device Repeatability Test Procedure*—Perform this procedure immediately after successfully completing the calibration error test for the opacity monitor. Do not make any adjustments to the opacity monitor until after this procedure has been completed. Make seven non-consecutive measurements of each internal device and record the opacity monitor responses.

7.11.2.1 Calculate the 95 % confidence coefficient using the same procedures as that used in the calibration error test. (See 7.8.2.4).

7.11.2.2 Determine conformance to the specification in 7.11.1.

7.11.2.3 Assign values to the upscale calibration device(s) relative to the calibration error test results. Construct a calibration curve by linear regression analysis through zero of the results of the calibration error test (x-axis are correct values and y-axis are the corresponding opacity monitor responses). Using the mean of the five measurement responses for each upscale calibration device as the y-axis value, determine in corresponding x-axis value from the calibration curve. Assign this value to the internal upscale calibration device.

8. Quality Assurance Guidelines for Opacity monitor Manufacturers

8.1 *General*—The products shall be manufactured under a quality program that ensures that like products, subsequently made, have the same reliability and quality as those originally examined to determine compliance with this design specification. To establish and maintain such a program, the manufacturer shall be guided by industry practice, its quality controls, and by this set of guidelines. These guidelines are supported by various standards and by industry practice.

8.1.1 *Applicable Documents*—This document is an adaptation of and the referred to the following standards for additional guidance:

ISO/DIS 9004 Quality Management and Quality System Elements-Guidelines

ANSI/NCSL Z 540-1-1994, Calibration Laboratories and Measuring Equipment - General Requirements

8.1.2 *General Vocabulary*—Terms used in this document are defined by:

ISO 842, Quality Vocabulary

8.2 *Quality System*:

8.2.1 *Management Responsibility*:

8.2.1.1 *Quality Policy*— The management of a company shall develop and promulgate a corporate quality policy. Management shall ensure that the corporate policy is understood, implemented and maintained.

8.2.1.2 *Quality Objectives*—Based on this policy, key quality objectives shall be defined, such as fitness for use, performance, reliability, safety, and so forth.

8.2.1.3 *Quality Management Systems*—A documented system shall be developed, established and implemented for the product as a means by which stated quality policies and objectives can be realized. The quality system should ensure that: (*1*) it is understood and effective; (*2*) products actually do satisfy customer expectations; (*3*) emphasis is placed on problem prevention rather than dependence on detection after occurrence; (*4*) causes, not only symptoms, of a problem are found, and that corrections are comprehensive, touching any activity that has a bearing on quality; and (*5*) feedback is generated that can be used at the product or process design stage for correcting problems and improving product. Management shall provide the resources essential to the implementation of quality policies and objectives.

8.2.2 *Quality System Documentation and Records*—The elements requirements and provisions adopted for the quality management system shall be documented in a systematic and orderly manner.

8.2.2.1 Documentation shall be legible, clean, readily, identifiable and maintained in an orderly manner.

8.2.2.2 The quality management system shall establish and require the means for identification, collection, filing, storage, maintenance, retrieval and disposition of pertinent quality documentation and records. Methods shall be established for making changes, modifications, revisions or additions to the contents of applicable documentation in a controlled manner.

8.3 *Corrective Action Program*:

8.3.1 *Introduction*— There shall be a comprehensive defect analysis/corrective action program for reporting and following-up on product and program deficiencies.

8.3.2 *Assignment of Responsibility*:

8.3.2.1 The responsibility and authority for instituting corrective action shall be defined as part of the quality system.

8.3.2.2 The coordination, recording and monitoring of corrective action shall be assigned to a specific person or group within the organization. (The analysis and execution of any corrective action may involve a variety of people from such areas as sales, design, production engineering, production and/or quality control.)

8.3.3 *Deficiencies*:

8.3.3.1 Deficiencies shall be evaluated in terms of their potential impact on product quality, reliability, safety, performance and customer satisfaction.

8.3.3.2 The relationship between cause and effect should be determined. The root cause should be determined before planning and implementing corrective measures. Careful analysis shall be given to the product and all related processes, operations, records, and so forth.

8.3.3.3 Controls of processes and procedures shall be implemented to prevent recurrence of the problem. When the corrective measures are implemented, their effect shall be monitored in order to ensure desired goals are met.

8.3.3.4 Permanent changes resulting from corrective action shall be incorporated into the work instructions, manufacturing processes, product specifications and/or the quality manual.

8.4 *Quality System Certification*—Companies with ISO 9001/9002 certification, companies meeting the requirements of ANSI/ASQC Q90 (Q91 or Q92), companies meeting the requirements of nationally recognized test laboratories (NRTLs) where the manufactured product bears the mark (or marks) of the NRTL(s), or companies with an equivalent independently and periodically verified quality system, and which adopt this specification as part of their product definition shall be deemed to meet all of the above quality assurance guidelines. Companies meeting these conditions shall attach the applicable certification to the manufacturer's certification of conformance report as proof of such designation.

9. Report

9.1 Summarize the design and performance (see Table 1, Table 2 and Table 3) data in the report. See Fig XI.1 for an example.

9.2 Include all descriptive information, such as:

9.2.1 Manufacturer or supplier information,

9.2.2 Opacity monitor information,

9.2.3 User information, and

9.2.4 Installation information.

10. Keywords

10.1 continuous opacity monitor; design specification; performance specification; transmissometer

APPENDIX

(Nonmandatory Information)

X1. DATA SUMMARY FORM

X1.1 Fig. X1.1 is an example data form to summarize data to certify conformance with design and performance specifications.

This document is provided by (company name), an (original manufacturer, supplier, remanufacturer, or service facility), of/for opacity monitoring systems that are intended to comply with standards of performance established by the US EPA 40CFR60, Appendix B, Performance Specification 1, Performance Specifications for Opacity Monitors. This EPA specification references the above ASTM Standard Practice, which may be used by the manufacturer or supplier to demonstrate that the designated opacity monitor meets those performance requirements that can be tested and verified by the supplier prior to field installation. Data in this summary document (Part I) have been generated in compliance with the procedures and specifications shown in the ASTM Standard Practice, SPXXXX. These data confirm that the designated opacity monitor meets or exceeds the requirements of this Standard Practice.

I. MANUFACTURER/SUPPLIER INFORMATION
Company name ____________________________
Location _________________________________

II. OPACITY MONITOR INFORMATION
Model______________________
Transceiver type _______________
Transceiver serial no. ___________
Reflector type _________________
Reflector serial no. ____________
Control unit serial no. ___________
Software version no. ____________

III. USER INFORMATION
Company _______________________________
Plant ____________________________________
Process/boiler ____________________________
Location _________________________________

IV. INSTALLATION INFORMATION
Monitoring pathlength (depth of effluent) ________
Installation pathlength (flange to flange) _________
Emission outlet pathlength (stack exit) __________
PLCF or (OPLR) _________
Facility opacity standard, % opacity ____________

FIG. X1.1 Data Summary Form

PART I—DESIGN AND PERFORMANCE SPECIFICATIONS-TESTED AT MANUFACTURER'S FACILITY

Conformance with design specifications is demonstrated by testing two separate opacity monitors, each of which is representative of standard production. One opacity monitor is selected and tested annually and the other is selected from either a production lot of instruments not to exceed 20 in size, or from monthly production, and tested in accordance with procedures described in the SPXXXX. The tests associated with each of the above selected analyzers is required to be repeated anytime there is a critical component change that is substantial, hardware or software change, or manufacturing process change that could affect performance with respect to said design specifications. The test data derived from each of the above two described analyzers is summarized below.

1. Design Specifications Verified Through Tests Prescribed For An Annually, or More Often, Selected Opacity Monitor

The opacity monitor that tested to demonstrate the following design parameters was selected on the basis of an annual selection ____ , or following a major change in the design or construction of the monitor ____.

OPACITY MONITOR INFORMATION

Model______________________
Transceiver type ______________
Transceiver serial no. ___________
Reflector type ________________
Reflector serial no. _____________
Control unit serial no. ___________
Software version no. ____________

TESTS PERFORMED BY:
______________________________ DATE: ________________

TEST DATA REVIEWED AND CERTIFIED BY:
______________________________ DATE: ________________

1.1 *Spectral Response*

Data listed below were obtained by calculation ____, or by actual measurement using a monochrometer ____. A description of either the calculations or the measurement test setup are included in Attachment A.

Parameter	Specification	Actual Test Result
Peak response	Between 500-600 nm	
Mean response	Between 500-600 nm	
Max response beyond 700 nm	Less than 10% of peak	
Max response less than 400 nm	Less than 10% of peak	

FIG. X1.1 Data Summary Form *(continued)*

1.2 *Thermal Stability*

Parameter	Specification	Actual Test Result
Tested range, min temp	Mfgr specified, °C (°F)	
Tested range, max temp	Mfgr specified, °C (°F)	
Nominal measurement value	0-10% opacity	
Measurement drift, max deviation from nominal measurement value	≤ 2% opacity/40 °C (°F)	
Zero drift from nominal without compensation	≤ 2% opacity/40 °C (°F)	
Zero drift from nominal with compensation	≤ 2% opacity/40 °C (°F)	
Span drift from nominal without compensation	≤ 2% opacity/40 °C (°F)	
Span drift from nominal with compensation	≤ 2% opacity/40 °C (°F)	

1.3 *Insensitivity to Ambient Light*

Parameter	Specification	Actual Test Result
Max solar intensity	900 W/m^2	
Nominal measurement value	0-10% opacity	
Measurement drift, max deviation from nominal measurement value	≤ 2% opacity	
Drift was corrected for thermal effects, yes or no	Mfgr specified	
Zero drift from nominal without compensation	≤ 2% opacity	
Zero drift from nominal with compensation	≤ 2% opacity	
Span drift from nominal without compensation	≤ 2% opacity	
Span drift from nominal with compensation	≤ 2% opacity	

1.4 *Calibration Device Availability*

Parameter	Specification	Availability/Value
External zero device	Optional	
Ext zero device repeatability	≤ 1% opacity	
External filter access	To be available	

FIG. X1.1 Data Summary Form *(continued)*

1.5 *Zero/upscale calibration check apparatus*

Parameter	Specification	Test Result
Indicated response to simulated zero calibration device	0 ± 0.5% opacity	
Simulated Zero Check	Simulated condition during which the energy reaching the detector is between 90 and 190% of the energy reaching the detector under actual clear path conditions *	
Response to upscale calibration device without electronic hardware or software modification	+10% opacity to highest calibration error attenuator value	
Does automatic zero and span calibration devices check all active optics and electronics?	Required	
Is automatic correction provided for zero drift?	Mfgr to specify (Y/N)	
	If yes, specify freq	
Is automatic correction provided for dust accumulation on exposed optics?	Mfgr to specify (Y/N)	
	If yes, specify freq	
Is automatic correction provided for span/cal drift?	Mfgr to specify (Y/N)	
	If yes, specify freq	

Note: * Negative opacity values of this magnitude can be calculated from the detector or preamplifier output by measuring the equivalent optical energy detected in the clear path condition and that produced by the zero calibration check device.

1.6 *PLCF (OPLR) Security Precautions*

Condition	Specification	As Supplied (Y/N)
Original certified value is fixed and not adjustable by user	One or more of listed conditions to be provided	
Value is output with zero and span values during each calibration cycle	One or more of listed conditions to be provided	
Flag (alarm) is activated when changed from original certified or permanently recorded value	One or more of listed conditions to be provided	

FIG. X1.1 Data Summary Form *(continued)*

1.7 *Faults and Alarm (Mfgr to specify)*

Fault Conditions (Note 1&3)	**Specified Indication**	**Actual Indication**
Conditions tested	Audible or visual, and electrical	Tested output
	Same	
	Same	
	Same	
Alarm Conditions (Note 2&3)	**Specified Indication**	**Actual Indication**
Conditions tested	Audible or visual, and electrical	Tested output
	Same	
	Same	
	Same	
	Same	
	Same	

Note 1) Fault conditions are those conditions which, when they occur, are deemed by the manufacturer to result in performance which is not in compliance with this performance specification.

Note 2) Alarm conditions are those conditions for which the manufacturer recommends review and/or corrective action by trained service personnel as appropriate to prevent further deterioration of instrument performance which could result in performance not in compliance with this specification.

Note 3) Manufacturer may use other nomenclature to designate either general or specific alarms and/or faults, as long as they are appropriately defined in the operators manual.

1.8 *Miscellaneous*

Parameter	**Specification**	**Test Result**
Resolution of visual measurement indication, if provided	≤ 0.5% opacity	
Resolution of analog output measurement indication	≤ 0.5% opacity	
Resolution of serial digital output, if provided	≤ 0.5% opacity	
Bipolar range of visual measurement indication	+50% opacity or more to -4% opacity or less	
Capability of analog output measurement indication to indicate negative values to at least -4% opacity	Required	
Are means available to monitor daily zero and span drift before correction?	Optional	
Is span drift corrected for zero drift in above method?	Optional	
Are means available to monitor dust accumulation on exposed optical surfaces?	Optional	

FIG. X1.1 Data Summary Form *(continued)*

What surfaces are monitored for dust accumulation?	Mfgr to specify, if applicable	
Is an alarm provided for excessive dust accumulation?	Mfgr to specify, if automatic correction is provided	
What level of dust accumulation triggers the above alarm?	Mfgr to specify, if applicable	
Is dust level measured separately from the accumulative zero drift?	Mfgr to specify	
Are all dust (if provided), zero, and span values corrected to stack exit conditions?	Required	
What is the normal update interval for opacity measurements?	10 sec max	
Do longer term opacity averages include at least 6 approximately equaly distributed individual measurement values per minute?	Required	

FIG. X1.1 Data Summary Form *(continued)*

2. Design Specifications Verified Through Tests Prescribed for an Opacity Monitor Selected on a Monthly Basis, or From Each Production Lot

The opacity monitor that was selected and tested to demonstrate the following design parameters was selected on the basis of a monthly selection ____, a manufacturing lot not to exceed 20 in size ____, or following a major change in the design or construction of the monitor ____.

OPACITY MONITOR INFORMATION
Model ____________________
Transceiver type ______________
Transceiver serial no. ___________
Reflector type _______________
Reflector serial no. _____________
Control unit serial no. ___________
Software version no. ____________

TESTS PERFORMED BY:
______________________________ DATE: ________________

TEST DATA REVIEWED AND CERTIFIED BY:
______________________________ DATE: ________________

2.1 *Angle of View*

Transmissometer is exempt from angle of view specification because the angle of projection has been demonstrated to be less than______degrees.

Portion of opacity monitor included in the test: __________________________
____

Portion of opacity monitor excluded in the test: __________________________
____

Light source used in the test: directional _____, or non-directional _____
Were detector/measurement electronics modified to measure response to designated light source: (Y/N) _______. If so, describe modifications in attachment B.

Parameter	**Specification**	**Actual Test Result**
Angle of view, horizontal	≤ 4° for all radiation providing a response of ≥ 2.5% of peak response	
Angle of view, vertical	≤ 4° for all radiation providing a response of ≥ 2.5% of peak response	

FIG. X1.1 Data Summary Form *(continued)*

2.2 *Angle of Projection*

Transmissometer is exempt from angle of projection specification because the angle of projection has been demonstrated to be less than______degrees.

Option 1 Procedure
Portion of opacity monitor included in the test:______________________________

Portion of opacity monitor excluded in the test: ______________________________

Photodetector used in test: ______________________________

____ If tests were conducted with dc coupled measurement circuit, was ambient light level less than 0.5% of peak light intensity? (Y/N) _______

____ If tests were conducted with ac coupled measurement circuit, was it demonstrated that ambient light levels did not saturate the detector? (Y/N) ______; and was it demonstrated that turning on/off ambient lights did not affect measurements? (Y/N) ______.

Parameter	Specification	Actual Test Result
Angle of projection, horizontal	≤ 4° for all radiation providing a response of ≥ 2.5% of peak response	
Angle of projection, vertical	≤ 4° for all radiation providing a response of ≥ 2.5% of peak response	

Option 2 Procedure (For transmissometer designs that have previously met the AOP specification using Option 1 procedure during the preceding 12 months)
Distance from transceiver/transmitter to target _____________
Beam dimension (diameter) in the vertical direction ___________
Beam dimension (diameter) in the horizontal direction __________
Option 2 Result: (total subtended angle):___________ degrees.
Option 1 Result (angle of projection): _____________ degrees
Difference (Option 1 result minus Option 2 result) ___________ degrees. If the results do not agree within 0.3 degrees, repeat the test using Option 1.

FIG. X1.1 Data Summary Form *(continued)*

2.3 *Insensitivity to supply voltage variations*

Manufacturers specified nominal voltage: __________
Manufacturers specified operating voltage range, if specified: ___________________

Parameter	**Specification**	**Actual Test Value**
Min test voltage	-10% from nom, or mfgrs min specified operating voltage, whichever is lesser	
Max test voltage	+10% from nom, or mfgrs max specified operating voltage, whichever is greater	
Nominal measurement value	0-10% opacity	
Measurement drift, max deviation from nominal measurement value from nominal to max ac voltage	± 1% opacity	
Measurement drift, max deviation from nominal measurement value from nominal to min ac voltage	± 1% opacity	
Zero drift from nominal to min ac voltage without compensation	± 1% opacity	
Zero drift from nominal to min ac voltage with compensation	± 1% opacity	
Span drift from nominal to min ac voltage without compensation	± 1% opacity	
Span drift from nominal to min ac voltage with compensation	± 1% opacity	
Zero drift from nominal to max ac voltage without compensation	± 1% opacity	
Zero drift from nominal to max ac voltage with compensation	± 1% opacity	
Span drift from nominal to max ac voltage without compensation	± 1% opacity	
Span drift from nominal to max ac voltage with compensation	± 1% opacity	

FIG. X1.1 Data Summary Form *(continued)*

3. Performance Specifications Verified by Tests Prescribed for Each Specific Opacity Monitor.

The following tests were performed individually on the specific instrument described in the beginning of this test report. Further, the following signatures attest to the fact that the design and performance specifications tested on previous opacity monitors, as described in Sections 1 and 2, are representative of the design and performance of this specific monitor.

TESTS PERFORMED BY:
_________________________________ DATE: ________________

TEST DATA REVIEWED AND CERTIFIED BY:
_________________________________ DATE: ________________

3.1 *Calibration error*

Filter	Specify Group, Group I or II	Actual Filter Value	Specified Cal Error	Actual Cal Error
Low	Group		3%	
Mid	Group		3%	
High	Group		3%	

Note: Group I filters are 5-10, 10-20, 20-40 percent opacity (low, mid, high)
Group II filters are 10-20, 20-30, 30-60 percent opacity (low, mid, high)

3.2 *Misalignment indication*

This opacity monitor uses (a) manual alignment and visual alignment sighting device (Y/N) ____, or b) automatic beam steering (Y/N) ______.

3.2.1 *For manually aligned opacity monitors with visual alignment sighting indicator:*

A. Rotational misalignment

Parameter	Specification	Test Result
Nominal measurement value	0-10% opacity	
Indication of centered alignment	Acceptable? (Y/N)	
Clear indication of misalignment for rotational misalignment for transceiver/transmitter in upward vertical direction which causes 2% opacity change	Acceptable? (Y/N)	
Clear indication of misalignment for rotational misalignment for transceiver/transmitter in downward vertical direction which causes 2% opacity change	Acceptable? (Y/N)	
Clear indication of misalignment for rotational misalignment for transceiver/transmitter in horizontal right direction which causes 2% opacity change	Acceptable? (Y/N)	
Clear indication of misalignment for rotational	Acceptable? (Y/N)	

FIG. X1.1 Data Summary Form *(continued)*

misalignment for transceiver/transmitter in horizontal left direction which causes 2% opacity change		

B. Lateral misalignment, same test conditions

Parameter	Specification	Test Result
Clear indication of misalignment for lateral movement to the left which causes 2% opacity change	Acceptable? (Y/N)	
Clear indication of misalignment for lateral movement to the right which causes 2% opacity change	Acceptable? (Y/N)	
Clear indication of misalignment for lateral movement in upward direction which causes 2% opacity change Clear indication of misalignment with above movement	Acceptable? (Y/N)	
Clear indication of misalignment for lateral movement in downward direction which causes 2% opacity change Clear indication of misalignment with above movement	Acceptable? (Y/N)	

3.2.2 *For opacity monitors with automatic beam steering.*

Parameter	Specification	Test Result
Nominal measurement value	0-10% opacity	
Indication of centered alignment	Acceptable? (Y/N)	
Degree of rotational misalignment for transceiver/transmitter in upward vertical direction which triggers alarm	Mfgr to specify	
Degree of rotational misalignment for transceiver/transmitter in downward vertical direction which triggers alarm	Mfgr to specify	
Degree of rotational misalignment for transceiver/transmitter in horizontal right direction which triggers alarm	Mfgr to specify	
Degree of rotational misalignment for transceiver/transmitter in horizontal left direction which triggers alarm	Mfgr to specify	

FIG. X1.1 Data Summary Form *(continued)*

Parameter	Specification	Test Result
Lateral movement of transceiver/transmitter in upward vertical direction which causes an indication of misalignment	Mfgr to specify movement	
What is maximum deviation of opacity from nom when opacity monitor is misaligned as above from centered to value noted?	≤ 2% opacity	
Lateral movement of transceiver/transmitter in downward vertical direction which causes an indication of misalignment	Mfgr to specify movement	
What is maximum deviation of opacity from nom when opacity monitor is misaligned as above from centered to value noted?	≤ 2% opacity	
Lateral movement of transceiver/transmitter in horizontal right direction which causes an indication of misalignment	Mfgr to specify movement	
What is maximum deviation of opacity from nom when opacity monitor is misaligned as above from centered to value noted?	≤ 2% opacity	
Lateral movement of transceiver/transmitter in horizontal left direction which causes an indication of misalignment	Mfgr to specify movement	
What is maximum deviation of opacity from nom when opacity monitor is misaligned as above from centered to value noted?	≤ 2% opacity	

3.3 *Spectral Response Repeatability*

Date of photopic filter calibration ____________________
Peak transmission of photopic filter ____________________
Calculated nominal response of analyzer to photopic filter ____________________, % opacity
Calculated allowable variation of the response to photopic filter:
OP, high ______________, OP, low ____________________
Above opacity values converted to stack exit values according to the specific PLCF (OPLR) established for this installation: PLCF (OPLR) ________________
OPc, nom ____________, OPc, high ______________, OPc, low ______________
Actual measured response of the instrument to listed photopic filter ____________ % opacity
Is measured response within previously calculated range (Y/N) ____________

FIG. X1.1 Data Summary Form *(continued)*

3.4 *Intrinsic opacity monitor settings/adjustments*

List all configurable parameters to obtain the performance described in this report. These parameters typically include calibration check intervals, calibration check correction, procedure settings relating to flange-to-flange separation distance, range, averaging time, alarms, etc.

____

____

____

____

____

4. Quality Assurance Program

4.1 *ISO, ANSI/ASQC, or other Quality System Certification*

Is the company which prepared this report certified according to ISO quality standards, ANSI/ASQC (QC 90 or 91) or other applicable quality standard (Y/N) ____________. If so, to what classification ________________ and on what date _______________. Attach certificate of such designation as attachment C.

4.2 *QA Guideline Compliance*

Has the company which prepared this document established and maintained a QA/QC program that is in compliance with the guidelines specified in the ASTM SPXXXXX, (Y/N) ________. If so, please attach a description of the quality program in attachment C, and indicate the person responsible for the integrity of this quality program ____________________________________

Suppliers who comply with 4.1 and not 4.2 are required to supply all supporting test data with this report.

FIG. X1.1 Data Summary Form *(continued)*

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 D6228: Standard Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Flame Photometric Detection

CFR Section(s): 40 CFR 60.334(h)(1)

Standards Body: American Society for Testing and Materials

APPROVED

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

Designation: D 6228 – 98

Standard Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Flame Photometric Detection[1]

This standard is issued under the fixed designation D 6228; 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 provides for the determination of individual volatile sulfur-containing compounds in gaseous fuels by gas chromatography (GC) with flame photometric detection (FPD). The detection range for sulfur compounds is from 20 to 20 000 picograms (pg) of sulfur. This is equivalent to 0.02 to 20 mg/m^3 or 0.014 to 14 ppmv of sulfur based upon the analysis of a 1-mL sample.

1.2 This test method describes a GC-FPD method using a specific capillary GC column. Other GC-FPD methods, with differences in GC column and equipment setup and operation, may be used as alternative methods for sulfur compound analysis with different range and precision, provided that appropriate separation of the sulfur compounds of interest can be achieved.

1.3 This test method does not intend to identify all individual sulfur species. Total sulfur content of samples can be estimated from the total of the individual compounds determined. Unknown compounds are calculated as monosulfur-containing compounds.

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

1.5 *This standard does not purport to address all 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 1072 Test Method for Total Sulfur in Fuel Gases[2]

D 1265 Practice for Sampling Liquefied Petroleum (LP) Gases–Manual Method[3]

D 1945 Test Method for Analysis of Natural Gas by Gas Chromatography[2]

D 3609 Practice for Calibration Techniques Using Permeation Tubes[4]

D 4468 Test Method for Total Sulfur in Gaseous Fuels by Hydrogenolysis and Rateometric Colorimetry[2]

D 4626 Practice for Calculation of Gas Chromatographic Response Factors[5]

D 5287 Practice for Automatic Sampling of Gaseous Fuels[2]

D 5504 Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Chemiluminescence Detection[2]

E 840 Practice for Using Flame Photometric Detectors in Gas Chromatography[6]

2.2 *EPA Standards:*

EPA–15 Determination of Hydrogen Sulfide, Carbonyl Sulfide and Carbon Disulfide Emissions from Stationary Sources, 40 CFR, Chapter 1, Part 60, Appendix A

EPA–16 Semicontinuous Determination of Sulfur Emissions from Stationary Sources, 40 CFR, Chapter 1, Part 60, Appendix A

3. Terminology

3.1 *Abbreviations*:

3.1.1 A common abbreviation of a hydrocarbon compound is to designate the number of carbon atoms in the compound. A prefix is used to indicate the carbon chain form, while a subscript suffix denotes the number of carbon atoms, for example, normal decane = n-C_{10}, isotetradecane = i-C_{14}.

3.1.2 Sulfur compounds commonly are referred to by their initials, chemical or formula, for example, methyl mercaptan = MeSH, dimethyl sulfide = DMS, carbonyl sulfide = COS, di-*t*-butyl trisulfide = DtB-TS, and tetrahydothiophene = THT or thiophane.

4. Summary of Test Method

4.1 Sulfur analysis ideally is performed on-site to eliminate potential sample deterioration during storage. The reactive nature of sulfur components may pose problems both in sampling and analysis. Samples should be collected and stored in containers that are nonreactive to sulfur compounds, such as

---

[1] This test method is under the jurisdiction of ASTM Committee D-3 on Gaseous Fuels and is the direct responsibility of Subcommittee D03.05 on Determination of Special Constituents of Gaseous Fuels.

Current edition approved March 10, 1998. Published May 1998.

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

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

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

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

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

Tedlar[7] bags. Sample containers should be filled and purged at least three times to ensure representative sampling. Laboratory equipment also must be inert, well conditioned, and passivated with a gas containing the sulfur compounds of interest to ensure reliable results. Frequent calibration and daily verification of calibration curve using stable standards are required. Samples should be analyzed within 24 h of collection to minimize sample deterioration. If the stability of analyzed sulfur components is proved experimentally, the time between collection and analysis may be lengthened.

4.2 A 1-mL sample of the fuel gas is injected into a gas chromatograph where it is passed through a 60-m, 0.53-mm inside diameter (ID), thick film, methyl silicone liquid phase, open tubular partitioning column, or a similar column capable of separating sulfur components.

4.3 *Flame Photometric Detectors*—When combusted in a hydrogen-rich flame, sulfur compounds emit light energy characteristic to all sulfur species. The light is detected by a photomultiplier tube (PMT). The PMT response is proportional to the concentration or the amount of sulfur. All sulfur compounds including sulfur odorants can be detected by this technique.

4.4 *Other Detectors*—This test method is written primarily for the flame photometric detector. The same gas chromatographic (GC) method can be used with other sulfur-specific detectors provided they have sufficient sensitivity and selectivity to all sulfur compounds of interest in the required measurement range.

4.5 *Other GC Test Methods*—The GC test methods using sulfur chemiluminescence, reductive rateometric, and electrochemical detectors are available or under development.

5. Significance and Use

5.1 Many sources of natural gas and petroleum gases contain varying amounts and types of sulfur compounds, which are odorous, corrosive to equipment, and can inhibit or destroy catalysts used in gas processing. Their accurate measurement is essential to gas processing, operation, and utilization.

5.2 Small amounts, typically, 1 to 4 ppmv of sulfur odorant compounds, are added to natural gas and liquefied petroleum (LP) gases for safety purposes. Some odorant compounds can be reactive and may be oxidized, forming more stable compounds having lower odor thresholds. These gaseous fuels are analyzed for sulfur odorants to help ensure appropriate odorant levels for safety.

5.3 This test method offers a technique to determine individual sulfur species in gaseous fuel and the total sulfur content by calculation. Gas chromatography is used commonly and extensively to determine other components in gaseous fuels including fixed gas and organic components (see Test Method D 1945). This test method dictates the use of a specific GC technique with one of the more common detectors for measurement.

6. Apparatus

6.1 *Chromatograph*—Any gas chromatograph that has the following performance characteristics can be used.

6.1.1 *Sample Inlet System*—Gas samples are introduced to the gas chromatograph using an automated or manually operated stainless steel gas sampling valve enclosed in a heated valve oven, which must be capable of operating continuously at a temperature of 50°C above the temperature at which the gas was sampled. TFE-fluorocarbon tubing made of fluorinated ethylene propylene (FEP), 316 stainless steel tubing, or other tubing made of nonpermeable, nonsorbing, and nonreactive materials, as short as possible and heat traced at the same temperature, should be used for transferring the sample from a sample container to the gas-sampling valve. A 1.0-mL sampling loop made of nonreactive materials, such as deactivated fused silica or 316 stainless steel is used to avoid possible decomposition of reactive sulfur species. Other size fixed-volume sampling loops may be used for different concentration ranges. A 1- to 2-m section of deactivated precolumn attached to the front of the analytical column is recommended. The precolumn is connected directly to the gas sampling valve for on-column injection. The inlet system must be well conditioned and evaluated frequently for compatibility with trace quantities of reactive sulfur compounds, such as *tert*-butyl mercaptan.

6.1.2 *Digital Pressure Transmitter*—A calibrated stainless steel pressure/vacuum transducer with a digital readout may be equipped to allow sampling at different pressures to generate calibration curves.

6.1.3 *Column Temperature Programmer*—The chromatograph must be capable of linear programmed temperature operation over a range from 30 to 200°C, in programmed rate settings of 0.1 to 30°C/min. The programming rate must be sufficiently reproducible to obtain retention time repeatability of 0.05 min (3 s).

6.1.4 *Carrier and Detector Gas Control*—Constant flow control of carrier and detector gases is critical to optimum and consistent analytical performance. Control is best provided by the use of pressure regulators and fixed flow restrictors. The gas flow rate is measured by any appropriate means and the required gas flow indicated by the use of a pressure gage. Mass flow controllers, capable of maintaining gas flow constant to ±1 % at the required flow rates also can be used. The supply pressure of the gas delivered to the gas chromatograph must be at least 69 kPa (10 psi) greater than the regulated gas at the instrument to compensate for the system back pressure. In general, a supply pressure of 552 kPa (80 psig) will be satisfactory.

6.1.5 *Detector*—A flame photometric detector calibrated in the sulfur-specific mode is used for this test method. Other detectors as mentioned in 4.4 will not be covered in this test method. This detector may be obtained from various manufacturers; however, there are variations in design. The pulsed flame photometric detector (PFPD) is one of the new FPD designs. The pressure and flow rate of the hydrogen and air gases used in the detector may be different. The selection of which detector to use should be based on its performance for the intended application. The detector should be set according to the manufacturer's specifications and tuned to the best performance of sensitivity and selectivity as needed.

---

[7] Registered trademark. Available from DuPont de Nemours, E. I., & Co., Inc., Barley Mill Plaza, Bldg. 10, Wilmington, DE 19880–0010.

6.1.5.1 When sulfur-containing compounds are burned in a hydrogen-rich flame, they quantitatively produce a S_2* species in an excited state (Eq 1 and Eq 2). The light emitted from this species is detected by a photomultiplier tube (PMT) (Eq 3). A 393-nm bandpass optical filter normally is used to enhance the selectivity of detection. The selectivity normally is about 10^4 to 1 by mass of sulfur to mass of carbon.

$$RS + O_2 \rightarrow n\,CO_2 + SO_2 \qquad (1)$$

$$2\,SO_2 + 4\,H_2 \rightarrow 4\,H_2O + S_2^* \qquad (2)$$

$$S_2^* \rightarrow S_2 + h\nu \qquad (3)$$

where:

$h\nu$ = emitted light energy.

6.1.5.2 The intensity of light is not linear with the sulfur concentration but is proportional approximately to the square of the sulfur concentration. The relationship between the FPD response (R_D) and the sulfur concentration (S) is given by Eq 4 and Eq 5. The n-factor usually is less than 2.0.

$$R_D \ \alpha\ [S]^n \qquad (4)$$

$$\text{Log}\,[S]\ \alpha\ 1/n\ \text{Log}\,R \qquad (5)$$

where:

n = exponential factor (1.7 to 2.0).

6.1.5.3 The linear calibration curve can be made using a log-log plot. Some instruments use an electronic linearizer to produce a signal with direct linear response. The dynamic range of this linear relationship is about 1×10^3.

6.2 *Column*—A 60- by 0.53-m ID fused silica open tubular column containing a 5-µm film thickness of bonded methyl silicone liquid phase is used. The column shall provide adequate retention and resolution characteristics under the experimental conditions described in 7.3. Other columns, which can provide equivalent separation can be used, as well.

6.3 *Data Acquisition*:

6.3.1 *Recorder*—A 0- to 1-mV range recording potentiometer or equivalent, with a full-scale response time of 2 s or less can be used.

6.3.2 *Integrator*—The use of an electronic integrating device or computer is recommended. The device and software must have the following capabilities:

6.3.2.1 Graphic presentation of the chromatogram.

6.3.2.2 Digital display of chromatographic peak areas.

6.3.2.3 Identification of peaks by retention time or relative retention time, or both.

7. Reagents and Materials

7.1 *Sulfur Permeation Tube Standards*—Gaseous standards generated from individual or a combination of certified permeation tubes at a constant temperature and flow rate shall be used for all calibrations. Each permeation tube will be weighed to the nearest 0.1 mg on a periodic basis after the permeation rate has equilibrated and remains constant. The standard concentration is calculated by mass loss and dilution gas flow rate. Impurities permeated from each tube must be detected, measured, and accounted for in the mass loss, if they are present above a level of 0.1 % of the permeated sulfur species. See Practice D 3609.

7.2 *Compressed Cylinder Gas Standards*—As an alternative, blended gaseous sulfur standards may be used if a means to ensure accuracy and stability of the mixture is available. These mixtures can be a source of error if their stability during storage cannot be guaranteed.

Note 1—**Warning:** Sulfur compounds may be flammable and harmful or fatal if ingested or inhaled.

7.3 *Carrier Gas*—Helium or nitrogen of high purity (99.999 % min purity) (**Warning**—See Note 2). Additional purification is recommended by the use of molecular sieves or other suitable agents to remove water, oxygen, and hydrocarbons. Available pressure must be sufficient to ensure a constant carrier gas flow rate (see 6.1.4).

Note 2—**Warning:** Helium and nitrogen used are compressed gases under high pressure.

7.4 *Hydrogen*—Hydrogen of high purity (99.999 % min purity) is used as fuel for the flame photometric detector (FPD) (**Warning**—See Note 3).

Note 3—**Warning:** Hydrogen is an extremely flammable gas under high pressure.

7.5 *Air*—High-purity (99.999 % min purity) compressed air is used as the oxidant for the flame photometric detector (FPD) (**Warning**—See Note 4).

Note 4—**Warning:** Compressed air is a gas under high pressure that supports combustion.

8. Preparation of Apparatus and Calibration

8.1 *Chromatograph*—Place in service in accordance with the manufacturer's instructions. Typical operating conditions are shown in Table 1 .

8.2 *FPD*—Place the detector in service in accordance with the manufacturer's instructions. Hydrogen and air flows are critical and must be adjusted properly in accordance with the instruction furnished by the manufacturer. With the FPD flame ignited, monitor the signal to verify compliance with the signal noise and drift specified by the manufacturer. The FPD flame should be maintained to give consistent and optimum sensitivity for the detection range.

8.2.1 *Sample Injection*—A sample loop of 1.0 mL of suitable size for sample injection may be used for performance check. A linear calibration curve may be determined by using standards of varying concentrations or by injecting a single calibration standard at different pressures from 13.3 to 133 kPa (100 to 1000 torr). If the latter method is used, the concentration of sulfur component for calibration is calculated using the following equation.

$$S_n = (P_s/P_o) \times C_n \qquad (6)$$

TABLE 1 Gas Chromatographic Operating Parameters

Gas Sample Loop:	1.0 mL at 120°C
Injection Type:	On-column
Carrier Gas:	He at 11.0 mL/min or at a flow rate allowing CH_4 elutes at approximately 2.1 min
Column Oven:	30°C hold 1.5 min, 15°C/min to 200°C, hold 8 min, or as needed
Detector:	H_2/air ratio specified by manufacturer, 250°C, 20 mL/min, helium makeup gas

where:

S_n = calculated concentration of the sulfur compound in the sampled gas on mole or volume basis,
P_s = sampling pressure as absolute,
P_o = laboratory ambient pressure as absolute, and
C_n = concentration of the sulfur compound in the calibration standard.

8.2.2 *Detector Response Calibration*—Analyze the calibration gas and obtain the chromatograms and peak areas. Determine the linear range of detector response using sample injection techniques illustrated in 8.2.1. A log/log plot or a linearized plot may be constructed with the linear correlation factor calculated. Calculate the relative sulfur response factor of each sulfur compound at ambient pressure by:

$$F_n = (S_n/A_n) \times L_n \quad (7)$$

where:

F_n = sulfur response factor of compound,
S_n = concentration of the sulfur compound in the sampled gas on mole or volume basis,
A_n = peak area of the sulfur compound measured, and
L_n = moles of sulfur in the compound.

Example:

Assume 1.0 ppmv of dimethyl sulfide (DMS) injected with a 1.0-mL sample loop.

1-ppmv DMS = 62.13/22.41 = 2.772 mg/m^3 (from Table 2). 1.0 mL of 1-ppmv DMS = 2772-pg DMS = 2772 × 51.61 % = 1430-pg S. If the peak area of DMS response is 15 850 counts, the response factor F_n (*S*/peak) is 1430/15 850 × 1 = 9.02 × 10^2 (pg sulfur/unit area). The response factor (F_n) of 1.0-mL injection = 1.0/15 850 × 1 = 63 × 10^{-6} (ppmv DMS/unit area).

All *mono*-sulfur compounds should have approximately the same response factor. The response factor (F_n) of each sulfur compound should be within 10 % of F_n for dimethyl sulfide. The day-to-day variation of F_n should not be greater than 5 %. The detector should be maintained and flow rates readjusted to optimize the detector performance if F_n exceeds this limitation. Table 2 lists common sulfur compounds found in gaseous fuel and their properties for calculation.

8.2.3 *Interferences*—There are two types of interferences that must be minimized for reliable quantitation.

8.2.3.1 *Hydrocarbon Quenching*—Hydrocarbons produce a quenching effect on sulfur detection as a result of the formation of a large amount of carbon dioxide in the flame suppressing the formation of SO_2. The quenching can be minimized by optimizing the chromatographic conditions to separate the sulfur components of interest from large hydrocarbons present in the sample matrix. A flame ionization detector (FID) or thermal conductivity detector (TCD) can be used to identify the presence of interfering hydrocarbons. Sample dilution or injection of a smaller volume of sample may be used to alleviate the quenching effect if sulfur concentration is significantly higher than the method detection limit.

TABLE 2 Physical Properties of Common Sulfur Compounds

Compound	Relative Molecular Mass (Molecular Weight)	% 5	Boiling Point, °C	Vapor Pressure kPa at 37.78°C
H_2S	34.08	94.09	−60.3	. . .
COS	60.08	53.37	−50.2	. . .
MeSH	48.11	66.65	6.2	214
EtSH	62.13	51.61	35.0	112
DMS	62.13	51.61	37.3	103
CS_2	76.14	84.23	46.5	. . .
iPrSH	76.16	42.10	52.6	61
TBM	90.19	35.55	64.0	41
nPrSH	76.16	42.10	67.0	35
MES	76.16	42.10	67.0	36
THT	88.17	36.37	120	4.6
di-EtS	90.19	35.55	92.0	. . .
DMDS	94.20	68.08	109.7	. . .
di-Et-DS	122.25	52.46	154.0	. . .

8.2.3.2 *Self-Quenching*—In other cases, the reverse of the reaction shown in Eq 3 produces self-quenching. This arises when the emitted light is reabsorbed before reaching the photomultiplier. It occurs when a very large concentration of any sulfur species is present in the flame above and beyond the linearity range of the detector. It often generates an M-shape peak with the inverted signal at a component's peak apex, which mistakenly can be identified as two close eluting compounds. Sample dilution or smaller sample injection may eliminate this effect.

8.3 *Chromatography*—A chromatogram of typical natural gas analysis is illustrated in Fig. 1 (relative response versus retention time). The retention times of selected sulfur components are listed for reference (Table 3). They may vary considerably depending on the chromatographic conditions. The eluting sequence and spread of sulfur peaks and their peak shape should remain the same. Adequate resolution defined as baseline separation of adjacent peaks shall be achieved. The baseline separation of two peaks is defined as the FPD signal of the first compound returns to a point at least below 5 % of the smallest peak of two.

9. Procedure

9.1 *Sampling and Preparation of Sample Aliquots*:

9.1.1 *Gas Samples*—Samples should be supplied to the laboratory in specially conditioned high-pressure sample containers or in Tedlar[7] bags at atmospheric pressure. The sample must be analyzed as soon as possible, preferably within 24 h of sampling.

9.2 *Instrument Setup*—Set up the GC-FPD in accordance with the chromatograph operating parameters listed in Table 1.

9.3 *Instrument Performance*—Analyze selected standards to verify the chromatographic performance (see 8.3), retention times (Table 3), and the response factors (see 8.2.2). The calibration made at the beginning and the end of each run or series of runs within 24-h period shall not exceed ±5 %.

9.4 *External Standard Calibration*—At least twice a day or as frequently as necessary, analyze the calibration standard mix to verify the calibration curve determined in 8.2.1 and 8.2.2 and determine the standard response factors for the sample analysis.

9.5 *Sample Analysis*—Evacuate and purge the lines from the sample container through the sample loop in the gas chromatograph. Inject 1.0 mL with a gas sampling valve as in 8.2.1. If the sample size exceeds the linear range of the detector, reduce the sample size using a smaller loop or lower sampling pressure. Run the analysis in accordance with the conditions specified in Table 1. Obtain the chromatographic

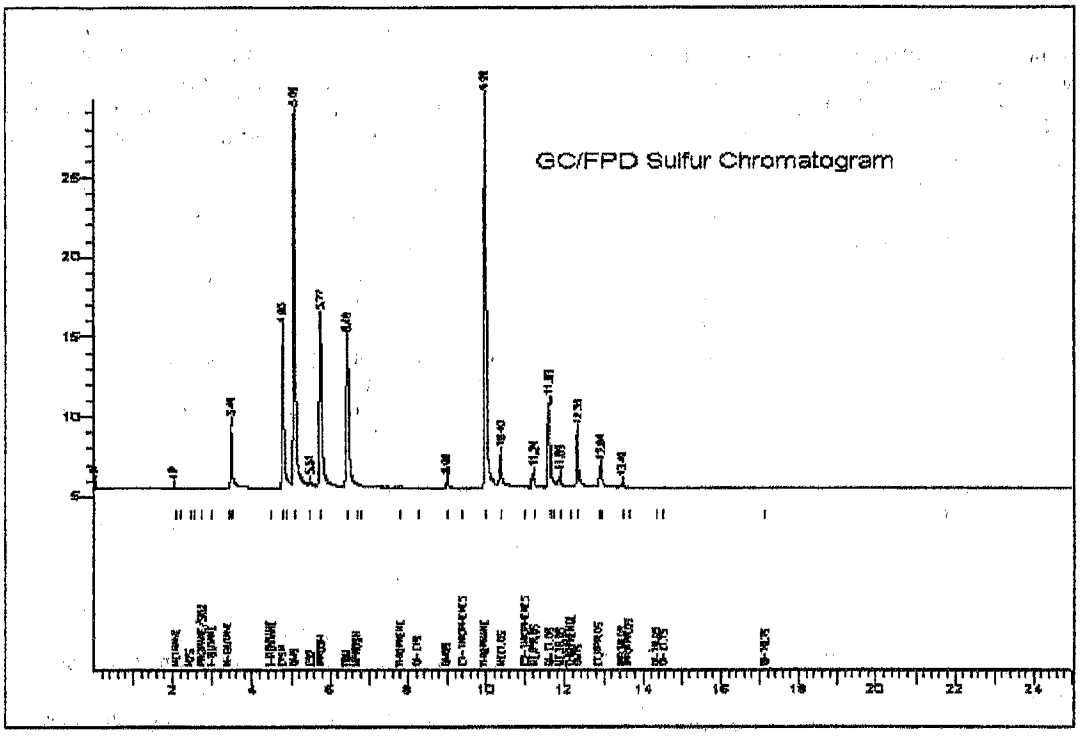


FIG. 1 Chromatogram of a Composite Odorized Natural Gas

TABLE 3 Retention Times of Various Sulfur Components

RT, min	Compound	*RT*, min	Compound	*RT*, min	Compound
2.09	methane	5.50	CS_2	11.23	M-iPr-DS
2.20	ethane	5.80	iPrSH	11.62	DEDS
2.45	H_2S	6.45	TBM	11.74	M-nPr-DS
2.55	COS	6.70	nPrSH	11.90	M-tB-DS
2.65	propane	6.80	MES	12.35	DMTS
3.00	*i*-butane	7.80	thiophene	12.87	E-nPr-DS
3.40	*n*-butane	8.25	DES	12.98	DiPr-DS
3.52	MeSH	9.00	DMDS	13.50	iPr-tB-DS
4.50	*i*-pentane	9.42	*M*-thiophenes	13.65	iPr-nPr-DS
4.75	EtSH	9.95	THT	14.35	DtB-DS
4.90	*n*-pentane	10.37	MEDS	14.55	DEt-TS
5.10	DMS	11.00	C_2-thiophenes	17.15	DtB-TS

data by means of a potentiometric record (graphic), digital integrator, or computer-based chromatographic data system. Examine the graphic display or digital data for any errors, for example, over-range component data, and repeat the injection and analysis, if necessary. The difference between corresponding peak areas of repeated runs should not exceed 5 %.

9.6 *Compound Identification*—Sulfur compounds are identified by their retention times established during calibration. All compounds without matching standards are identified as individual unknowns.

10. Calculation

10.1 Determine the chromatographic peak area of each component and use the response factor (Eq 7) obtained from the calibration run to calculate the amount of each sulfur compound present corrected for injection pressure. The amount of each unknown sulfur compound is calculated using the response factor of the closest adjacent identified compound, unless that compound shows abnormal peak shape.

$$C_n = (A_n/F_n)\,(P_o/P_s)\,/\,L_n \qquad (8)$$

where:

C_n = concentration of the sulfur compound in the gas on mole or volume basis,
A_n = peak area of the sulfur compound measured,
F_n = sulfur response factor of compound,
P_o = laboratory ambient pressure,
P_s = sampling pressure, and
L_n = moles of sulfur in the compound.

11. Report

11.1 Report the identification and concentration of each individual sulfur compound in ppmv. Report the sum of all sulfur components detected to the nearest ppmv or pg as total sulfur.

12. Precision and Bias

12.1 *Precision*—The precision of this test method is determined based on a sulfur standard mix in methane, which is stable during the testing period. The statistical examination of the laboratory test results is as follows:

12.1.1 *Repeatability (Single-Operator and Apparatus)*—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 this test method, exceed the following values by only one case in twenty.

Sulfur Compound	ppmv	Repeatability
COS	2.07	±0.06
DMS	3.63	±0.12
NPM	3.72	±0.12
DMDS	2.00	±0.06
THT	6.44	±0.16

12.1.2 *Reproducibility (Different Operators, Apparatus, and Laboratories)*—Since reference samples stable over a long testing period, which are required for this determination, are not available at this time, reproducibility cannot be determined.

12.2 *Bias*—Since there is no accepted reference material for determining the bias, no statement on bias can be made.

13. Keywords

13.1 flame photometric detection; gas chromatography; sulfur compounds, odorants

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:

CFR Section(s):

Standards Body:

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

Designation: D 6420 – 99

Standard Test Method for Determination of Gaseous Organic Compounds by Direct Interface Gas Chromatography-Mass Spectrometry[1]

This standard is issued under the fixed designation D 6420; 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 employs a direct interface gas chromatograph/mass spectrometer (GCMS) to identify and quantify the 36 volatile organic compounds (or sub-set of these compounds) listed as follows. The individual Chemical Abstract Service (CAS) numbers are listed after each compound.

Benzene-71432
Bromodichloromethane-75274
Carbon disulfide-75150
Chloroform-67663
Methyl iso-Butyl ketone-108101
Styrene-100425
Tetrachloroethylene-127184
Toluene-108883
Bromoform-75252
Vinyl acetate-108054
Vinyl chloride-75014
Chloromethane-74873
cis-1,2-Dichloroethene-156592
Dibromochloromethane-124481
1,1-Dichloroethane-107062
1,2-Dichloropropane-78875
Ethylbenzene-100414
Ethyl chloride-75003
Methylene chloride-75092
1,1,2,2-Tetrachloroethane-79349
1,1,1-Trichloroethane-71556
1,1,2-Trichloroethane-79005
p-Xylene-106423
Bromomethane-74839
Carbon tetrachloride-56235
Chlorobenzene-108907
c-1,3-Dichloropropene-10061015
1,2-Dichloroethane-156592
1,1-Dichloroethene-75354
t-1,2-Dichloroethene-156605
Methyl ethyl ketone-78933
2-Hexanone-591786
t-1,3-Dichloropropene-542756
Trichloroethene-79016
m-Xylene-108383
o-Xylene-95476

1.2 The test method incorporates a performance-based approach, which validates each GCMS analysis by placing boundaries on the instrument response to gaseous internal standards and their specific mass spectral relative abundance. Using this approach, the test method may be extended to analyze other compounds.

1.3 The test method provides on-site analysis of extracted, unconditioned, and unsaturated (at the instrument) gas samples from stationary sources. Gas streams with high moisture content may require conditioning to prevent moisture condensation within the instrument. For these samples, quality assurance (QA) requirements are provided in the test method to validate the analysis of polar, water-soluble compounds.

1.4 The instrument range should be sufficient to measure the listed volatile organic compounds from 150 ppb(v) to 100 ppm(v), using a full scan operation (between 45 and 300 atomic mass units). The range may be extended to higher or lower concentrations using either of the following procedures:

1.4.1 The initial three-point calibration concentrations and the continuing calibration checks are adjusted to match the stack concentrations, or

1.4.2 The three-point calibration is extended to include additional concentrations to cover the measurement range.

1.5 The minimum quantification level is 50 % of the lowest calibration concentration. Responses below this level are considered to be estimated concentrations, unless a calibration standard check is conducted at a lower concentration to demonstrate linearity. The sensitivity of the GCMS measurement system for the individual target analytes depends upon:

1.5.1 The specific instrument response for each target analyte and the number of mass spectral quantification ions available.

1.5.2 The amount of instrument noise, and

1.5.3 The percent moisture content of the sample gas.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Additional safety precautions are described in Section 9.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres[2]

D 3195 Practice for Rotameter Calibration[2]

2.2 *EPA Test Methods:*

Method 1–Sample and Velocity Traverses for Stationary Sources[3]

Method 2–Determination of Stack Gas Velocity and Volumetric Flow Rate (Type S Pitot Tube)[3]

Method 3–Gas Analysis for Carbon Dioxide, Oxygen, Excess Air, and Dry Molecular Weight[3]

Method 4–Determination of Moisture Content in Stack Gases[3]

Method 624–Purgables[4]

---

[1] This test method is under the jurisdiction of ASTM Committee D-22 on Sampling and Analysis of Atmospheres and is the direct responsibility of Subcommittee D22.03 on Ambient Atmospheres and Source Emissions.

Current edition approved May 10, 1999. Published July 1999.

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

[3] Code of Federal Regulations 40 CFR Part 60, Appendix A, available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

[4] Code of Federal Regulations 40 CFR Part 136, Appendix A, available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

3. Terminology

3.1 See Terminology D 1356 for definition of terms used in this test method.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *blank analysis, n*—injecting zero air or nitrogen into the GCMS to determine background levels of the target analytes.

3.2.2 *CCC, n—continuing calibration check*—injecting calibration gas standards into the GCMS to verify the calibration status.

3.2.2.1 *Discussion*—The continuing calibration check is performed before each testing day, before resuming sampling after instrument shutdown or malfunction, and before resuming sampling after 12 h of continuous instrument operation.

3.2.3 *quantification ion, n*—a specific ion in the analytes mass spectrum that is used for quantification.

3.2.4 *system calibration, n*—calibration obtained by injecting the calibration standard(s) through the entire sampling system.

3.2.5 *system zero, n*—zero obtained by injecting dry nitrogen or zero gas through the entire sampling system to determine the system background levels of the target analytes.

4. Summary of Test Method

4.1 *Analysis*—Volatile Organic Hazardous Air Pollutants (VOHAP) are analyzed using gas chromatography (GC) to separate the individual compounds and mass spectrometry (MS) to identify the compounds. The MS scans a defined mass range (usually from 45 to 300 atomic mass units (amu) for combustion sources) to identify the specific fragments for each molecule. The target analytes are identified positively by: (*1*) comparing eluting analyte GC peak retention times in the total ion chromatograph (TIC) to those contained in a three-point calibration, and (2) examining the mass spectral pattern of the eluted peaks. Internal standards are used to correct for hardware-related errors such as different injection volumes, operational temperature fluctuations, and electron multiplier drift.

4.2 *Sampling*—Samples are extracted from the stack or duct at a constant rate, filtered, conditioned (if required), and transported to the GCMS for analysis. Calibration gases are introduced at the extractive probe outlet, upstream of the primary particulate filter. All sample extraction components are maintained at temperatures that prevent moisture condensation within the measurement system components.

5. Significance and Use

5.1 This field test method determines the mass concentration of VOHAPs (or any subset) listed in Section 1.

5.2 Multiplying the mass concentration by the effluent volumetric flow rate (see 2.2) yields mass emission rates.

5.3 This field test method employs the typical laboratory GCMS techniques and QA/QC procedures.

5.4 This field test method provides data with accuracy and precision similar to most laboratory GCMS instrumentation.

NOTE 1—Supporting data are available from ASTM Headquarters Request RR:________.

6. Interferences

6.1 *Analytical Interferences*—Analytical interferences occur when chromatographic peak(s) and quantification ion(s) overlap to such an extent that quantification of specific target compounds is prohibited. The nature of the GCMS technique virtually eliminates these types of analytical interferences. However, compounds having very simple mass spectra (that is, only one or two mass fragments) may be difficult to identify positively.

6.2 *Sampling System Interferences*—Sampling system interferences occur when target analytes are not transported to the instrumentation or when compounds damage the measurement system components. Water, reactive particulate matter, adsorptive sites within the sampling system components, and reactive gases are examples of such potential sampling system interferences. Specific provisions and performance criteria are included in this test method to detect and prevent the presence of sampling system interferences.

7. Apparatus

7.1 *Analytical Instrumentation*:

7.1.1 *Gas Chromatograph/Mass Spectrometer (GCMS)*, capable of separating the analyte mixture and detecting compounds in the 45 to 300 atomic mass unit (amu) range.

7.1.2 *Personal Computer*, with compatible GCMS software for control of the GCMS and for data quantification.

7.2 *Sampling System*:

7.2.1 *Sampling Probe*, glass, stainless steel, or other appropriate material of sufficient length and physical integrity to sustain heating, prevent adsorption of analytes, and to reach the gas sampling point.

7.2.2 *Calibration Assembly*, typically fabricated by user, to introduce calibration standards into the sampling system at the probe outlet, upstream of the primary particulate filter, at the same pressure and temperature as that of the effluent samples, with provisions for monitoring the sample pressure and temperature during continuing calibrations and effluent sampling.

7.2.3 *Particulate Filters*, rated at 0.3 μm, placed immediately after the heated probe and after the sample condenser system.

7.2.4 *Pump*, leak-free, with heated head, capable of maintaining an adequate sample flow rate (at least 1.5 L/min).

7.2.5 *Sampling Line*, of suitable internal diameter, heated to prevent sample condensation, made of stainless steel, tetrafluorocarbon polymer, or other material that minimizes adsorption of analytes, of minimal length.

7.2.6 *Sample Condenser System*, a refrigeration unit capable of reducing and removing the moisture of the sample gas to a level acceptable for sample injection.

7.2.7 *Sample Flow Rotameters*, capable of withstanding sample gas conditions, calibrated according to Practice D 3195.

7.2.8 *Sample Transfer Line*, to transport sample from sample interface to GCMS, heated to prevent sample condensation and fabricated of stainless steel, tetrafluorocarbon polymer, or other material to minimize adsorption of analytes, of minimal length.

7.3 *Auxiliary Equipment*:

7.3.1 *Calibration Gas Manifold*, capable of delivering nitrogen or calibration gases through sampling system or directly to the instrumentation, with provisions to provide for accurate dilution of the calibration gases as necessary. See Fig. 1 for an example schematic.

7.3.2 *Mass Flow Meters or Controllers*, with a stated accuracy and calibrated range (±2 % of scale from 0 to 500 mL/min or 0 to 5 L/min).

7.3.3 *Digital Bubble Meter (or equivalent)*, having a NIST-traceable calibration and accuracy of ±2 % of reading, with an adequate range to calibrate mass flow meters or controllers and rotameters at the specific flow rates (within ±10 %) required to perform the test method.

7.3.4 *Tubing, tetrafluorocarbon polymer* (or other material), of suitable diameter and length to connect cylinder regulators and minimize the adsorption of analytes on the tubing surface.

7.3.5 *Tubing*, 316 stainless steel (or other material), of suitable diameter and length for heated connections.

7.3.6 *Gas Regulators*, appropriate for individual gas cylinders, constructed of materials that minimize adsorption of analytes.

8. Reagents and Materials

8.1 *Calibration Gases*, gas standards (in nitrogen balance or other inert gas) for those compounds identified in Section 1, certified by the manufacturer to be accurate to 5 % or better, used for the initial and continuing calibrations.

NOTE 2—The analytical accuracy of the calibration standards must be known. The analytical accuracy for gas mixtures may be concentration dependent.

8.2 *Internal Standards*, manufacturer-certified mixtures for co-injection with sample gas.

8.3 *High Purity (HP) Nitrogen or Zero Air*, for purging sample lines and sampling system components, dilutions, and blank runs.

9. Hazards

9.1 *Target Analytes*—Many of the compounds listed in Section 1 are toxic and carcinogenic. Therefore, avoid exposure to these chemicals. Calibration standards are contained in compressed gas cylinders; exercise appropriate safety precautions to avoid accidents in their transport and use.

9.2 *Sampling Location*—This test method may involve sampling locations with high positive or negative pressures, high temperatures, elevated heights, or high concentrations of hazardous or toxic pollutants.

9.3 *Mobile or Remote Laboratory*—To avoid exposure to hazardous pollutants and to protect personnel in the laboratory, perform a leak check of the sampling system and inspect the sample exhaust equipment before sampling the calibration standards or effluent. Properly vent the exhaust gases.

10. Calibration and Standardization

10.1 *Calibration Standards*—Because of the incompatibility of some target compounds, many gas blends at each concentration may be needed to construct a calibration curve for all of the 36 target analytes listed in 1.1. Obtain or generate calibration standards of each target compound at nominal concentrations of 300 ppb(v), 1 ppm(v), and 10 ppm(v) by either of the following options:

10.1.1 *Option 1*—Obtain calibration gas standards for the target compounds at the three specified nominal concentrations.

10.1.2 *Option 2*—Obtain 10 ppm(v) calibration standards for the target analytes. Then successively dilute the 10 ppm(v) standard with ultra-pure nitrogen using mass flow meters. Dilute the 10 ppm(v) standard to 1 ppm(v) and then the 1 ppm(v) to 300 ppb(v). If Option 2 is used, analyze the calibration check (see Table 5) compounds directly as a QA audit of the dilution technique. The audit result using the calibrated GCMS must be within ±20 % for the calibration to be valid.

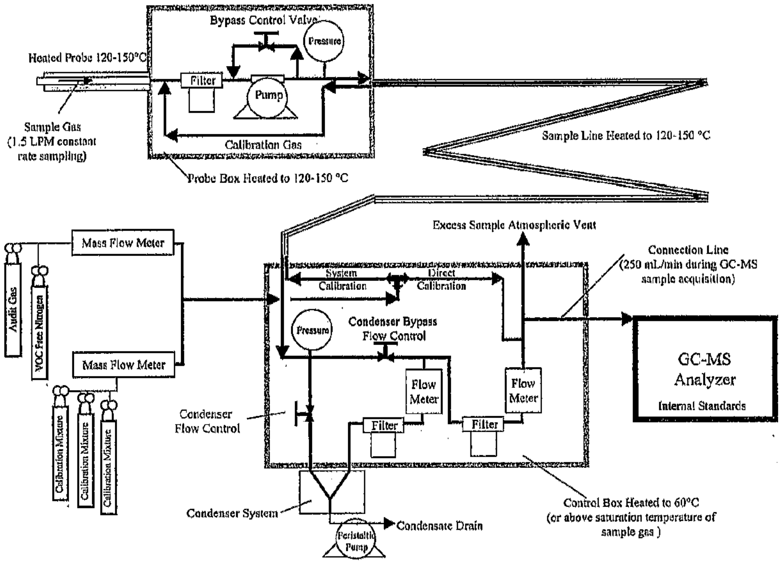


FIG. 1 Example Direct Interface GCMS Measurement System

TABLE 1 Calibration and Sampling QA/QC Criteria

Operational Mode	IS Recommended Requirements	GC Retention Time Requirements	Extracted Ion Chromatographic Criteria	Accuracy and Sensitivity
Mass Spectrometer Tune	See Table 3			
Three-Point Calibration	See Table 4	RTs for individual VOHAPS must be within ±6 % of each other from run to run.	% RSDs calculated from the individual RRFs at each calibration point must be ±20 % for each target analyte. The RFs of the internal standards must be within –50 - 100 % of the mean for the initial three-point calibration.	ARRFs must be > 0.25 to ensure proper instrumental response. A signal to noise of 10:1 (measured in accordance with the instrument manufacturer's procedures) is recommended for the low concentration level.
Surrogate Continuing Calibration Check (CCC)	See Table 4	RTs for individual VOHAPS must be within± 6 % of the initial three-point calibration.	The RFs of the internal standards must be within –50 - 100 % of their ARFs from the initial three-point calibration.	Surrogate continuing system calibration results must be within ±20 % of the manufacturers certified value from analysis by the three-point calibration for valid continuing calibration.
Sampling	See Table 4	RTs for detected VOHAPS must be within ±6 % of those in the initial three-point calibration.	The RFs of the internal standards must be within –50 - 100 % of their ARFs from the initial three-point calibration.	Spectral ions of greater than 10 % abundance in the identified compounds mass spectrum must also be contained in the reference calibration spectrum for that particular target analyte.

TABLE 2 Relative Ion Abundance Criteria for Bromofluorobenzene

Mass Fragment	Ion Abundance Criteria
50	15-40 %
75	30-60 %
95	Base peak
96	5-9 % of mass 95
173	<2 % of mass 174
174	>50 % of mass 95
175	5-9 % of mass 174
176	>95 % but <101 % of mass 174
177	5-9 % of mass 174

TABLE 3 Instrument Performance for Blended TRIS/BPFB Internal Standard Mixture in Tune

Mass Fragment	Recommended Percent Relative Low Abundance Criteria	Recommended Percent Relative High Abundance Criteria
50	5	8
55	5	8
69	33	36
93	39	45
117	100	100
167	50	65
248	30	99
263	20	50
282	10	30

TABLE 4 Instrument Performance for Separated Internal Standard Mixture

Internal Standard	Mass	Recommended Ion Abundance Criteria
TRIS	50	5-20 % of mass 69
	69	Base Peak
	75	40-60 % of mass 69
	213	50-90 % of mass 69
	263	75-95 % of mass 69
	282	30-70 % of mass 69
BPFB	93	20-50 % of mass 117
	117	Base Peak
	167	45-75 % of mass 117
	245	<2 % of mass 246
	246	>25 % of mass 117
	247	5-9 % of mass 246
	248	>25 % of mass 117
	249	5-9 % of mass 248

TABLE 5 Surrogate System Continuing Calibration Compounds

NOTE 1—The compounds listed in Table 5 represent certain class(s) of analytes known as surrogate mixture.

Compound	Class Representing	Molecular Weight	Quantification-Ion	Retention Time[A]
Methylene Chloride	Chlorinated	84	84	2:41 min
Methyl Ethyl Ketone (MEK)	Polar	72	72	2:57 min
Carbon tetrachloride	Chlorinated	152	117	3:35 min
Toluene	Aromatic	92	91	5:08 min
Chlorobenzene	Chlorinated aromatic	112	112	7:22 min
O-xylene	Aromatic	91	91	9:44 min

[A] Retention time based on 60°C isothermal separation on a SPB-1 GC column 30 m long and 0.32 mm inside diameter.

10.1.3 Option 2 for preparation of the three-point calibration curve may also generate concentration levels above and below the suggested concentration range. It is necessary, when using this option, to audit the calibration curve using a certified calibration standard independent from those used to prepare the curve.

10.1.4 If the QA audit results are not within 20 % of the expected value, corrective action must be taken.

10.2 *Mass Flow Meters*—For Option 2, calibrate the mass flow meter using a digital bubble meter having a NIST-traceable calibration at the specific flow rates (±10 %) necessary for diluting the calibration standards.

10.3 *MS Tune*—Follow the manufacturer's written instructions for the set-up, tune, operation, and calibration of the GCMS instrument.

10.3.1 If NIST library searchable mass spectra are needed to identify compounds not included in the three-point calibration or to facilitate comparison with other mass spectral analyses, the mass spectrometer tune must be able to produce mass spectra for bromofluorobenzene (BFB) that meet the relative abundance criteria in Table 2.

NOTE 3—BFB is a compound typically used to tune mass spectrometers for use in quantifying volatile organic compounds according to EPA Method 624.[4]

10.3.2 Table 3 presents a specific example of applicable MS tune limits for the mixture of two recommended gaseous internal standards—1,3,5 trifluoromethylbenzene (tris) and bromopentafluorobenzene (BPFB). These criteria have been used to demonstrate that the instrument produces an acceptable instrumental response for BFB. Table 4 presents a specific example of applicable ion abundance criteria for the two co-injected, GC separated gaseous internal standards. Meeting the QA criteria, in Tables 3 and 4 ensures proper and consistent GCMS response in each run, and thus allows meaningful searches of the NIST mass spectral library for data acquired under these conditions.

10.4 *Initial Three-Point Calibration*—Perform an initial three-point calibration for each target compound at each of the three nominal concentrations in 10.1 using duplicate analyses. Calculate relative response factors (RRFs) and average relative response factors (ARRFs) for each target compound at each of the three concentrations (Section 12, Eq 1 and 2). Calculate the percent RSD from these analyses for each target analyte. Verify that the QA/QC performance criteria in Table 1 are met.

10.5 *System Continuing Calibration Check (CCC)*:

10.5.1 Introduce the six calibration check compounds identified in Table 5 at the calibration assembly port, and determine their concentrations using the appropriate three-point calibration curves generated for the 36 analytes listed in 1.1. Allow sufficient time for the system to equilibrate. The system equilibration time should be no longer than the GCMS run time. (The compounds listed in 1.1, and any subset of these compounds, and the internal standards can be separated and detected in a 10 to 15 min isothermal GC run.) Calculate the percent differences from the respective certified values. Percent differences within ±20 % indicate that the calibration of the GCMS system for the analytes is still valid.

10.5.2 Perform analysis of the CCC each day before measuring the effluent, before resuming sampling after each instrument shut down for maintenance or corrective action, and before analyzing additional samples after twelve hours of continuous operation. Repeat procedure if difference is greater than 20 % of expected value for any target VOHAP.

NOTE 4—If only a subset of compounds identified in Section 1 are the target analytes for the test situation, then only those surrogates needed to verify the calibration status of the subset must be analyzed. (See Table 5 for the list of surrogates and compounds for which they represent.) Alternately, all of the target analytes can be used to verify continuing calibration status.

10.5.3 If a moisture condenser is used, conduct an additional CCC immediately after each test run (that is, while the potential for residual moisture in the sampling system is greatest) when analyzing for polar, water-soluble compounds. This QA check is to determine whether loss of water-soluble compounds in the system occurred. Take corrective action, if necessary, before repeating the sample run.

10.6 *Consistency During Runs*—Use the same instrument conditions to quantify effluent and QA samples that were used to establish the three-point calibration curve.

11. Procedure

11.1 *Pretest Preparations and Evaluations*:

11.1.1 *Flow Rate and Moisture Determination*—If the effluent volumetric flow rate is required, perform EPA Methods 1 through 3. Determine the moisture content to within ±2 % using EPA Method 4, wet-bulb dry-bulb measurements, saturation calculations, or other applicable means. If the moisture content of the flue gas is greater than the applicable instrument operating limit, remove the moisture (using a condenser system or other suitable apparatus) before introduction into the GCMS.

11.1.2 *Sample Interface Preparation*—Assemble the sampling system and allow the sample interface system components to reach operating temperatures. See Fig. 1 for an example schematic. Operate the sampling system at a constant sample flow rate during the entire test.

11.1.3 *Continuing Calibration Check*—Perform a CCC according to 10.5. Verify that the results agree to within ±20 % of the certified value before proceeding.

11.1.4 *System Zero Analysis*—After the CCC, perform a system zero (through the calibration assembly port) using nitrogen or zero air. Analyze nitrogen samples until the measurement system background levels are less than 50 ppb(v) for the target analytes of interest.

11.2 *Sampling and Analysis*:

11.2.1 Extract effluent sample gas for a period equal to the sample equilibration time (appropriate to the individual sampling system) before acquiring and analyzing the first sample. Co-inject the internal standards with each sample. Continuously extract the effluent between consecutive GCMS sample acquisitions to ensure constant sample equilibration within the sample interface system.

NOTE 5—The gaseous internal standards must be co-injected with the sample gas on each GCMS run. The concentration should be no greater than 10 times the expected value of the sample, but in practice this may not be possible for some sources.

11.2.2 Analyze the sample using prepared calibration files and quantification algorithms. Identify and determine the concentration of the target VOHAP according to 12.6. Verify that the QA/QC criteria listed in Table 1 are met for each run. Each sample analysis represents the emissions concentration over a period of approximately 15 min.

11.2.3 Typical test run durations are from 45 to 60 min. During each test run, analyze a minimum of three samples, unless otherwise specified.

11.3 *Data Storage*—Identify all samples with a unique file name. Store backup copies of data files.

12. Calculation

12.1 *Relative Response Factor (RRF)*—Calculate RRF as follows:

$$RRF = \frac{A_X}{A_{IS}} \frac{C_{IS}}{C_X} \qquad (1)$$

where

RRF = relative response factor,

A_X = peak area of selected target VOHAP quantion,
A_{IS} = peak area of corresponding selected internal standard quantion,
C_{IS} = concentration of corresponding selected internal standard, and
C_X = concentration of target VOHAP.

12.2 *Average Relative Response Factor (ARRF)*—Calculate ARRF as follows:

$$ARRF = \frac{1}{n}\sum_{i=1}^{n} RRF_i \qquad (2)$$

where:
$ARRF$ = average relative response factor,
RRF = individual RRFs calculated from calibration run (12.1).
n = 6, sample size. (Duplicate samples at each of three concentration levels.)

12.3 *Standard Deviation(s)*—Calculate as follows:

$$s = \sqrt{\frac{\sum_{i=1}^{n}(RRF_i - ARRF)^2}{n-1}} \qquad (3)$$

where:
s = standard deviation,
RRF_I = individual relative response factor,
$ARRF$ = average relative response factor, and
n = 6, sample size.

12.4 *Percent Relative Standard Deviation (%RSD).* Calculate % RSD as follows:

$$\%\,RSD = \frac{s}{ARRF} \times 100 \qquad (4)$$

where:
$\%\,RSD$ = percent relative standard deviation.

12.5 *Continuing Calibration Check (CCC) Percent Difference (%D).* Calculate % D as follows:

$$\%\,D = \frac{(ARRF - RRF_{CCC})}{ARRF} \times 100 \qquad (5)$$

where:
$\%\,D$ = percent difference between RRF_{CCC} and ARRF,
RRF_{CCC} = target VOHAP RRF obtained from the continuing (system) calibration check, and
$ARRF$ = average relative response factor from three-point calibration.

12.6 *Quantification of Results*—Calculate the VOHAP concentrations in gas samples as follows:

$$Target\ VOHAP,\ \text{ppm(v)} = \frac{A_X}{ARRF}\,\frac{C_{IS}}{A_{IS}} \qquad (6)$$

where:
A_X = peak area of target VOHAP quantion,
A_{IS} = peak area of corresponding selected internal standard quantion,
C_{IS} = concentration of corresponding selected internal standard, and
$ARRF$ = average relative response factor of target VOHAP calculated from three-point calibration.

12.7 *Alternative Quantification Calculations*—Alternative quantification algorithms, such as regression analyses, may be used to develop calibration files and sample analysis quantification. In some cases, calculation procedures allowing a non-zero y-axis intercept improve the accuracy and RSDs of measurement results. If the alternative is used, apply the same numerical procedure for the three-point calibration and all sample analyses for the test series.

13. Report

13.1 Report the results for the individual GCMS analyses, and the mean of all samples for each target analyte for each run.

13.2 Include copies of the three-point calibration including % RSD, RRFs and ARRFs, calibration check continuing system calibration(s) results and other test method QA/QC activities in the test report.

13.3 Store and include records of the manufacturer's certificates of calibration standards and internal standards.

14. Precision and Bias

14.1 *Data Quality Objectives*—The overall data quality objectives are within ±20 % of the expected value. A precision value of 10 % for each measurement value has been achieved using this method as documented in the research report. Achieving the performance criteria listed in Tables 1-4 has demonstrated that these objectives can be met.[5]

15. Keywords

15.1 gas chromatography; mass spectrometry; stack gas analysis; stationary source; volatile organic hazardous air pollutant

---

[5] "Evaluation of HAPSITE and a Direct Interface GCMS Test Method for Measurement of Volatile Organic Compounds in Stationary Source Effluent," Vols I and II, July 1997. Available from ASTM Headquarters. Request RR: D22-1028 .

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:

CFR Section(s):

Standards Body:

APPROVED

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

Designation: D 6503 – 99

Standard Test Method for Enterococci in Water Using Enterolert™[1]

This standard is issued under the fixed designation D 6503; 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 describes a simple procedure for the detection of enterococci in water and wastewater. It is based on IDEXX's patented Defined Substrate Technology® (DST™). This product, Enterolert, utilizes a nutrient indicator that fluoresces when metabolized. It can detect these bacteria at one colony forming unit (CFU)/100 mL within 24 h. The presence of this microorganism in water is an indication of fecal contamination and the possible presence of enteric pathogens.

1.2 This test method can be used successfully with drinking water, source water, recreational (fresh and marine) water, and bottled water. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

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 1193 Specification for Reagent Water[2]

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

3. Terminology

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

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *enterococci, n*—a gram positive bacteria possessing the enzyme β-D-glucosidase, which cleaves the nutrient indicator and produces fluorescence under a long wave length (366 nm) ultraviolet (UV) light.

3.2.2 *most probable number (MPN), n*—a statistical method for determining bacterial density based on the Poisson distribution.

3.2.3 *presence-absence, n*—a term used to indicate if enterococci is present in a water sample. It is a qualitative value, "yes" or "no" for reporting results.

3.2.4 *quanti-tray™, n*—a system for the quantification of enterococci. It consists of a sealer and trays which have multi-wells and can enumerate up to 2000 CFU/100 mL without dilution.

3.2.5 *snap pack, n*—a package containing Enterolert reagent for testing 100-mL sample either in the P/A format or quantitatively, that is, Quanti-Tray™ system).

4. Summary of Test Method [3]

4.1 This test method is used for the detection of enterococci, such as *E. faecium, E. faecalis* in drinking water, source water, recreational waters (marine water and fresh), and bottled water. When the reagent is added to the sample and incubated at 41 ± 0.5°C for 24 h, Enterolert can detect these bacteria at 1 CFU/100 mL. Fluorescence is produced when enterococci metabolizes the nutrient indicator. Enterolert can be used as a presence-absence test or for quantification (5-tube, 10-tube MPN, 15-tube serial dilution or the Quanti-Tray system).

5. Significance and Use

5.1 This test provides an easy and reliable method for the detection of enterococci in water within 24 h. For recreational water (fresh and marine) testing is performed to insure areas are safe for swimming. Enterolert also can be used for testing bottled water and drinking water.

6. Interferences

6.1 The presence of Bacillus spp. can interfere with the testing of marine water samples. To eliminate interference, a 1:10 dilution is required with sterile water (deionized or distilled).

7. Apparatus

7.1 *Ultraviolet Lamp*, 6-watt long wavelength (366 nm).

7.2 *41°C Incubator (± 0.5°C)*, air or water bath.

7.3 *Vessels*, sterile, nonfluorescent.

7.4 *Quanti-Tray Sealer*[4].

7.5 Quanti-Tray or Quanti-Tray 2000[4].

8. Reagents and Materials

8.1 *Purity of Water*—Unless otherwise indicated, references

---

[1] This test method is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.24 on Microbiology.

Current edition approved Dec. 10, 1999. Published April 2000.

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

[3] This test method is based on Enterolert, a product of IDEXX Laboratories, Westbrook, ME 04092.

[4] Available from IDEXX Laboratories, One Idexx Dr., Westbrook, ME 04092.

to water shall be understood to mean reagent water conforming to Specification D 1193, Type IV. Sterilize the water by either autoclaving or by sterile filtration (0.22 micron-filtered water).

8.2 *Enterolert Test Kit*[4].

9. Precautions

9.1 The analyst must observe the normal good laboratory practices and safety procedures required in a microbiology laboratory while preparing, using, and disposing of cultures, reagents and materials and while operating sterilization equipment and other equipment.

10. Sampling

10.1 Collect the sample as described in detail in the USEPA microbiological methods manual[5] and in accordance with Practices D 3370.

10.2 *Sample Storage Temperature and Handling Conditions*—Ice or refrigerate water samples at a temperature of 2 to 8°C during transit to the laboratory. Use insulated containers to ensure proper maintenance of storage temperatures. Take care that sample bottles are not totally immersed in water during transit or storage.

10.3 *Holding Time Limitations*—Examine samples, as soon as possible, after collection. Do not hold samples longer than 6 h between collection and initiation of analyses.

11. Quality Control Check

11.1 Check and record temperatures in incubators daily to insure temperature is within stated limits.

11.2 Quality control should be conducted on each new lot of Enterolert. See package insert for the recommended quality control procedure, which consists of the following protocol:

11.2.1 For each type of the American Type Culture Collection (ATCC) bacterial strain listed below, streak the culture onto labeled TSA or blood agar plates and incubate at 35°C for 18–24 h.

11.2.2 For each bacterial strain, touch a 1-µl loop to a colony and use it to inoculate a labeled test tube containing 5 mL of sterile deionized water. Close cap and shake thoroughly.

11.2.3 For each bacterial strain, take a 1-µl loop from the test tube and use it to inoculate a labeled vessel containing 100 mL.

11.2.4 Follow the Enterolert presence/absence steps listed above to test these controls. Compare the test results to the following expected results:

Control	ATTC No.	Expected Result
Enterococcus faecium	335667	Fluorescence
Serratia marcescens (g, –)	43862	No fluorescence
Aerococcus viridians (g, +)	10400	No fluorescence

12. Procedure

12.1 *Presence/Absence*—See package insert.

12.1.1 Samples should be brought to room temperature (18–30°C).

12.1.2 Carefully separate one snap pack from the strip.

12.1.3 Tap the snap pack to insure that all of the powder is towards the bottom of the pack.

12.1.4 Open the pack by snapping back the top of the score line. Do not touch the opening of pack.

12.1.5 Add the reagent to a 100-mL water sample, which is in a sterile, transparent, nonfluorescent vessel.

12.1.6 Aseptically cap and seal the vessel.

12.1.7 Shake until dissolved.

12.1.8 Incubate Enterolert for 24 h at 41 ± 0.5°C,

12.1.9 Read results at 24 h. If the sample is inadvertently incubated over 28 h without observation, the following guidelines apply: Lack of fluorescence after 28 h is a valid negative test. Fluorescence after 28 h is an invalid result.

12.1.10 Check for fluorescence by placing a 6-W 366-nm UV light within 5 in. of the sample in a dark environment. Be sure the light is facing away from your eyes and towards the vessel. If fluorescence is observed, the presence of enterococci is confirmed.

12.2 *MPN*—Quanti-tray enumeration test procedure for 100-mL sample (see package insert).

12.2.1 Follow steps 12.1.1-12.1.7.

12.2.2 Pour the reagent sample into the Quanti-Tray avoiding contact with the foil tab and seal the tray according to the Quanti-Tray package insert.

12.2.3 Incubate for 24 h at 41 ± 0.5°C.

12.2.4 Follow the same interpretation instructions from 12.1.9 through 12.1.10, and count the number of positive wells. Refer to the MPN table (see Table 1) provided with the Quanti-Tray to determine the CFU/100 mL.

12.3 *MPN*—5-tube × 20 mL, 10-tube × 10 mL and 15-tube serial dilution.

12.3.1 Follow 12.1.1-12.1.7.

12.3.2 sterile nonfluorescent tubes or transfer 20 mL of the reagent sample into five sterile nonfluorescent tubes.

12.3.3 Incubate for 24 h at 41 ± 0.5°C.

12.3.4 Follow 12.1.9 and 12.1.10 for interpretation.

12.3.5 Refer to the MPN tables (see Tables 2-4) to determine the CFU/100 mL.

13. Calculation

13.1 For P/A, there are no calculations. For quantification, refer to Quanti-Tray MPN tables and for the 5, 10, and 15 tube test results refer to the respective MPN tables.[6]

14. Report

14.1 Report as positive or negative for presence/absence testing.

14.2 Reporting of results is based on calculation of enterococci density determined from the appropriate MPN tables.

15. Precision and Bias [7]

15.1 *Precision*—A limited collaborative study was conducted. Nine technicians from three laboratories tested three different matrixes at three levels following Practice D 2777. Outliers were rejected in accordance with the statistical tests outlined in Practice D 2777. All data from one technician was

---

[5] Bordner, R.H., Winter, J.A., and Scarpino, P.V., Eds., *Microbiological Methods for Monitoring the Environment, Water, and Wastes*, EPA-600/8-78-017.

[6] *Standard Methods for the Examination of Water and Waste Water*, 19th Edition.

[7] Supporting data for this test method are available from ASTM Headquarters. Request RR: D 19-1167.

rejected for recreational water-marine and single values were rejected for both recreational water-fresh at the low level and for recreational water-marine at the low level. The mean count, the overall standard deviation (St), and the single operator standard deviation (so), are indicated in Table 5.

15.2 *Bias*—The mean value obtained for the samples (drinking water, recreational water fresh and marine) from the nine technicians for the low-, mid- and high-spiked samples all fall within the 95 % confidence interval (poisson distribution) of the actual values obtained from plating on blood agar.

15.3 Results of this collaborative study may not be typical of results for matrices other than those studied.

16. Keywords

16.1 bottled water; drinking water; enterococci; Enterolert; most probable number; presence-absence; Quanti-Tray; recreational water; source water

TABLE 1 51-Well Quanti-Tray® MPN Table

No. of Wells Giving Positive Reaction	MPN/100-mL Sample	95 % Confidence Limits	
		Lower	Upper
0	<1	0.0	3.7
1	1.0	0.3	5.6
2	2.0	0.6	7.3
3	3.1	1.1	9.0
4	4.2	1.7	10.7
5	5.3	2.3	12.3
6	6.4	3.0	13.9
7	7.5	3.7	15.5
8	8.7	4.5	17.1
9	9.9	5.3	18.8
10	11.1	6.1	20.5
11	12.4	7.0	22.1
12	13.7	7.9	23.9
13	15.0	8.8	25.7
14	16.4	9.8	27.5
15	17.8	10.8	29.4
16	19.2	11.9	31.3
17	20.7	13.0	33.3
18	22.2	14.1	35.2
19	23.8	15.3	37.3
20	25.4	16.5	39.4
21	27.1	17.7	41.6
22	28.8	19.0	43.9
23	30.6	20.4	46.3
24	32.4	21.8	48.7
25	34.4	23.3	51.2
26	36.4	24.7	53.9
27	38.4	26.4	56.6
28	40.6	28.0	59.5
29	42.9	29.7	62.5
30	45.3	31.5	65.6
31	47.8	33.4	69.0
32	50.4	35.4	72.5
33	53.1	37.5	76.2
34	56.0	39.7	80.1
35	59.1	42.0	84.4
36	62.4	44.6	88.8
37	65.9	47.2	93.7
38	69.7	50.0	99.0
39	73.8	53.1	104.8
40	78.2	56.4	111.2
41	83.1	59.9	118.3
42	88.5	63.9	126.2
43	94.5	68.2	135.4
44	101.3	73.1	146.0
45	109.1	78.6	158.7
46	118.4	85.0	174.5
47	129.8	92.7	195.0
48	144.5	102.3	224.1
49	165.2	115.2	272.2
50	200.5	135.8	387.6
51	>200.5	146.1	Infinite

TABLE 2 IDEXX Quanti-Tray/2000 MPN Table (cfu/100 mL)

No. Large Wells Positive	No. Small Wells Positive																							
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
0	<1	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0	11.0	12.0	13.0	14.0	15.1	16.1	17.1	18.1	19.1	20.2	21.2	22.2	23.2
1	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.1	9.1	10.1	11.1	12.1	13.2	14.2	15.2	16.2	17.3	18.3	19.3	20.4	21.4	22.4	23.5	24.5
2	2.0	3.0	4.1	5.1	6.1	7.1	8.1	9.2	10.2	11.2	12.2	13.3	14.3	15.3	16.4	17.4	18.5	19.5	20.6	21.6	22.6	23.7	24.8	25.8
3	3.1	4.1	5.1	6.1	7.2	8.2	9.2	10.3	11.3	12.4	13.4	14.4	15.5	16.5	17.6	18.6	19.7	20.8	21.8	22.9	23.9	25.0	26.1	27.1
4	4.1	5.2	6.2	7.2	8.3	9.3	10.4	11.4	12.5	13.5	14.6	15.6	16.7	17.8	18.8	19.9	21.0	22.0	23.1	24.2	25.2	26.3	27.4	28.5
5	5.2	6.3	7.3	8.4	9.4	10.5	11.5	12.6	13.7	14.7	15.8	16.9	17.9	19.0	20.1	21.2	22.2	23.3	24.4	25.5	26.6	27.7	28.8	29.9
6	6.3	7.4	8.4	9.5	10.6	11.6	12.7	13.8	14.9	15.9	17.0	18.1	19.2	20.3	21.4	22.5	23.6	24.7	25.8	26.9	28.0	29.1	30.2	31.3
7	7.4	8.5	9.6	10.7	11.8	12.8	13.9	15.0	16.1	17.2	18.3	19.4	20.5	21.6	22.7	23.8	24.9	26.0	27.1	28.3	29.4	30.5	31.6	32.8
8	8.6	9.7	10.8	11.9	13.0	14.1	15.2	16.3	17.4	18.5	19.6	20.7	21.8	22.9	24.1	25.2	26.3	27.4	28.6	29.7	30.8	32.0	33.1	34.3
9	9.8	10.9	12.0	13.1	14.2	15.3	16.4	17.5	18.7	19.8	20.9	22.0	23.2	24.3	25.4	26.6	27.7	28.9	30.0	31.2	32.3	33.5	34.6	35.8
10	11.0	12.1	13.2	14.3	15.5	16.6	17.7	18.9	20.0	21.1	22.3	23.4	24.6	25.7	26.9	28.0	29.2	30.3	31.5	32.7	33.8	35.0	36.2	37.4
11	12.2	13.4	14.5	15.6	16.8	17.9	19.1	20.2	21.4	22.5	23.7	24.8	26.0	27.2	28.3	29.5	30.7	31.9	33.0	34.2	35.4	36.6	37.8	39.0
12	13.5	14.6	15.8	16.9	18.1	19.3	20.4	21.6	22.7	23.9	25.1	26.3	27.5	28.6	29.8	31.0	32.2	33.4	34.6	35.8	37.0	38.2	39.4	40.7
13	14.8	16.0	17.1	18.3	19.5	20.6	21.8	23.0	24.2	25.4	26.6	27.8	29.0	30.2	31.4	32.6	33.8	35.0	36.2	37.5	38.7	39.9	41.1	42.4
14	16.1	17.3	18.5	19.7	20.9	22.1	23.3	24.4	25.7	26.9	28.1	29.3	30.5	31.7	33.0	34.2	35.4	36.7	37.9	39.1	40.4	41.6	42.9	44.2
15	17.5	18.7	19.9	21.1	22.3	23.5	24.7	25.9	27.2	28.4	29.6	30.9	32.1	33.3	34.6	35.8	37.1	38.4	39.6	40.9	42.2	43.4	44.7	46.0
16	18.9	20.1	21.3	22.6	23.8	25.0	26.2	27.5	28.7	30.0	31.2	32.5	33.7	35.0	36.3	37.5	38.8	40.1	41.4	42.7	44.0	45.3	46.6	47.9
17	20.3	21.6	22.8	24.0	25.3	26.5	27.8	29.1	30.3	31.6	32.9	34.1	35.4	36.7	38.0	39.3	40.6	41.9	43.2	44.5	45.9	47.2	48.5	49.8
18	21.8	23.1	24.3	25.6	26.9	28.1	29.4	30.7	32.0	33.3	34.6	35.9	37.2	38.5	39.8	41.1	42.4	43.8	45.1	46.4	47.8	49.1	50.5	51.9
19	23.3	24.6	25.9	27.2	28.5	29.8	31.1	32.4	33.7	35.0	36.3	37.6	39.0	40.3	41.6	43.0	44.3	45.7	47.1	48.4	49.8	51.2	52.6	54.0
20	24.9	26.2	27.5	28.8	30.1	31.4	32.8	34.1	35.4	36.8	38.1	39.5	40.8	42.2	43.6	44.9	46.3	47.7	49.1	50.5	51.9	53.3	54.7	56.1
21	26.5	27.8	29.2	30.5	31.8	33.2	34.5	35.9	37.3	38.6	40.0	41.4	42.8	44.1	45.5	46.9	48.4	49.8	51.2	52.6	54.1	55.5	56.9	58.4
22	28.2	29.5	30.9	32.3	33.6	35.0	36.4	37.7	39.1	40.5	41.9	43.3	44.7	46.2	47.6	49.0	50.5	51.9	53.4	54.8	56.3	57.8	59.3	60.7
23	29.9	31.3	32.7	34.1	35.4	36.8	38.2	39.7	41.1	42.5	43.9	45.4	46.8	48.3	49.7	51.2	52.7	54.2	55.6	57.1	58.6	60.2	61.7	63.2
24	31.7	33.1	34.5	35.9	37.3	38.8	40.2	41.6	43.1	44.6	46.0	47.5	49.0	50.5	51.9	53.4	55.0	56.5	58.0	59.5	61.1	62.6	64.2	65.8
25	33.5	35.0	36.4	37.9	39.3	40.8	42.2	43.7	45.2	46.7	48.2	49.7	51.2	52.7	54.3	55.8	57.3	58.9	60.5	62.0	63.6	65.2	66.8	68.4
26	35.5	36.9	38.4	39.9	41.3	42.8	44.3	45.9	47.4	48.9	50.4	52.0	53.5	55.1	56.7	58.2	59.8	61.4	63.0	64.7	66.3	67.9	69.6	71.2
27	37.4	38.9	40.4	41.9	43.5	45.0	46.5	48.1	49.6	51.2	52.8	54.4	56.0	57.6	59.2	60.8	62.4	64.1	65.7	67.4	69.1	70.8	72.5	74.2
28	39.5	41.0	42.6	44.1	45.7	47.2	48.8	50.4	52.0	53.6	55.2	56.9	58.5	60.1	61.8	63.5	65.2	66.9	68.6	70.3	72.0	73.7	75.5	77.3
29	41.6	43.2	44.8	46.4	48.0	49.6	51.2	52.8	54.5	56.1	57.8	59.5	61.2	62.9	64.6	68.3	68.0	69.8	71.5	73.3	75.1	76.9	78.7	80.5
30	43.9	45.5	47.1	48.7	50.4	52.0	53.7	55.4	57.1	58.8	60.5	62.2	64.0	65.7	67.5	69.3	71.0	72.8	74.7	76.5	78.3	80.2	82.1	84.0
31	46.2	47.9	49.5	51.2	52.9	54.6	56.3	58.1	59.8	61.6	63.3	65.1	66.9	68.7	70.5	72.4	74.2	76.1	78.0	79.9	81.8	83.7	85.7	87.6
32	48.7	50.4	52.1	53.8	55.6	57.3	59.1	60.9	62.7	64.5	66.3	68.1	70.0	71.9	73.8	75.7	77.6	79.5	81.5	83.5	85.4	87.5	89.5	91.5
33	51.2	53.0	54.7	56.5	58.3	60.1	62.0	63.8	65.7	67.6	69.5	71.4	73.3	75.2	77.2	79.2	81.2	83.2	85.2	87.3	89.3	91.4	93.5	95.7
34	53.9	55.7	57.6	59.4	61.3	63.1	65.0	66.9	68.9	70.8	72.8	74.8	76.8	78.8	80.8	82.9	85.0	87.1	89.2	91.4	93.5	95.7	97.9	100.1
35	56.8	58.6	60.5	62.4	64.4	66.3	68.3	70.3	72.3	74.3	76.3	78.4	80.5	82.6	84.7	86.9	89.1	91.3	93.5	95.7	98.0	100.3	102.6	105.0
36	59.8	61.7	63.7	65.7	67.7	69.7	71.7	73.8	75.9	78.0	80.1	82.3	84.5	86.7	88.9	91.2	93.5	95.8	98.1	100.5	102.9	105.3	107.7	110.2
37	62.9	65.0	67.0	69.1	71.2	73.3	75.4	77.6	79.8	82.0	84.2	86.5	88.8	91.1	93.4	95.8	98.2	100.6	103.1	105.6	108.1	110.7	113.3	115.9
38	66.3	68.4	70.6	72.7	74.9	77.1	79.4	81.6	83.9	86.2	88.6	91.0	93.4	95.8	98.3	100.8	103.4	105.9	108.6	111.2	113.9	116.6	119.4	122.2
39	69.9	72.2	74.4	76.6	78.9	81.3	83.6	86.0	88.4	90.9	93.3	95.9	98.4	101.0	103.6	106.3	109.0	111.8	114.5	117.4	120.3	123.2	126.1	129.2
40	73.8	76.2	78.5	80.9	83.3	85.7	88.2	90.7	93.3	95.9	98.5	101.2	103.9	106.7	109.5	112.4	115.3	118.2	121.2	124.2	127.3	130.5	133.7	137.0
41	78.0	80.5	83.0	85.5	88.0	90.6	93.3	95.9	98.7	101.4	104.3	107.1	110.0	113.0	116.0	119.1	122.2	125.4	128.7	132.0	135.3	138.8	142.3	145.9
42	82.6	85.2	87.8	90.5	93.2	96.0	98.8	101.7	104.6	107.6	110.6	113.7	116.9	120.1	123.3	126.7	130.1	133.6	137.1	140.8	144.5	148.3	152.2	156.1
43	87.6	90.4	93.2	96.0	99.0	101.9	105.0	108.1	111.2	114.5	117.8	121.1	124.6	128.1	131.7	135.4	139.1	143.0	147.0	151.0	155.1	159.4	163.8	168.2
44	93.1	96.1	99.1	102.2	105.4	108.6	111.9	115.3	118.7	122.3	125.9	129.6	133.4	137.4	141.4	145.5	149.7	154.1	158.5	163.1	167.8	172.7	177.7	182.9
45	99.3	102.5	105.8	109.2	112.6	116.2	119.8	123.6	127.4	131.3	135.4	139.6	143.9	148.3	152.9	157.6	162.4	167.4	172.6	177.9	183.5	189.2	195.1	201.2
46	106.3	109.8	113.4	117.2	121.0	125.0	129.1	133.3	137.6	142.1	146.7	151.5	156.5	161.6	166.9	172.5	178.2	184.2	190.4	196.8	203.5	210.5	217.8	225.4
47	114.3	118.3	122.4	126.6	130.9	135.4	140.1	145.0	150.0	155.3	160.7	166.4	172.3	178.5	185.0	191.8	198.9	206.3	214.2	222.4	231.0	240.0	249.5	259.5
48	123.9	128.4	133.1	137.9	143.0	148.3	153.9	159.7	165.8	172.2	178.9	186.0	193.5	201.4	209.8	218.7	228.2	238.2	248.9	260.2	272.3	285.1	298.7	313.0
49	135.5	140.8	146.4	152.3	158.5	165.0	172.0	179.3	187.2	195.6	204.6	214.3	224.7	235.9	248.1	261.3	275.5	290.9	307.6	325.5	344.8	365.4	387.3	410.6

TABLE 3 IDEXX Quanti-Tray/2000 MPN Table (cfu/100 mL)

	No. Small Wells Positive																							
No.	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48
	25.3	26.3	27.4	28.4	29.5	30.5	31.5	32.6	33.6	34.7	35.7	36.8	37.8	38.9	39.9	41.0	42.1	43.1	44.2	45.3	46.3	47.4	48.5	49.5
	26.6	27.6	28.7	29.7	30.8	31.9	32.9	34.0	35.0	36.1	37.2	38.2	39.3	40.4	41.4	42.5	43.6	44.7	45.7	46.8	47.9	49.0	50.1	51.2
	27.9	29.0	30.0	31.1	32.2	33.2	34.3	35.4	36.5	37.5	38.6	39.7	40.8	41.9	42.9	44.0	45.1	46.2	47.3	48.4	49.5	50.6	51.7	52.8
	29.3	30.3	31.4	32.5	33.6	34.7	35.7	36.8	37.9	39.0	40.1	41.2	42.3	43.4	44.5	45.6	46.7	47.8	48.9	50.0	51.2	52.3	53.4	54.5
	30.7	31.7	32.8	33.9	35.0	36.1	37.2	38.3	39.4	40.5	41.6	42.8	43.9	45.0	46.1	47.2	48.3	49.5	50.6	51.7	52.9	54.0	55.1	56.3
	32.1	33.2	34.3	35.4	36.5	37.6	38.7	39.8	41.0	42.1	43.2	44.3	45.5	46.6	47.7	48.9	50.0	51.2	52.3	53.5	54.6	55.8	56.9	58.1
	33.5	34.6	35.8	36.9	38.0	39.1	40.3	41.4	42.6	43.7	44.8	46.0	47.1	48.3	49.4	50.6	51.7	52.9	54.1	55.2	56.4	57.6	58.7	59.9
	35.0	36.2	37.3	38.4	39.6	40.7	41.9	43.0	44.2	45.3	46.5	47.7	48.8	50.0	51.2	52.3	53.5	54.7	55.9	57.1	58.2	59.4	60.6	61.8
	36.5	37.7	38.9	40.0	41.2	42.3	43.5	44.7	45.9	47.0	48.2	49.4	50.6	51.8	53.0	54.1	55.3	56.5	57.7	58.9	60.2	61.4	62.6	63.8
	38.1	39.3	40.5	41.6	42.8	44.0	45.2	46.4	47.6	48.8	50.0	51.2	52.4	53.6	54.8	56.0	57.2	58.4	59.7	60.9	62.1	63.4	64.6	65.8
	39.7	40.9	42.1	43.3	44.5	45.7	46.9	48.1	49.3	50.6	51.8	53.0	54.2	55.5	56.7	57.9	59.2	60.4	61.6	62.9	64.2	65.4	66.7	67.9
	41.4	42.6	43.8	45.0	46.3	47.5	48.7	49.9	51.2	52.4	53.6	54.9	56.1	57.4	58.6	59.9	61.2	62.4	63.7	65.0	66.2	67.5	68.8	70.1
	43.1	44.3	45.6	46.8	48.1	49.3	50.5	51.8	53.1	54.3	55.6	56.8	58.1	59.4	60.7	61.9	63.2	64.5	65.8	67.1	68.4	69.7	71.0	72.3
	44.9	46.1	47.4	48.6	49.9	51.2	52.4	53.7	55.0	56.3	57.6	58.9	60.2	61.5	62.8	64.1	65.4	66.7	68.0	69.3	70.7	72.0	73.3	74.7
	46.7	48.0	49.3	50.5	51.8	53.1	54.4	55.7	57.0	58.3	59.6	60.9	62.3	63.6	64.9	66.3	67.6	68.9	70.3	71.6	73.0	74.4	75.7	77.1
	48.6	49.9	51.2	52.5	53.8	55.1	56.4	57.8	59.1	60.4	61.8	63.1	64.5	65.8	67.2	68.5	69.9	71.3	72.6	74.0	75.4	76.8	78.2	79.6
	50.5	51.8	53.2	54.5	55.8	57.2	58.5	59.9	61.2	62.6	64.0	65.3	66.7	68.1	69.5	70.9	72.3	73.7	75.1	76.5	77.9	79.3	80.8	82.2
	52.5	53.9	55.2	56.6	58.0	59.3	60.7	62.1	63.5	64.9	66.3	67.7	69.1	70.5	71.9	73.3	74.8	76.2	77.6	79.1	80.5	82.0	83.5	84.9
	54.6	56.0	57.4	58.8	60.2	61.6	63.0	64.4	65.8	67.2	68.6	70.1	71.5	73.0	74.4	75.9	77.3	78.8	80.3	81.8	83.3	84.8	86.3	87.8
	56.8	58.2	59.6	61.0	62.4	63.9	65.3	66.7	68.2	69.7	71.1	72.6	74.1	75.5	77.0	78.5	80.0	81.5	83.1	84.6	86.1	87.6	89.2	90.7
	59.0	60.4	61.9	63.3	64.8	66.3	67.7	69.2	70.7	72.2	73.7	75.2	76.7	78.2	79.8	81.3	82.8	84.4	85.9	87.5	89.1	90.6	92.2	93.8
	61.3	62.8	64.3	65.8	67.3	68.8	70.3	71.8	73.3	74.9	76.4	77.9	79.5	81.0	82.6	84.2	85.8	87.4	89.0	90.6	92.2	93.8	95.4	97.1
	63.7	65.3	66.8	68.3	69.8	71.4	72.9	74.5	76.1	77.6	79.2	80.8	82.4	84.0	85.6	87.2	88.9	90.5	92.1	93.8	95.5	97.1	98.8	100.5
	66.3	67.8	69.4	71.0	72.5	74.1	75.7	77.3	78.9	80.5	82.1	83.8	85.4	87.1	88.7	90.4	92.1	93.8	95.5	97.2	98.9	100.6	102.3	104.1
	68.9	70.5	72.1	73.7	75.3	77.0	78.6	80.2	81.9	83.6	85.2	86.9	88.6	90.3	92.0	93.8	95.5	97.2	99.0	100.7	102.5	104.3	106.1	107.9
	71.7	73.3	75.0	76.6	78.3	80.0	81.6	83.3	85.0	86.8	88.5	90.2	92.0	93.7	95.5	97.3	99.1	100.9	102.7	104.5	106.3	108.2	110.0	111.9
	74.6	76.3	78.0	79.7	81.4	83.1	84.8	86.6	88.4	90.1	91.9	93.7	95.5	97.3	99.2	101.0	102.9	104.7	106.6	108.5	110.4	112.3	114.2	116.2
	77.6	79.4	81.1	82.9	84.6	86.4	88.2	90.0	91.9	93.7	95.5	97.4	99.3	101.2	103.1	105.0	106.9	108.8	110.8	112.7	114.7	116.7	118.7	120.7
	80.8	82.6	84.4	86.2	88.1	89.9	91.8	93.7	95.6	97.5	99.4	101.3	103.3	105.2	107.2	109.2	111.2	113.2	115.2	117.3	119.3	121.4	123.5	125.6
	84.2	86.1	87.9	89.8	91.7	93.6	95.6	97.5	99.5	101.5	103.5	105.5	107.5	109.5	111.6	113.7	115.7	117.8	120.0	122.1	124.2	126.4	128.6	130.8
	87.8	89.7	91.7	93.6	95.6	97.6	99.6	101.6	103.7	105.7	107.8	109.9	112.0	114.1	116.3	118.5	120.6	122.8	125.1	127.3	129.5	131.8	134.1	136.4
	91.6	93.6	95.6	97.7	99.7	101.8	103.9	106.0	108.2	110.3	112.5	114.7	116.9	119.1	121.4	123.6	125.9	128.2	130.5	132.9	135.3	137.7	140.1	142.5
	95.7	97.7	99.9	102.0	104.2	106.3	108.5	110.7	113.0	115.2	117.5	119.8	122.1	124.5	126.8	129.2	131.6	134.0	136.5	139.0	141.5	144.0	146.6	149.1
	100.0	102.2	104.4	106.6	108.9	111.2	113.5	115.8	118.2	120.5	122.9	125.3	127.8	130.3	132.8	135.3	137.8	140.4	143.0	145.6	148.3	150.9	153.6	156.4
	104.7	107.0	109.3	111.7	114.0	116.4	118.9	121.3	123.8	126.3	128.8	131.4	134.0	136.6	139.2	141.9	144.6	147.3	150.1	152.9	155.7	158.6	161.5	164.4
	109.7	112.2	114.6	117.1	119.6	122.1	124.7	127.3	129.9	132.6	135.3	138.0	140.8	143.6	146.4	149.2	152.1	155.0	158.0	161.0	164.0	167.1	170.2	173.3
	115.2	117.8	120.4	123.0	125.7	128.4	131.1	133.9	136.7	139.5	142.4	145.3	148.3	151.3	154.3	157.3	160.4	163.6	166.8	170.0	173.3	176.6	179.9	183.3
	121.3	124.0	126.8	129.6	132.4	135.3	138.2	141.2	144.2	147.2	150.3	153.5	156.6	159.9	163.1	166.4	169.8	173.2	176.7	180.2	183.7	187.3	191.0	194.7
	127.9	130.8	133.8	136.8	139.9	143.0	146.1	149.3	152.6	155.9	159.2	162.6	166.1	169.6	173.2	176.8	180.4	184.2	188.0	191.8	195.7	199.6	203.7	207.7
	135.3	138.5	141.7	145.0	148.3	151.7	155.1	158.6	162.1	165.7	169.4	173.1	176.9	180.7	184.7	188.6	192.7	196.8	201.0	205.3	209.6	214.0	218.5	223.0
	143.7	147.1	150.6	154.2	157.8	161.5	165.3	169.1	173.0	177.0	181.1	185.2	189.4	193.7	198.1	202.5	207.0	211.7	216.4	221.1	226.0	231.0	236.0	241.1
	153.2	157.0	160.9	164.8	168.9	173.0	177.2	181.4	185.8	190.3	194.8	199.5	204.2	209.1	214.0	219.0	224.2	229.4	234.8	240.2	245.8	251.5	257.2	263.1
	164.3	168.6	172.9	177.3	181.9	186.5	191.3	196.1	201.1	206.2	211.4	216.7	222.1	227.7	233.4	239.2	245.2	251.3	257.5	263.8	270.3	276.9	283.6	290.5
	177.5	182.3	187.3	192.4	197.6	202.9	208.4	214.0	219.8	225.8	231.8	238.1	244.5	251.0	257.7	264.6	271.7	278.9	286.3	293.8	301.5	309.4	317.4	325.6
	193.6	199.3	205.0	211.0	217.2	223.5	230.0	236.7	243.6	250.7	258.1	265.6	273.3	281.2	289.4	297.8	306.3	315.1	324.1	333.3	342.8	352.4	362.3	372.4
	214.1	220.9	227.9	235.1	242.7	250.4	258.4	266.7	275.3	284.1	293.2	302.6	312.3	322.3	332.5	343.0	353.8	364.9	376.2	387.9	399.8	412.0	424.5	437.4
	241.5	250.0	258.9	268.2	277.8	287.7	298.1	308.8	319.9	331.4	343.3	355.5	368.1	381.1	394.5	408.3	422.5	437.0	452.0	467.4	483.3	499.5	516.3	533.5
	280.9	292.4	304.4	316.9	330.0	343.6	357.8	372.5	387.7	403.4	419.8	436.6	454.1	472.1	490.7	509.9	529.8	550.4	571.7	593.8	616.7	640.5	665.3	691.0
	344.1	360.9	378.4	396.8	416.0	436.0	456.9	478.6	501.2	524.7	549.2	574.8	601.5	629.4	658.6	689.3	721.5	755.5	791.5	829.7	870.4	913.9	960.6	1011.1
	461.1	488.4	517.2	547.5	579.4	613.1	648.8	686.7	727.0	770.1	816.4	866.4	920.8	980.4	1046.2	1119.9	1203.3	1299.7	1413.6	1553.1	1732.9	1986.3	2419.2	>2419.2

TABLE 4 MPN Index and 95 % Confidence Limits for Various Combinations of Positive Results When Five Tubes are Used/Dilution (10 mL, 1.0 mL, 0.1 mL)^A

Combination of Positives	MPN Index/100 mL	95 % Confidence Limits		Combination of Positives	MPN Index/100 mL	95 % Confidence Limits	
		Lower	Upper			Lower	Upper
				4-2-0	22	9.0	56
0-0-0	<2	—	—	4-2-1	26	12	65
0-0-1	2	1.0	10	4-3-0	27	12	67
0-1-0	2	1.0	10	4-3-1	33	15	77
0-2-0	4	1.0	13	4-4-0	34	16	80
				5-0-0	23	9.0	86
1-0-0	2	1.0	11	5-0-1	30	10	110
1-0-1	4	1.0	15	5-0-2	40	20	140
1-1-0	4	1.0	15	5-1-0	30	10	120
1-1-1	6	2.0	18	5-1-1	50	20	150
1-2-0	6	2.0	18	5-1-2	60	30	180
2-0-0	4	1.0	17	5-2-0	50	20	170
2-0-1	7	2.0	20	5-2-1	70	30	210
2-1-0	7	2.0	21	5-2-2	90	40	250
2-1-1	9	3.0	24	5-3-0	80	30	250
2-2-0	9	3.0	25	5-3-1	110	40	300
2-3-0	12	5.0	29	5-3-2	140	60	360
3-0-0	8	3.0	24	5-3-3	170	80	410
3-0-1	11	4.0	29	5-4-0	130	50	390
3-1-0	11	4.0	29	5-4-1	170	70	480
3-1-1	14	6.0	35	5-4-2	220	100	580
3-2-0	14	6.0	35	5-4-3	280	120	690
3-2-1	17	7.0	40	5-4-4	350	160	820
				5-5-0	240	100	940
4-0-0	13	5.0	38	5-5-1	300	100	1300
4-0-1	17	7.0	45	5-5-2	500	200	2000
4-1-0	17	7.0	46	5-5-3	900	300	2900
4-1-1	21	9.0	55	5-5-4	1600	600	5300
4-1-2	26	12	63	5-5-5	≥1600	—	—

^{A}Based on *Standard Methods for the Examination of Water and Wastewater*, 19th ed.

TABLE 5 Mean Count, Overall Standard Deviation and Single Operator Standard Deviation

NOTE 1—All calculations were made from the statistical summary given as Table One in the study file

Summary Table	Low Level				Middle Level				High Level			
Background Matrix	n	X MPN/100 mL	St %	So %	n	X MPN/100 mL	St %	So %	n	X MPN/100 mL	St %	So %
Drinking water	9	9.1	27.7	24.2	9	26.2	15.1	15	9	61.0	10.2	9.5
Rec. water Fresh	9	9.4^A	30.2^A	23.4^A	9	29.1	14.1	6.9	9	64.3	10.6	11
Rec. water Marine	8	7.9^A	25.2^A	17.7^A	8	29.4	17.4	13	8	67.5	8.0	7.6

^{A}One value rejected to make this estimate.

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:

CFR Section(s):

Standards Body:

APPROVED

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

Designation: D 665 – 98$^{\epsilon1}$

An American National Standard

Designation: 135/93

Standard Test Method for Rust-Preventing Characteristics of Inhibited Mineral Oil in the Presence of Water[1]

This standard is issued under the fixed designation D 665; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

ϵ^1 NOTE—Paragraph 6.3.2 was corrected editorially in August 1999.

1. Scope

1.1 This test method is used to evaluate the ability of inhibited mineral oils, particularly steam-turbine oils, to aid in preventing the rusting of ferrous parts should water become mixed with the oil. This test method is also used for testing other oils, such as hydraulic oils and circulating oils. Provision is made in the procedure for testing heavier-than-water fluids.

NOTE 1—For synthetic fluids, such as phosphate ester types, the plastic holder and beaker cover should be made of a chemically resistant material, such as polytetrafluoroethylene (PTFE).

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:*

A 108 Specification for Steel Bars, Carbon, Cold-Finished, Standard Quality[2]

A 240/A 240M Specification for Heat-Resisting Chromium and Chromium-Nickel Stainless Steel Plate, Sheet, and Strip for Pressure Vessels[3]

D 91 Test Method for Precipitation Number of Lubricating Oils[4]

D 1193 Specification for Reagent Water[5]

D 1401 Test Method for Water Separability of Petroleum Oils and Synthetic Fluids[4]

D 2422 Classification of Industrial Fluid Lubricants by Viscosity System[4]

D 3603 Test Method for Rust-Preventing Characteristics of Steam Turbine Oil in the Presence of Water (Horizontal Disk Method)[6]

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products[6]

E 1 Specification for ASTM Thermometers[7]

Motor Fuels, Section I, Annex A2, Reference Materials and Blending Accessories[8]

2.2 *Other Documents:*

Specifications-IP Standard Thermometers, Appendix A[9]

Specifications for IP Standard Reference Liquids, Appendix B[9]

SAE Standard J 405 Chemical Composition of SAE Wrought Stainless Steels[10]

BS 871 Specification for abrasive papers and cloths[9]

BS 970: Part 1: Carbon and Carbon Manganese Steels Including Free Cutting Steels[9]

3. Summary of Test Method

3.1 A mixture of 300 mL of the oil under test is stirred with 30 mL of distilled water or synthetic sea water, as required, at a temperature of 60°C (140°F) with a cylindrical steel test rod completely immersed therein. It is customary to run the test for 24 h; however, the test period may, at the discretion of the contracting parties, be for a shorter or longer period. The test rod is observed for signs of rusting and, if desired, degree of rusting.

4. Significance and Use

4.1 In many instances, such as in the gears of a steam turbine, water can become mixed with the lubricant, and

---

[1] This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricantsand is the direct responsibility of Subcommittee DO2.C on Turbine Oils.

In the IP, this test method is under the jurisdiction of the Standardization Committee. This test method was adopted as a joint ASTM – IP standard in 1964.

Current edition approved June 10, 1998. Published September 1998. Originally published as D 665 – 42 T. Last previous edition D 665 – 95.

[2] *Annual Book of ASTM Standards*, Vol 01.05.

[3] *Annual Book of ASTM Standards*, Vol 01.03.

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

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

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

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

[8] *Annual Book of ASTM Standards*, Vol 05.04.

[9] *Annual Book of IP Standard Methods for Analysis and Testing of Petroleum and Related Products*, Vol 2.

[10] *1995 SAE Handbook*, Vol 1.

rusting of ferrous parts can occur. This test indicates how well inhibited mineral oils aid in preventing this type of rusting. This test method is also used for testing hydraulic and circulating oils, including heavier-than-water fluids. It is used for specification of new oils and monitoring of in-service oils.

Note 2—This test method was used as a basis for Test Method D 3603. Test Method D 3603 is used to test the oil on separate horizontal and vertical test rod surfaces, and can provide a more discriminating evaluation.

5. Apparatus

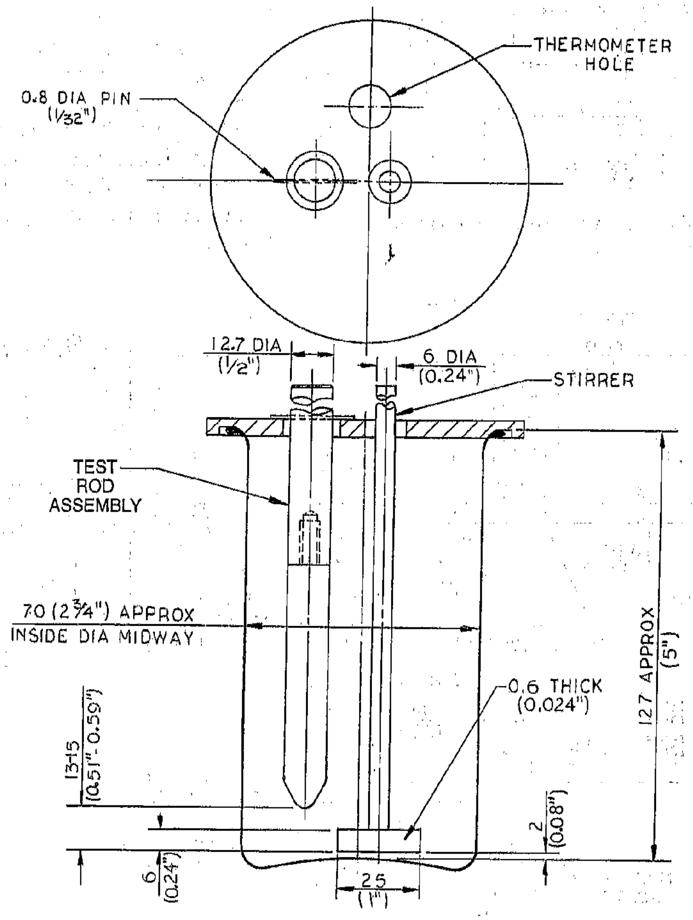
5.1 *Oil Bath*—A thermostatically controlled liquid bath capable of maintaining the test sample at a temperature of 60 ± 1°C (140 ± 2°F) (see Note 3). An oil having a viscosity of approximately ISO VG 32 (see Classification D 2422) is suitable for the bath. The bath shall have a cover with holes to accommodate the test beakers.

Note 3—ASTM Thermometer 9C (9F), as prescribed in Specification E 1, or IP Thermometer 21C in accordance with IP Volume 2, Appendix A, is suitable to indicate the temperature. Alternatively, calibrated thermocouples may be used.

5.2 *Beaker*—A 400-mL, Berzelius-type, tall-form heat-resistant glass[11] beaker without pourout, as shown in Fig. 1, approximately 127 mm (5 in.) in height measured from the inside bottom center and approximately 70 mm (2¾ in.) in inside diameter measured at the middle.

5.3 *Beaker Cover*—A flat beaker cover of glass or poly(methyl methacrylate) (PMMA) (Note 4), kept in position by suitable means such as a rim or groove. Two holes shall be provided on any diameter of the cover; one for a stirrer 12 mm (¹⁵⁄₃₂ in.) in diameter with its center 6.4 mm (¼ in.) from the center of the cover; and the other, on the opposite side of the center of the cover, for the test rod assembly (see Section 8), 18 mm (⁴⁵⁄₆₄ in.) in diameter with its center 16 mm (⅝ in.) from the center of the cover. In addition, a third hole 12 mm (¹⁵⁄₃₂ in.) in diameter shall be provided for a temperature measuring device, with its center 22.5 mm (⅞ in.) from the center of the cover and on a diameter of the cover at right angles to the diameter through the other two holes.

Note 4—An inverted petri dish makes a suitable cover, as the sides of the dish aid in keeping it in position. Fig. 2 shows a PMMA resin cover

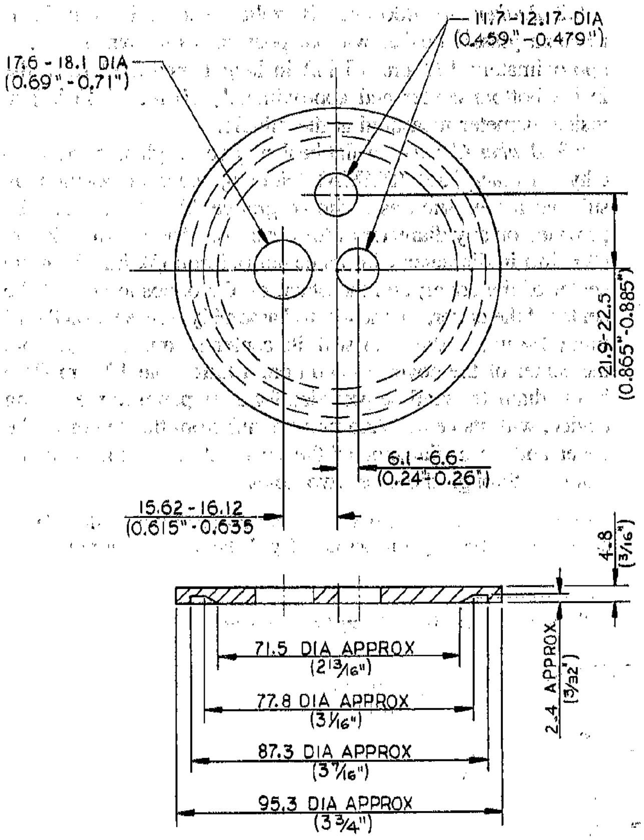


Note 1—All units are in millimetres, unless otherwise specified.

FIG. 1 Rusting Test Apparatus

---

[11] Borosilicate glass is satisfactory for this purpose.



Note 1—All units are in millimetres, unless otherwise specified.

FIG. 2 Beaker Cover

for the beaker which has been found to be suitable. An optional feature is shown, consisting of a slot, 1.6 by 27 mm (1/16 by 1 1/16 in.), which is centered on a diameter of the stirrer hole at right angles to the cover diameter through the test rod hole and stirrer hole. This feature allows withdrawal of the stirrer while the beaker cover is in place. When the test method test is used for other fluids such as synthetics, the beaker cover should be made from chemically resistant material such as polymonochlorotrifluoroethylene (PCTFE).

5.4 The plastic holder shall be made of PMMA resin in accordance with the dimensions shown in Fig. 3 (two types of holders are illustrated). When testing synthetic fluids, the plastic holder should be made from chemically resistant material such as polytetrafluoroethylene (PTFE).

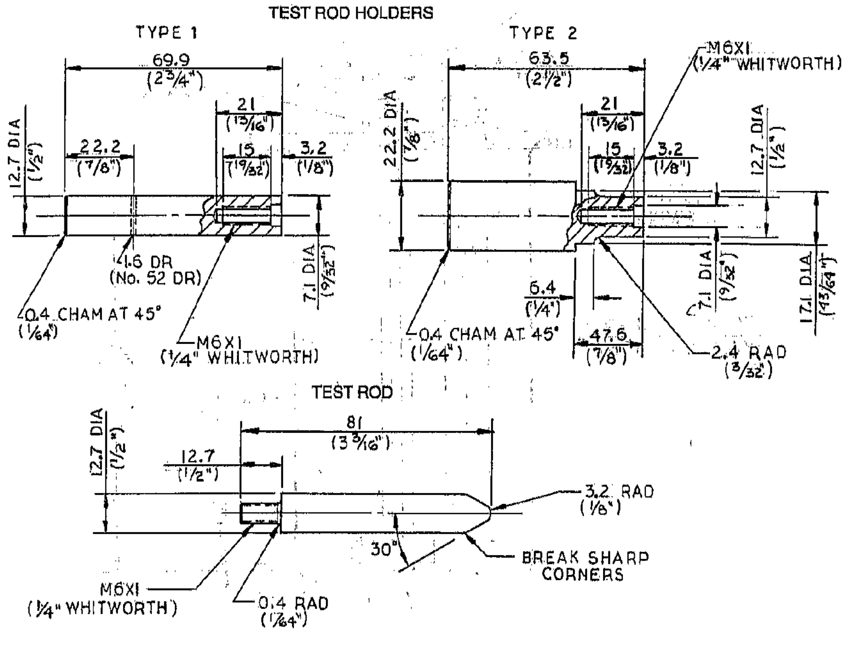
5.5 *Stirrer*—A stirrer constructed entirely from stainless steel (Note 5 and Note 6) in the form of an inverted T. A flat blade 25 by 6 by 0.6 mm (1 by 0.24 by 0.024 in.) shall be attached to a 6-mm (0.24-in.) rod in such a way that the blade is symmetrical with the rod and has its flat surface in the vertical plane.

Note 5—A suitable material is an 18 % chromium, 8 % nickel alloy steel conforming to Type 304, of Specification A 240, or SAE No. 30304 (see SAE J405), or BS 970: Part 1: 1983: 302S31.[9]

Note 6—If stainless steel is not obtainable, stirrers made of heat-resistant glass[11] and having approximately the same dimensions as the stainless steel stirrers specified can be used.

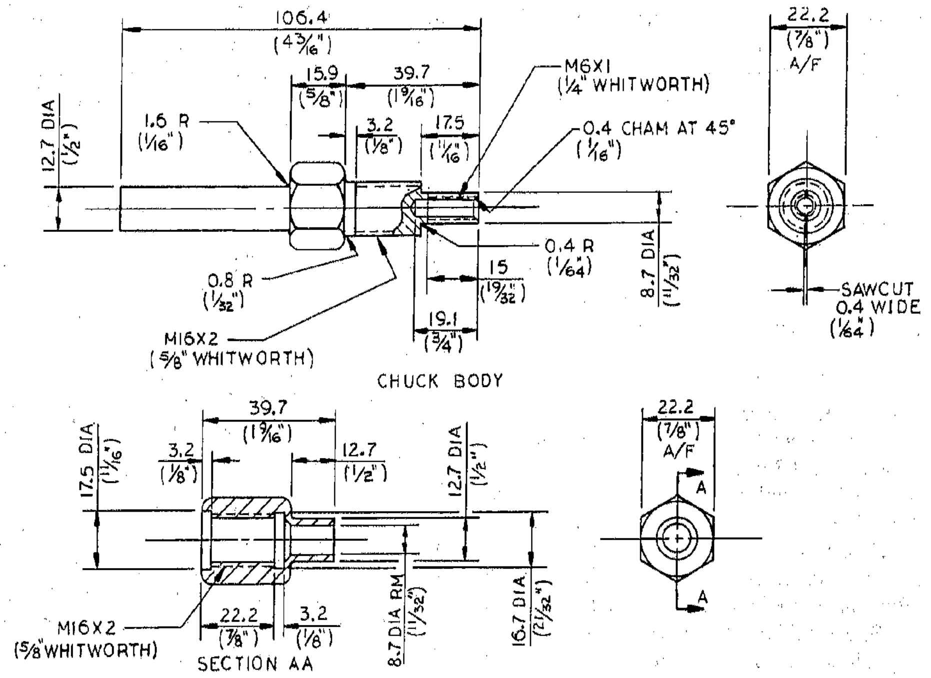
5.6 *Stirring Apparatus*—Any convenient form of stirring apparatus capable of maintaining a speed of 1000 ± 50 rpm.

5.7 *Grinding and Polishing Equipment*—A 150-grit[9] (99-µm) and a 240-grit[9] (58-µm) in accordance with BS 871 or its equivalent, metalworking aluminum oxide abrasive cloth coat on a jeans backing, a suitable chuck (see Fig. 4) for holding the test rod, and a means of rotating the test rod at a speed of 1700 to 1800 rpm.



Note 1—All units are in millimetres, unless otherwise specified.

FIG. 3 Test Rod and Holders



NOTE 1—All units are in millimetres, unless otherwise specified.

FIG. 4 Chuck for Polishing Test Rods

5.8 *Oven*, capable of maintaining a temperature of 65°C (150°F).

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 conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[12] 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*— Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II of Specification D 1193.

6.3 The synthetic sea water shall have the following composition:

Salt	g/L
NaCl	24.54
$MgCl_2 \cdot 6H_2O$	11.10
Na_2SO_4	4.09
$CaCl_2$	1.16
KCl	0.69
$NaHCO_3$	0.20
KBr	0.10
H_3BO_3	0.03
$SrCl_2 \cdot 6H_2O$	0.04
NaF	0.003

6.3.1 The solution can be conveniently prepared as follows. This procedure avoids any precipitation in concentrated solutions with subsequent uncertainty of complete resolution. Using certified pure (cp) chemicals and distilled water, prepare the following stock solutions (also see Test Method D 1401, Section 6):

Stock Solution No. 1:

$MgCl_2 \cdot 6H_2O$	3885 g
$CaCl_2$(anhydrous)	406 g
$SrCl_2 \cdot 6H_2O$	14 g

Dissolve and dilute to 7 L.

Stock Solution No. 2:

KCl	483 g
$NaHCO_3$	140 g
KBr	70 g
H_3BO_3	21 g
NaF	2.1 g

Dissolve and dilute to 7 L.

6.3.2 To prepare the synthetic sea water, dissolve 245.4 g of NaCl and 40.94 g of Na_2SO_4 in a few litres of distilled water, add 200 mL of Stock Solution No. 1 and 100 mL of Stock Solution No. 2 and dilute to 10 L. Stir the 10-L batch and add 0.1 *N* Na_2CO_3 solution until the pH is between 7.8 and 8.2. One or two millilitres of the carbonate solution will be required.

6.4 *Precipitation Naphtha*, as specified in Test Method D 91. (**Warning**—Flammable. Health hazard.)

6.5 *Isooctane*, as specified in Table 32, Motor Fuels Section

---

[12] *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.

I, Annex A2, Reference Materials and Blending Accessories. (**Warning**—Flammable. Health hazard.)

6.6 *IP 60/80 Petroleum Spirit*, as specified by IP Standard Reference Liquids. (**Warning**—Flammable. Health hazard.)

6.7 *Steel Test Rod*, as specified in Section 8.

7. Sampling

7.1 Sample for this test can come from tanks, drums, small containers, or even operating equipment, and they should be truly representative of the entire quantity. Therefore, use the applicable apparatus and techniques described in Practice D 4057, or other comparable standard practice.

8. Test Rod and Its Preparation

8.1 For each test oil, prepare two steel test rods. These may either be new or from a previous test (seeNote 7) and shall be prepared in accordance with 8.2 and 8.3.

8.2 The test rod assembly shall consist of a round steel test rod fitted to a plastic holder. The round steel test rod when new shall be 12.7 mm (0.5 in.) in diameter and approximately 68 mm ($2\frac{11}{16}$ in.) in length exclusive of the threaded portion which screws into the plastic holder and shall be tapered at one end as shown in Fig. 3. It shall be made of steel conforming to Grade 10180 of Specification A 108 or to BS 970 Part I: 1983-070M20. If these steels are not available, other equivalent steels may be used, provided they are found to be satisfactory by comparative test using this Test Method D 665 – IP 135.

NOTE 7—When making a check test, the steel test rod that showed rust should not be reused. Test rods that repeatedly show rust in tests of various oils can be imperfect. Such test rods should be used with oils known to pass the test. If rusting occurs in repeat tests, these test rods should be discarded.

8.3 *Preliminary Grinding*—If the test rod has been used previously and is free of rust or other irregularities, the preliminary grinding may be omitted, and it may be subjected only to final polishing as prescribed in 8.4. If the test rod is new or if any part of its surface shows rust or other irregularities, clean it with ASTM precipitation naphtha or *iso*octane or IP 60/80 petroleum spirit and grind with medium 150-grit aluminum oxide cloth to remove all irregularities, pits, and scratches, as determined by visual inspection (Note 8). Perform the grindings by mounting the test rod in the chuck of the grinding and polishing apparatus, and turning it at a speed of 1700 to 1800 rpm while applying the 150-grit aluminum oxide cloth. Old 150-grit aluminum oxide cloth may be used to remove rust or major irregularities, but complete the grinding with new cloth. Proceed at once with the final polishing with 240-grit aluminum oxide cloth, or remove the test rod from the chuck and store in *iso*octane until needed. Discard reused test rods when the diameter is reduced to 9.5 mm (0.375 in.).

NOTE 8—Do not touch the test rods with the hands at any stage after cleaning with naphtha or *iso*octane or the petroleum spirit (which precedes either preliminary grinding or final polishing) until the test is completed. Forceps or a clean, lintless cloth may be used.

8.4 *Final Polishing*:

8.4.1 Just before the test is to be made, subject the test rod to final polishing with 240-grit aluminum oxide cloth. If the preliminary grinding has just been completed, stop the motor that rotates the test rod. Otherwise, remove the test rod from the *iso*octane (previously used unrusted test rods shall be stored in this reagent), dry with a clean cloth, and place in the chuck. Rub a new piece of 240-grit aluminum oxide cloth longitudinally over the static test rod until the rounded end, and the entire surface show visible scratches. Rotate the test rod at a speed of 1700 to 1800 rpm. Take the cloth and place it halfway around the test rod, and apply a firm but gentle downward pull to the loose ends of the cloth for about 1 to 2 min so as to produce a uniform finely scratched surface free of longitudinal scratches. Carry out the final stages of the polishing with new cloth.

8.4.2 To ensure that the flat shoulder (that portion of the test rod perpendicular to the threaded stem) is free of rust, polish this area. This can be done by holding a strip of 240-grit aluminum oxide cloth between the chuck and the shoulder while rotating the test rod for a brief period.

8.4.3 Remove the test rod from the chuck without touching with the fingers; wipe lightly with a clean, dry, lintless cloth or tissue (or brush the test rod lightly with a camel's hair brush); attach to the plastic holder; and immediately immerse in the oil to be tested. This can be either the hot oil sample (see 9.1) or a clean test tube containing a portion of the sample. The test rod can be removed later from this tube and allowed to drain briefly before being placed in the hot oil.

9. Procedure A for Distilled Water

9.1 Clean the beaker in accordance with good laboratory procedure, wash with distilled water, and dry in an oven. Clean glass beaker cover and a glass stirrer by the same procedure. To clean a stainless steel stirrer and a PMMA cover, use ASTM precipitation naphtha or *iso*octane or IP 60/80 petroleum spirit, wash thoroughly with hot water and finally with distilled water, and dry in an oven at a temperature not over 65°C (150°F). Pour 300 mL of the oil to be tested (see Practice D 4057) into the beaker and place the beaker in the oil bath held at a temperature that will maintain the oil sample at 60 ± 1°C (140 ± 2°F). Insert the beaker into a hole of the bath cover and suspend in the hole with the beaker rim resting on the bath cover. The oil level in the bath shall not be below the oil level in the test beaker. Cover the beaker with the beaker cover with the stirrer in position in the proper opening. Adjust the stirrer so that the shaft is 6 mm (0.24 in.) off center in the beaker containing the oil sample and the blade is not more than 2 mm (0.08 in.) from the bottom of the beaker. Then suspend a temperature measuring device through the hole in the cover intended for that purpose so that it is immersed to a depth of 56 mm (2.2 in.). Start the stirrer and when the temperature reading reaches 60 ± 1°C (140± 2°F), insert the steel test rod prepared in accordance with Section 8.

9.2 Insert the test rod assembly through the test rod hole in the beaker cover and suspend so that its lower end is 13 to 15 mm (0.51 to 0.59 in.) from the bottom of the beaker. Either type of plastic test rod holder (see Fig. 3) may be used. The hole through which the test rod is suspended shall be unobstructed (see Note 9).

NOTE 9—Fig. 1 shows the arrangement of the apparatus.

9.3 Continue stirring for 30 min to ensure complete wetting of the steel test rod. With the stirrer in motion, remove the temperature measuring device temporarily and add 30 mL of distilled water through this hole, discharging the water on the bottom of the beaker, and replace the temperature measuring device. Continue stirring at a speed of 1000 ± 50 rpm for 24 h (see Note 10) from the time water was added, maintaining the temperature of the oil-water mixture at 60 ± 1°C (140 ± 2°F). Stop stirring at the end of the 24-h period, remove the test rod, allow to drain, and then wash with ASTM precipitation naphtha or *iso*octane, or IP 60/80 petroleum spirit. If desired, the test rod may be preserved by lacquering.

NOTE 10—In general, observations of rusting made at the end of the 12-h testing time are indicative as to whether the oil will pass or fail. It is customary to run the test for 24 h; however, the test period may, at the discretion of the contracting parties, be for a shorter or longer period.

10. Procedure B for Synthetic Sea Water

10.1 The procedure for rust-preventing characteristics of inhibited mineral oils in the presence of synthetic sea water shall be identical with that described in 9.1, 9.2, and 9.3, except use synthetic sea water in place of distilled water in that portion of the procedure described in 9.3.

11. Procedure C for Heavier-Than-Water Fluids

11.1 The stirring action provided by the stirrer prescribed in 5.4 is not sufficient to mix thoroughly the water and test sample when the fluid under test is heavier than water. This section is meant to define changes in the test method to accommodate heavier-than-water fluids. Except as specifically stated, all the requirements of the previous Sections 1-10 shall apply. Since this procedure can be performed with distilled water or synthetic sea water, take care to include this information in the report.

11.2 *Apparatus*:

11.2.1 *Beaker Cover*— Same as prescribed in 5.3 (see Note 11).

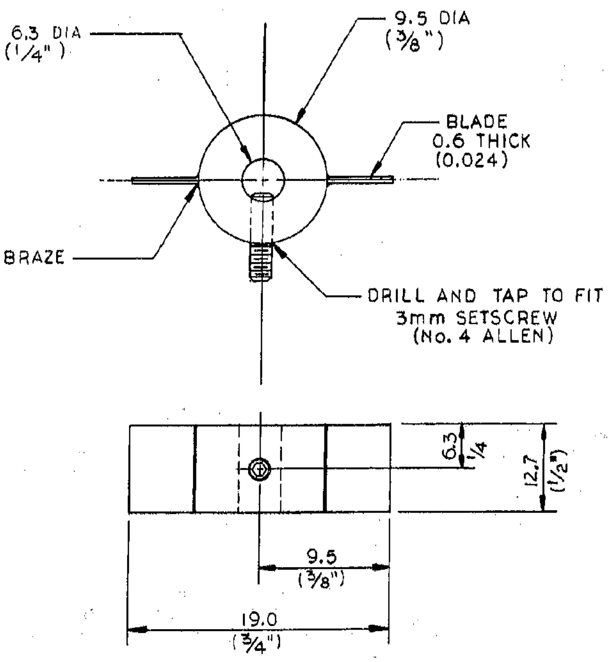
NOTE 11—Some heavier-than-water fluids can attack or dissolve PMMA beaker covers and test rod holders. It is recommended that PCTFE beaker covers and PTFE test rod holders be used when testing heavier-than-water fluids.

11.2.2 *Stirrer*—Same as prescribed in 5.4 but with an auxiliary blade attached to the stirrer shaft. The auxiliary blade shall be of stainless steel, 19.0 by 12.7 by 0.6 mm (0.75 by 0.50 by 0.25 in.) as shown in Fig. 5. The auxiliary blade shall be positioned on the stirrer shaft so that the bottom edge of the auxiliary blade is 57 mm (2.25 in.) above the top edge of the fixed lower blade, and so that the flat surfaces of both blades are in the same vertical plane.

11.3 *Test Rod and Its Preparation*—Same as prescribed in Section 8.

12. Interpretation of Results

12.1 Perform all inspections at the end of the test to determine the condition of test rods without magnification under normal light. For the purpose of this test, normal light is considered to be illumination of about 60 footcandles (650 lx). Within the meaning of this test method, a rusted test rod is one on which any rust spot or rust streak is visible by the above inspection procedure.



NOTE 1—All units are in millimetres, unless otherwise specified.

FIG. 5 Auxiliary Stirrer Blade (not to scale)

12.2 For the purpose of this test method, rust is an area of corrosion of the test surface that is identified by color and is confirmed by the presence of pits or roughness if the surface is wiped with a lintless cloth or tissue paper. Neither surface discoloration nor specks, which can easily be removed with a lintless or tissue paper cloth with no evidence of pitting or roughness, shall be considered to be rust.

12.3 In order to report an oil as passing or failing, conduct the test in duplicate. Report an oil as passing the test if both test rods are rust-free at the end of the test period. Report an oil as failing the test if both test rods are rusted at the end of the test period (see Note 12). If one test rod is rusted while the other is free of rust, test two additional test rods (see Note 7). If either of these latter test rods shows rusting, report the oil as not passing the test. If neither of these latter test rods shows rusting, report the oil as passing the test.

NOTE 12—An indication of the degree of rusting occurring in this test may be desired. For uniformity in such cases, use of the following classifications of rusting severity is recommended:

Light Rusting—Rusting confined to not more than six spots, each of which is 1 mm or less in diameter.

Moderate Rusting—Rusting in excess of the above but confined to less than 5% of the surface of the test rod.

Severe Rusting—Rusting covering more than 5% of the surface of the test rod.

12.4 A reference oil with a Pass in Procedure A and a Fail in Procedure B can be prepared as follows: Add 0.0150 mass %

of an additive concentrate[13] to a white mineral oil.[14] The additive concentrate consists of 60 mass % of dodecenyl succinic acid and 40 mass % of normal paraffin oil, ISO VG 22 (see Classification D 2422).[15]

13. Report

13.1 The test report shall contain the following:

13.1.1 The type and identification of the product used.

13.1.2 The date of the test.

13.1.3 A reference to this ASTM-IP standard, indicating whether Procedure A, B, or C was used. Since Procedure C may be followed with either distilled water or sea water, be sure to include the type of water used in this case.

13.1.4 The duration of the tests.

13.1.5 Any deviation from the procedure specified.

13.1.6 The result of the test, including degree of severity of rusting, if desired.

14. Precision and Bias

14.1 *Precision*—It is not practicable to specify the precision of the procedure in this test method because the results of the test are only intended to give a pass/fail rating to the oil being tested.

14.2 *Bias*—The procedure in this test method has no bias because the value of rust-preventing characteristics is defined only in terms of this test method.

15. Keywords

15.1 circulating oils; heavier-than-water fluids; hydraulic oils; inhibited mineral oil; rust-preventing characteristics; steam-turbine oils

---

[13] A suitable additive concentrate is Lubrizol 850, as used in the ASTM round robin. Lubrizol 850 is available from Lubrizol Corporation, Wickliffe, OH.

[14] A suitable white mineral oil is USP Mineral Oil with a viscosity in the order of ISO VG 32 (Penreco Drakeol 19 was used in the ASTM round robin and is available from Penreco, Kams City, PA).

[15] The results of the cooperative test program using this reference oil are available from ASTM Headquarters as RR:D02-1284.

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 D814: Standard Test Method for Rubber Property--Vapor Transmission of Volatile Liquids

CFR Section(s): 40 CFR 1051.245(e)(1)

Standards Body: American Society for Testing and Materials

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

Designation: D 814 – 95

Standard Test Method for Rubber Property— Vapor Transmission of Volatile Liquids[1]

This standard is issued under the fixed designation D 814; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the measurement of the rate of vapor transmission of volatile liquids through a rubber sheet, disk, or diaphragm.

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 Document

2.1 *ASTM Standard:*

D 3767 Practice for Rubber—Measurement of Dimensions[2]

3. Significance and Use

3.1 The rate of transmission of a liquid through a rubber sheet, that acts as a barrier, is important in rubber diaphragm performance and other similar industrial applications. This transmission is referred to as vapor transmission since the liquid diffuses through the rubber in a molecular sense and escapes into free atmosphere in vapor form.

3.2 This test method is applicable only to the materials in sheet form of moderate thickness and is principally useful for comparing the relative vapor transmission of different liquids in the same rubber or of the same liquid through different rubbers. Comparisons should not be made in which both different rubbers and different liquids are used.

4. Apparatus

4.1 The test apparatus shall consist essentially of glass vapor transmission jars (4.2) for each liquid, on which the test specimens are mounted, and a suitable rack for supporting the jars in an inverted position in such a way as to allow free circulation of air over the surface of the specimen. The apparatus shall be kept in a constant temperature cabinet or room at 23 ± 2°C (73.4 ± 3.6°F).

4.2 *Vapor Transmission Jar*—A glass jar of approximately 236-cm^3 (½-pt) capacity with an opening of 60.3 ± 0.4 mm (2.375 ± 0.015 in.) in inside diameter and a wall 3.2 mm (0.125 in.) in thickness at the opening, which shall be ground flat without rounded edges to a smooth ground-glass finish at the contact surface. The opening shall be equipped with a metal screw ring clamp holding a smooth-edged, flat, sheet-metal ring 55.6 ± 0.4 mm (2.188 ± 0.015 in.) in inside diameter and approximately 68.3 mm (2.69 in.) in outside diameter. The ring clamp and ring serve as a clamping device for holding the specimen against the ground-glass-edge of the jar with a circular specimen area 55.6 mm (2.188 in.) in diameter exposed to the air while permitting the screw clamp to be tightened to form a leak-proof seal without subjecting the specimen to torsional strain. When testing extensible materials, a circular disk of 16 to 20-mesh screen shall be placed inside the screw ring clamp between it and the flat metal ring to prevent stretching of the specimen during the test. The screen disk may be soldered in place on top of the sheet metal ring if desired.

NOTE 1—A suitable vapor transmission jar may be prepared from a ½-pt Mason jar equipped with a Kerr-type screw cap, provided the edge of the jar is properly ground and finished with fine emery and the cap is cut with smooth, flattened edges to form the required circular opening.

4.3 *Dial Micrometer*—The dial micrometer shall conform to the requirements of Method A of Practice D 3767.

4.4 *Balance*—The balance shall be of suitable capacity capable of weighing to 0.005 g.

5. Test Specimens

5.1 The test specimens shall consist of circular disks 68 mm (2.69 in.) in diameter, cut with a sharp-edged die from a sheet of the material being tested. The thickness of the sheet, which shall not exceed 3.2 mm (0.125 in.), shall be measured using the dial micrometer described in 4.3.

5.2 For evaluating the vapor transmission of a particular liquid with respect to a given rubber, three specimens having the same nominal thickness within a tolerance of ±3 % shall be tested. The vapor transmission of the liquid shall be taken as the average of the values obtained from the two rubber specimens giving the lowest results, providing these check within ±20 % of the average so determined.

6. Procedure

6.1 With the vapor transmission jar in an upright position, place 200 cm^3 of the test liquid in it, after which fit the test specimen over the mouth of the jar, place the ring and wire screen in position, and screw down the screw ring clamp lightly. Hold the assembly in the constant temperature cabinet or room at 23 ± 2°C (73.4 ± 3.6°F) with the test disk lightly in place until temperature equilibrium is obtained. Then screw down the ring tightly and allow the assembly to stand in an upright position for 2 h. Make a tare assembly using a duplicate jar and a test specimen of the same size but without the addition of the test liquid. Place suitable weighting material such as lead shot in the tare jar to bring its

---

[1] This test method is under the jurisdiction of ASTM Committee D-11 on Rubber and is the direct responsibility of Subcommittee D11.10 on Physical Testing.

Current edition approved May 15, 1995. Published July 1995. Originally published as D 814 – 44 T. Last previous edition D 814 – 86 (1991)$^{\epsilon 1}$.

[2] *Annual Book of ASTM Standards*, Vol 09.01.

mass to approximately that of the assembled jar and contents. Condition the tare jar at the test temperature, seal it, and handle throughout the test in a manner similar to that used for the test jar. Place the test jar on a balance of suitable capacity capable of weighing to 0.005 g, and counterbalance it against the tare jar, adding weights as required for equilibrium. Take the original mass of the test assembly as that of the tare corrected for the added weights and record to the nearest 0.005 g.

6.2 After weighing, invert each test jar assembly and place on the rack, supporting each in such a way that the entire inner surface of the specimen remains in contact with the liquid throughout the test. If the rack is located in a conditioning cabinet, take care to remove diffused vapors from the chamber and to assure free circulation of fresh air by means of a fan or other suitable device. Twenty-four hours after inverting the jar, again weigh it against the tare jar. Any excessive loss of mass indicates that leakage due to improper seal is occurring. Remove such test assemblies and replace them by new assemblies properly prepared. Return the test assembly to the rack and reweigh against the tare after periods of 120 ± 2 h and 192 ± 2 h from the initial inversion. Consider the difference in mass between those obtained at 120 h (5 days) and at 192 h (8 days) divided by 3 as the average mass of liquid lost per 24 h.

NOTE 2—In this test, the specimens are allowed to remain in contact with the liquid for 5 days before starting measurement of the loss in order to permit the rate of diffusion of the liquid to become uniform.

7. Calculation

7.1 Express the vapor transmission rate (VTR) of each test liquid with respect to the rubber employed and calculate as follows:

$$\text{Vapor transmission rate (VTR), mg/(s}\cdot\text{m}^2) = 4.77 \times \text{average mass in grams of liquid lost per 24 h}$$

8. Report

8.1 The report shall include the following:

8.1.1 Identification of the test rubber,

8.1.2 Thickness of the test rubber to the nearest 0.025 mm (0.001 in.),

8.1.3 Identification of the test liquid, and

8.1.4 Vapor transmission rate (VTR) of the liquid, expressed in milligrams per second per square metre of wetted area.

9. Precision

9.1 Due to a lack of laboratories willing to participate in round-robin testing, no precision data are available for this test method.

10. Keywords

10.1 vapor transmission; volatile liquids