Exhibit 177
(Part 2)

Designation: D 975 – 07

An American National Standard

Standard Specification for Diesel Fuel Oils[1]

This standard is issued under the fixed designation D 975; 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 (∈) indicates an editorial change since the last revision or reapproval.

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

1. Scope*

1.1 This specification covers seven grades of diesel fuel oils suitable for various types of diesel engines. These grades are described as follows:

1.1.1 *Grade No. 1-D SI5*—A special-purpose, light middle distillate fuel for use in diesel engine applications requiring a fuel with 15 ppm sulfur (maximum) and higher volatility than that provided by Grade No. 2-D S15 fuel.[2]

1.1.2 *Grade No. 1-D S500*—A special-purpose, light middle distillate fuel for use in diesel engine applications requiring a fuel with 500 ppm sulfur (maximum) and higher volatility than that provided by Grade No. 2-D S500 fuel.[2]

1.1.3 *Grade No. 1-D S5000—A* special-purpose, light middle distillate fuel for use in diesel engine applications requiring a fuel with 5000 ppm sulfur (maximum) and higher volatility than that provided by Grade No. 2-D S5000 fuels.

1.1.4 *Grade No. 2-D S15*—A general purpose, middle distillate fuel for use in diesel engine applications requiring a fuel with 15 ppm sulfur (maximum). It is especially suitable for use in applications with conditions of varying speed and load.[2]

1.1.5 *Grade No. 2-D S500*—A general-purpose, middle distillate fuel for use in diesel engine applications requiring a fuel with 500 ppm sulfur (maximum). It is especially suitable for use in applications with conditions of varying speed and load.[2]

1.1.6 *Grade No. 2-D S5000*—A general-purpose, middle distillate fuel for use in diesel engine applications requiring a fuel with 5000 ppm sulfur (maximum), especially in conditions of varying speed and load.

1.1.7 *Grade No. 4-D*—A heavy distillate fuel, or a blend of distillate and residual oil, for use in low- and medium-speed diesel engines in applications involving predominantly constant speed and load.

NOTE 1—A more detailed description of the grades of diesel fuel oils is given in X1.2.

NOTE 2—The Sxxx designation has been adopted to distinguish grades by sulfur rather than using words such as "Low Sulfur" as previously because the number of sulfur grades is growing and the word descriptions were thought to be not precise. S5000 grades correspond to the so-called "regular" sulfur grades, the previous No. 1-D and No. 2-D. S500 grades correspond to the previous "Low Sulfur" grades. S15 grades were not in the previous grade system and are commonly referred to as "Ultra-Low Sulfur" grades or ULSD.

1.2 This specification, unless otherwise provided by agreement between the purchaser and the supplier, prescribes the required properties of diesel fuels at the time and place of delivery.

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

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

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

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D 56 Test Method for Flash Point by Tag Closed Cup Tester

D 86 Test Method for Distillation of Petroleum Products at Atmospheric Pressure

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

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

D 130 Test Method for Corrosiveness to Copper from Petroleum Products by Copper Strip Test

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

D 482 Test Method for Ash from Petroleum Products

[1] This specification is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.E0.02 on Diesel Fuel Oils.

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[2] This fuel complies with 40 CFR Part 80—Control of Air Pollution from New Motor Vehicles: Heavy-Duty Engines and Vehicle Standards and Highway Diesel Fuel Sulfur Control Requirements: Final Rule. Regulation of Fuels and Fuel Additives: Fuel Quality Regulations for Highway Diesel Fuel Sold in 1993 and Later Calendar Years.

[3] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

***A Summary of Changes section appears at the end of this standard.**

1

D 524 Test Method for Ramsbottom Carbon Residue of Petroleum Products

D 613 Test Method for Cetane Number of Diesel Fuel Oil

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

D 1319 Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption

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

D 1796 Test Method for Water and Sediment in Fuel Oils by the Centrifuge Method (Laboratory Procedure)

D 2274 Test Method for Oxidation Stability of Distillate Fuel Oil (Accelerated Method)

D 2500 Test Method for Cloud Point of Petroleum Products

D 2622 Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry

D 2709 Test Method for Water and Sediment in Middle Distillate Fuels by Centrifuge

D 2880 Specification for Gas Turbine Fuel Oils

D 2887 Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography

D 3117 Test Method for Wax Appearance Point of Distillate Fuels

D 3120 Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry

D 3828 Test Methods for Flash Point by Small Scale Closed Cup Tester

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

D 4294 Test Method for Sulfur in Petroleum and Petroleum Products by Energy-Dispersive X-ray Fluorescence Spectrometry

D 4306 Practice for Aviation Fuel Sample Containers for Tests Affected by Trace Contamination

D 4539 Test Method for Filterability of Diesel Fuels by Low-Temperature Flow Test (LTFT)

D 4737 Test Method for Calculated Cetane Index by Four, Variable Equation

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

D 5453 Test Method for Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence

D 5771 Test Method for Cloud Point of Petroleum Products (Optical Detection Stepped Cooling Method)

D 5772 Test Method for Cloud Point of Petroleum Products (Linear Cooling Rate Method)

D 5773 Test Method for Cloud Point of Petroleum Products (Constant Cooling Rate Method)

D 5842 Practice for Sampling and Handling of Fuels for Volatility Measurement

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

D 6078 Test Method for Evaluating Lubricity of Diesel Fuels by the Scuffing Load Ball-on-Cylinder Lubricity Evaluator (SLBOCLE)

D 6079 Test Method for Evaluating Lubricity of Diesel Fuels by the High-Frequency Reciprocating Rig (HFRR)

D 6217 Test Method for Particulate Contamination in Middle Distillate Fuels by Laboratory Filtration

D 6371 Test Method for Cold Filter Plugging Point of Diesel and Heating Fuels

D 6468 Test Method for High Temperature Stability of Distillate Fuels

D 6469 Guide for Microbial Contamination in Fuels and Fuel Systems

D 6890 Test Method for Determination of Ignition Delay and Derived Cetane Number (DCN) of Diesel Fuel Oils by Combustion in a Constant Volume Chamber

D 6898 Test Method for Evaluating Diesel Fuel Lubricity by an Injection Pump Rig

2.2 *Other Documents:*

26 CFR Part 48 Manufacturers and Realtors Excise Taxes[4]

40 CFR Part 80 Regulation of Fuels and Fuel Additives[4]

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *S(numerical specification maximum)*—indicates the maximum sulfur content, in weight ppm (µg/g), allowed by this specification in a diesel fuel grade.

3.1.1.1 *Discussion*—Of the seven diesel fuel grades specified in this standard, six have important distinguishing maximum sulfur regulatory requirements. These are Grades No. 1-D S15, No. 1-D S500, No. 1-D S5000, No. 2-D S15, No. 2-D S500 and No. 2-D S5000. The seventh grade, No. 4-D, is distinguished from these other grades by many major properties in addition to sulfur (unregulated maximum), and therefore is not included in this designation system. Thus, Grade No. 4-D does not have the designation S20000 as part of its grade name.

4. Sampling, Containers, and Sample Handling

4.1 It is strongly advised to review all test methods prior to sampling to understand the importance and effects of sampling technique, proper containers, and special handling required for each test method.

4.2 Correct sampling procedures are critical to obtaining a representative sample of the diesel fuel oil to be tested. Refer to Appendix X2 for recommendations. The recommended procedures or practices provide techniques useful in the proper sampling or handling of diesel fuels.

5. Test Methods

5.1 The requirements enumerated in this specification shall be determined in accordance with the following methods:

5.1.1 *Flash Point*—Test Methods D 93, except where other methods are prescribed by law. For all grades, Test Method D 3828 may be used as an alternate with the same limits. For Grades No. 1-D S15, No. 1-D S500 , No. 1-D S5000, No. 2-D

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

S15, No. 2-D S500, and No. 2-D S5000, Test Method D 56 may be used as an alternate with the same limits, provided the flash point is below 93°C and the viscosity is below 5.5 mm^2/s at 40°C. This test method will give slightly lower values. In cases of dispute, Test Methods D 93 shall be used as the referee method. Test Method D 56 can not be used as the alternate method for Grade No. 4-D because its minimum viscosity limit is 5.5 mm^2/s at 40°C.

5.1.2 *Cloud Point*—Test Method D 2500. For all fuel grades in Table 1, the automatic Test Methods D 5771, D 5772, or D 5773 can be used as alternates with the same limits. Test Method D 3117 can also be used since it is closely related to Test Method D 2500. In case of dispute, Test Method D 2500 shall be the referee method.

5.1.3 *Water and Sediment*—Test Method D 2709 is used for fuel Grades No. 1-D S15, No. 1-D S500, No. 1-D S5000, No. 2-D S15, No. 2-D S500, and No. 2-D S5000. Test Method D 1796 is used for Grade No. 4-D.

5.1.4 *Carbon Residue*—Test Method D 524 is used for fuel Grades No. 1-D S15, No. 1-D S500, No. 1-D S5000, No. 2-D

TABLE 1 Detailed Requirements for Diesel Fuel Oils^A

Property	ASTM Test Method^B	Grade						
		No. 1-D S15	No. 1-D S500^C	No. 1-D S5000^D	No. 2-D S15	No. 2-D S500^{C,E}	No. 2-D S5000^{D,E}	No. 4-D^D
Flash Point, °C, min.	D 93	38	38	38	52^E	52^E	52^E	55
Water and Sediment, % vol, max	D 2709	0.05	0.05	0.05	0.05	0.05	0.05	...
	D 1796	...	...	...	...	...	...	0.50
Distillation: one of the following requirements shall be met:								
1. Physical Distillation Distillation Temperature, °C 90 %, % vol recovered	D 86							
min		...	...	...	282^E	282^E	282^E	...
max		288	288	288	338	338	338	...
2. Simulated Distillation Distillation Temperature, °C 90 %, % vol recovered	D 2887							
min						300^E	300^E	
max			304	304		356	356	
Kinematic Viscosity, mm^2/S at 40°C	D 445							
min		1.3	1.3	1.3	1.9^E	1.9^E	1.9^E	5.5
max	...	2.4	2.4	2.4	4.1	4.1	4.1	24.0
Ash % mass, max	D 482	0.01	0.01	0.01	0.01	0.01	0.01	0.10
Sulfur, ppm (µg/g)^F max	D 5453	15	...	...	15	...	...	...
% mass, max	D 2622^G	...	0.05	...	...	0.05	...	...
% mass, max	D 129	...	...	0.50	...	...	0.50	2.00
Copper strip corrosion rating max 3 h at 50°C	D 130	No. 3	No. 3	No. 3	No. 3	No. 3	No. 3	...
Cetane number, min^H	D 613	40^I	40^I	40^I	40^I	40^I	40^I	30^I
One of the following properties must be met:								

Property	ASTM Test Method[B]	Grade						
		No. 1-D S15	No. 1-D S500[C]	No. 1-D S5000[D]	No. 2-D S15	No. 2-D S500[C,E]	No. 2-D S5000[D,E]	No. 4-D[D]
(1) Cetane index, min.	D 976–80[G]	40	40	...	40	40	...	...
(2) Aromaticity, % vol, max	D 1319[G]	35	35	...	35	35	...	...
Operability Requirements								
Cloud point, °C, max	D 2500	J	J	J	J	J	J	...
or								
LTFT/CFPP, °C, max	D 4539/D 6371							
Ramsbottom carbon residue on 10 % distillation residue, % mass, max	D 524	0.15	0.15	0.15	0.35	0.35	0.35	...
Lubricity, HFRR @ 60°C, micron, max	D 6079	520	520	520	520	520	520	...

Property	ASTM Test Method[B]	Grade						
		No. 1-D S15	No. 1-D S500[C]	No. 1-D S5000[D]	No. 2-D S15	No. 2-D S500[C,E]	No. 2-D S5000[D,E]	No. 4-D[D]

[A] To meet special operating conditions, modifications of individual limiting requirements may be agreed upon between purchaser, seller, and manufacturer.

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

[C] Under United States regulations, if Grades No. 1-D S500 or No. 2-D S500 are sold for tax exempt purposes then, at or beyond terminal storage tanks, they are required by 26 CFR Part 48 to contain the dye Solvent Red 164 at a concentration spectrally equivalent to 3.9 lb per thousand barrels of the solid dye standard Solvent Red 26, or the tax must be collected.

[D] Under United States regulations, Grades No.1-D S5000, No. 2-D S5000, and No. 4-D are required by 40 CFR Part 80 to contain a sufficient amount of the dye Solvent Red 164 so its presence is visually apparent. At or beyond terminal storage tanks, they are required by 26 CFR Part 48 to contain the dye Solvent Red 164 at a concentration spectrally equivalent to 3.9 lb per thousand barrels of the solid dye standard Solvent Red 26.

[E] When a cloud point less than −12°C is specified, as can occur during cold months, it is permitted and normal blending practice to combine Grades No. 1 and No. 2 to meet the low temperature requirements. In that case, the minimum flash point shall be 38°C, the minimum viscosity at 40°C shall be 1.7 mm^2/s, and the minimum 90 % recovered temperature shall be waived.

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

[G] These test methods are specified in 40 CFR Part 80.

[H] Where cetane number by Test Method D 613 is not available, Test Method D 4737 can be used as an approximation.

[I] Low ambient temperatures as well as engine operation at high altitudes may require the use of fuels with higher cetane ratings.

[J] It is unrealistic to specify low temperature properties that will ensure satisfactory operation at all ambient conditions. In general, cloud point (or wax appearance point) Low Temperature Flow Test, and Cold Filter Plugging Point Test may be used as an estimate of operating temperature limits for Grades No. 1-D S500; No. 2-D S500; and No. 1-D S5000 and No. 2-D S5000 diesel fuel oils. However, satisfactory operation below the cloud point (or wax appearance point) may be achieved depending on equipment design, operating conditions, and the use of flow-improver additives as described in X5.1.2. Appropriate low temperature operability properties should be agreed upon between the fuel supplier and purchaser for the intended use and expected ambient temperatures. Test Methods D 4539 and D 6371 may be especially useful to estimate vehicle low temperature operability limits when flow Improvers are used. Due to fuel delivery system, engine design, and test method differences, low temperature operability tests may not provide the same degree of protection in various vehicle operating classes. Tenth percentile minimum air temperatures for U.S. locations are provided in Appendix X5 as a means of estimating expected regional temperatures. The tenth percentile minimum air temperatures may be used to estimate expected regional target temperatures for use with Test Methods D 2500, D 4539, and D 6371. Refer to X5.1.3 for further general guidance on test application.

3 S15, No. 2-D S500 and No. 2-D S5000. Grade No. 4-D does not have a limit for carbon residue.

5.1.5 *Ash*—Test Method D 482 is used for all grades in Table 1.

5.1.6 *Distillation*—Test Method D 86 is used for Grades No. 1-D S15, No. 1-D S500, No. 1-D S5000, No. 2-D S15, No. 2-D S500 and No. 2-D S5000. For all grades, Test Method D 2887 can be used as an alternate with the limits listed in Table 1. In case of dispute, Test Method D 86 shall be the referee method. Grade No. 4-D does not have distillation requirements.

5.1.7 *Viscosity*—Text Method D445 is used for all fuel grades in Table 1.

5.1.8 *Sulfur*—The following list shows the referee test methods and alternate test methods for sulfur, the range over which each test method applies and the corresponding fuel grades.

Sulfur Test Method	Range	Grades
D 129 (referee)	>0.1 mass %	No. 1-D S5000, No. 2-D S5000, No. 4-D
D 1266	0.0005 to 0.4 mass % 5 to 4000 mg/kg (wt ppm)	No. 1-D S500, No. 2-D S500
D 1552	>0.06 mass %	No. 1-D S5000, No. 2-D S5000, No. 4-D
D 2622 (referee for S500 Grades)	0.0003 to 5.3 mass % 3 to 53 000 mg/kg (wt ppm)	All Grades
D 3120	3.0 to 100 mg/kg (wt ppm)	No. 1-D S15, No. 2-D S15 No. 1-D S500, No. 2-D S500 (S500 grades must be diluted before testing)
D 4294	0.0150 to 5.00 mass% 150 to 50 000 mg/kg (wt ppm)	No. 1-D S5000, No. 2-D S5000, No. 4-D
D 5453 (referee for S15 grades)	0.0001 to 0.8 mass % 1.0 to 8000 mg/kg (wt ppm)	All Grades

NOTE 4—The units used to report results in the above test methods are:

D 129	mass %
D 1266	mass %
D 1552	mass %
D 2622	mass %
D 3120	ppm (µg/g)
D 4294	mass%
D 5453	ppm (µg/g)

Results reported in mg/kg and in ppm (µ/g) are numerically the same. The units used in Table 1 for the sulfur requirements are the units in which results for the referee test are reported.

5.1.9 *Copper Corrosion*—Test Method D 130, 3 h test at 50°C. This test method is used for fuel Grades No. 1-D S15, No. 1-D S500, No. 1-D S5000, No. 2-D S15, No. 2-D S500 and No. 2-D S5000. Grade No. 4-D does not have a copper corrosion requirement.

5.1.10 *Cetane Number*—Test Method D 613 is used for all fuel grades in Table 1. Test Method D 6890 is used for all No. 1-D and No. 2-D grades with the DCN result being compared to the cetane number specification requirement of 40. Test Method D 613 shall be the referee method.

5.1.11 *Cetane Index*—Test Methods D 976-80 is used for fuel Grades No. 1-D S15, No. 1-D S500, No. 2-D S15 and No. 2-D S500. Grades No. 1-D S5000, No. 2-D S5000 and No. 4-D do not have an aromatics content requirement, so do not use this test method as a surrogate for aromatics content.

5.1.12 *Aromaticity*—Test Method D 1319. This test method provides an indication of the aromatics content of fuels. For fuels with a maximum final boiling point of 315°C, this method is a measurement of the aromatic content of the fuel. This test method is used for fuel Grades No. 1-D S15, No. 1-D S500, No. 2-D S15 and No. 2-D S500. Grades No. 1-D S5000, No. 2-D S5000 and No. 4-D do not have an aromatics content requirement.

5.1.13 *Lubricity*—Test Method D 6079.

6. Workmanship

6.1 The diesel fuel shall be visually free of undissolved water, sediment, and suspended matter.

7. Requirements

7.1 The grades of diesel fuel oils herein specified shall be hydrocarbon oils conforming to the detailed requirements shown in Table 1.

7.2 *Grades No. 2-D S15, No. 2 D S500 and No. 2-D S5000*—When a cloud point less than −12°C is specified, as can occur during cold months, it is permitted and normal blending practice to combine Grades No. 1 and No. 2 to meet the low temperature requirements. In that case, the minimum flash point shall be 38°C, the minimum viscosity at 40°C shall be 1.7 mm^2/s, and the minimum 90 % recovered temperature shall be waived.

8. Keywords

8.1 diesel; fuel oil; petroleum and petroleum products

APPENDIXES
(Nonmandatory Information)

X1. SIGNIFICANCE OF ASTM SPECIFICATION FOR DIESEL FUEL OILS

X1.1 Introduction

X1.1.1 The properties of commercial fuel oils depend on the refining practices employed and the nature of the crude oils from which they are produced. Distillate fuel oils, for example, may be produced within the boiling range of 150 and 400°C having many possible combinations of various properties, such as volatility, ignition quality, viscosity, and other characteristics.

X1.2 Grades

X1.2.1 This specification is intended as a statement of permissible limits of significant fuel properties used for specifying the wide variety of commercially available diesel fuel oils. Limiting values of significant properties are prescribed for seven grades of diesel fuel oils. These grades and their general applicability for use in diesel engines are broadly indicated as follows:

X1.2.2 *Grade No. 1-D S15*—Grade No. 1-D S15 comprises the class of very low sulfur, volatile fuel oils from kerosine to the intermediate middle distillates. Fuels within this grade are applicable for use in *(1)* high-speed diesel engines and diesel engine applications that require ultra-low sulfur fuels, *(2)* applications necessitating frequent and relatively wide variations in loads and speeds, and *(3)* applications where abnormally low operating temperatures are encountered.

X1.2.3 *Grade No. 1-D S500*—Grade No. 1-D S500 comprises the class of low-sulfur, volatile fuel oils from kerosine to the intermediate middle distillates. Fuels within this grade are applicable for use in *(1)* high-speed diesel engines that require low sulfur fuels, *(2)* in applications necessitating frequent and relatively wide variations in loads and speeds, and *(3)* in applications where abnormally low operating temperatures are encountered.

X1.2.4 *Grade No. 1-D S5000*—Grade No. 1-D S5000 comprises the class of volatile fuel oils from kerosine to the intermediate middle distillates. Fuels within this grade are applicable for use in high-speed diesel engines applications necessitating frequent and relatively wide variations in loads and speeds, and also for use in cases where abnormally low operating temperatures are encountered.

X1.2.5 *Grade No. 2-D S15*—Grade No. 2-D S15 includes the class of very low sulfur, middle distillate gas oils of lower volatility than Grade No. 1-D S15. These fuels are applicable for use in *(1)* high speed diesel engines and diesel engine applications that require ultra-low sulfur fuels, *(2)* applications necessitating relatively high loads and uniform speeds, or *(3)* diesel engines not requiring fuels having higher volatility or other properties specified in Grade No. 1-D S15.

X1.2.6 *Grade No. 2-D S500*—Grade No. 2-D S500 includes the class of low-sulfur, middle distillate gas oils of lower volatility than Grade No. 1-D S500. These fuels are applicable for use in *(1)* high-speed diesel engine applications that require low sulfur fuels, *(2)* applications necessitating relatively high loads and uniform speeds, or *(3)* diesel engines not requiring fuels having higher volatility or other properties specified for Grade No. 1-D S500.

X1.2.7 *Grade No. 2-D S5000*—Grade No. 2-D S5000 includes the class of middle distillate gas oils of lower volatility than Grade No. 1-D S5000. These fuels are applicable for use in *(1)* high-speed diesel engines in applications necessitating relatively high loads and uniform speeds, or *(2)* in diesel engines not requiring fuels having higher volatility or other properties specified for Grade No. 1-D S5000.

X1.2.8 *Grade No. 4-D*—Grade No. 4-D comprises the class of more viscous middle distillates and blends of these middle distillates with residual fuel oils. Fuels within this grade are applicable for use in low- and medium-speed diesel engines in applications necessitating sustained loads at substantially constant speed.

X1.3 Selection of Particular Grade

X1.3.1 The selection of a particular diesel fuel oil from one of these seven ASTM grades for use in a given engine requires consideration of the following factors:

X1.3.1.1 Fuel price and availability,

X1.3.1.2 Maintenance considerations,

X1.3.1.3 Engine size and design,

X1.3.1.4 Emission control systems,

X1.3.1.5 Speed and load ranges,

X1.3.1.6 Frequency of speed and load changes, and

X1.3.1.7 Atmospheric conditions. Some of these factors can influence the required fuel properties outlined as follows:

X1.4 Cetane Number

X1.4.1 Cetane number is a measure of the ignition quality of the fuel and influences combustion roughness. The cetane number requirements depend on engine design, size, nature of speed and load variations, and on starting and atmospheric conditions. Increase in cetane number over values actually required does not materially improve engine performance. Accordingly, the cetane number specified should be as low as possible to assure maximum fuel availability.

X1.5 Distillation

X1.5.1 The fuel volatility requirements depend on engine design, size, nature of speed and load variations, and starting and atmospheric conditions. For engines in services involving rapidly fluctuating loads and speeds as in bus and truck operation, the more volatile fuels may provide best performance, particularly with respect to smoke and odor. However, best fuel economy is generally obtained from the heavier types of fuels because of their higher heat content.

5

X1.6 Viscosity

X1.6.1 For some engines it is advantageous to specify a minimum viscosity because of power loss due to injection pump and injector leakage. Maximum viscosity, on the other hand, is limited by considerations involved in engine design and size, and the characteristics of the injection system.

X1.7 Carbon Residue

X1.7.1 Carbon residue gives a measure of the carbon depositing tendencies of a fuel oil when heated in a bulb under prescribed conditions. While not directly correlating with engine deposits, this property is considered an approximation.

X1.8 Sulfur

X1.8.1 The effect of sulfur content on engine wear and deposits appears to vary considerably in importance and depends largely on operating conditions. Fuel sulfur can affect emission control systems performance. To assure maximum availability of fuels, the permissible sulfur content should be specified as high as is practicable, consistent with maintenance considerations.

X1.9 Flash Point

X1.9.1 The flash point as specified is not directly related to engine performance. It is, however, of importance in connection with legal requirements and safety precautions involved in fuel handling and storage, and is normally specified to meet insurance and fire regulations.

X1.10 Cloud Point

X1.10.1 Cloud point is of importance in that it defines the temperature at which a cloud or haze of wax crystals appears in the oil under prescribed test conditions which generally relates to the temperature at which wax crystals begin to precipitate from the oil in use.

X1.11 Ash

X1.11.1 Ash-forming materials may be present in fuel oil in two forms: *(1)* abrasive solids, and *(2)* soluble metallic soaps. Abrasive solids contribute to injector, fuel pump, piston and ring wear, and also to engine deposits. Soluble metallic soaps have little effect on wear but may contribute to engine deposits.

X1.12 Copper Strip Corrosion

X1.12.1 This test serves as a measure of possible difficulties with copper and brass or bronze parts of the fuel system.

X1.13 Aromaticity

X1.13.1 This test is used as an indication of the aromatics content of diesel fuel. Aromatics content is specified to prevent an increase in the average aromatics content in Grades No. 1-D S15, No. 1-D S500, No. 2-D S15 and No. 2-D S500 fuels and is required by 40 CFR Part 80. Increases in aromatics content of fuels over current levels may have a negative impact on emissions.

X1.14 Cetane Index

X1.14.1 Cetane Index is specified as a limitation on the amount of high aromatic components in Grades No. 1-D S15, No. 1-D S500, No. 2-D S15 and No. 2-D S500.

X1.15 Other

X1.15.1 *Microbial Contamination*—Refer to Guide D 6469 for a discussion of this form of contamination.

X2. SAMPLING, CONTAINERS AND SAMPLE HANDLING

X2.1 Introduction

X2.1.1 This appendix provides guidance on methods and techniques for the proper sampling of diesel fuel oils. As diesel fuel oil specifications become more stringent and contaminants and impurities become more tightly controlled, even greater care needs to be taken in collecting and storing samples for quality assessment.

X2.2 Sampling, Containers and Sample Handling Recommendations

X2.2.1 Appropriate manual method sampling procedures can be found in Practice D 4057 and automatic method sampling is covered in Practice D 4177.

X2.2.2 The correct sample volume and appropriate container selection are also important decisions that can impact test results. Practice D 4306 for aviation fuel container selection for tests sensitive to trace contamination may be useful. Practice D 5854 for procedures on container selection and sample mixing and handling is recommended. For cetane number determination protection from light is important. Collection and storage of diesel fuel oil samples in an opaque container, such as a dark brown glass bottle, metal can, or a minimally reactive plastic container to minimize exposure to UV emissions from sources such as sunlight or fluorescent lamps, is recommended. According to Paragraph 8.2 of Test Method D 6079, “Because of sensitivity of lubricity measurements to trace materials, sample containers shall be only fully epoxy-lined metal, amber borosilicate glass, or polytetrafluoroethylene as specified in Practice D 4306.”

X2.2.3 For volatility determination of a sample, Practice D 5842 for special precautions recommended for representative sampling and handling techniques may be appropriate.

6

X3. STORAGE AND THERMAL STABILITY OF DIESEL FUELS

X3.1 Scope

X3.1.1 This appendix provides guidance for consumers of diesel fuels who may wish to store quantities of fuels for extended periods or use the fuel in severe service or high temperature applications. Fuels containing residual components are excluded. Consistently successful long-term fuel storage or use in severe applications requires attention to fuel selection, storage conditions, handling and monitoring of properties during storage and prior to use.

X3.1.2 Normally produced fuels have adequate stability properties to withstand normal storage and use without the formation of troublesome amounts of insoluble degradation products. Fuels that are to be stored for prolonged periods or used in severe applications should be selected to avoid formation of sediments or gums, which can overload filters or plug injectors. Selection of these fuels should result from supplier-user discussions.

X3.1.3 These suggested practices are general in nature and should not be considered substitutes for any requirements imposed by the warranty of the distillate fuel equipment manufacturer or by federal, state, or local government regulations. Although they cannot replace a knowledge of local conditions or good engineering and scientific judgment, these suggested practices do provide guidance in developing an individual fuel management system for the middle distillate fuel user. They include suggestions in the operation and maintenance of existing fuel storage and handling facilities and for identifying where, when, and how fuel quality should be monitored or selected for storage or severe use.

X3.2 Definitions

X3.2.1 *bulk fuel*—fuel in the storage facility.

X3.2.2 *fuel contaminants*—foreign materials that make fuel less suitable or unsuitable for the intended use.

X3.2.2.1 *Discussion*—Fuel contaminants include materials introduced subsequent to the manufacture of fuel and fuel degradation products.

X3.2.3 *fuel-degradation products*—those materials that are formed in fuel during extended storage or exposure to high temperatures.

X3.2.3.1 *Discussion*—Insoluble degradation products may combine with other fuel contaminants to reinforce deleterious effects. Soluble degradation products (soluble gums) are less volatile than fuel and may carbonize to form deposits due to complex interactions and oxidation of small amounts of olefinic or sulfur-, oxygen- or nitrogen-containing compounds present in fuels. The formation of degradation products may be catalyzed by dissolved metals, especially copper salts. When dissolved copper is present it can be deactivated with metal deactivator additives.

X3.2.4 *long-term storage*—storage of fuel for longer than 12 months after it is received by the user.

X3.2.5 *severe use*—use of the fuel in applications which may result in engines operating under high load conditions that may cause the fuel to be exposed to excessive heat.

X3.3 Fuel Selection

X3.3.1 Certain distilled refinery products are generally more suitable for long-term storage and severe service than others. The stability properties of middle distillates are highly dependent on the crude oil sources, severity of processing, use of additives and whether additional refinery treatment has been carried out.

X3.3.2 The composition and stability properties of middle distillate fuels produced at specific refineries may be different. Any special requirements of the user, such as long-term storage or severe service, should be discussed with the supplier.

X3.3.3 Blends of fuels from various sources may interact to give stability properties worse than expected based on the characteristics of the individual fuels.

X3.4 Fuel Additives

X3.4.1 Available fuel additives can improve the suitability of marginal fuels for long-term storage and thermal stability, but may be unsuccessful for fuels with markedly poor stability properties. Most additives should be added at the refinery or during the early weeks of storage to obtain maximum benefits.

X3.4.2 Biocides or biostats destroy or inhibit the growth of fungi and bacteria, which can grow at fuel-water interfaces to give high particulate concentrations in the fuel. Available biocides are soluble in both the fuel and water or in the water phase only.

X3.5 Tests for Fuel Quality

X3.5.1 At the time of manufacture, the storage stability of fuel may be assessed using Test Method D 2274 or D 5304. However, these accelerated stability tests may not correlate well with field storage stability due to varying field conditions and to fuel composition.

X3.5.2 Performance criteria for accelerated stability tests that assure satisfactory long-term storage of fuels have not been established.

X3.5.3 Test Method D 6468, provides an indication of thermal oxidative stability of middle distillate fuels when heated to temperatures near 150°C.

X3.6 Fuel Monitoring

X3.6.1 A plan for monitoring the quality of bulk fuel during prolonged storage is an integral part of a successful program. A plan to replace aged fuel with fresh product at established intervals is also desirable.

X3.6.2 Stored fuel should be periodically sampled and its quality assessed. Practice D 4057 provides guidance for sampling. Fuel contaminants and degradation products will usually settle to the bottom of a quiescent tank. A “Bottom” or “Clearance” sample, as defined in Practice D 4057, should be included in the evaluation along with an “All Level” sample.

X3.6.3 The quantity of insoluble fuel contaminants present in fuel can be determined using Test Method D 6217.

X3.6.4 Test Method D 6468, can be used for investigation of operational problems that might be related to fuel thermal stability. Testing samples from the fuel tank or from bulk storage may give an indication as to the cause of filter plugging. It is more difficult to monitor the quality of fuels in vehicle tanks since operation may be on fuels from multiple sources.

X3.6.5 Some additives exhibit effects on fuels tested in accordance with Test Method D 6468 that may or may not be observed in the field. Data have not been developed that correlate results from the test method for various engine types and levels of operating severity.

X3.7 Fuel Storage Conditions

X3.7.1 Contarnination levels in fuel can be reduced by storage in tanks kept free of water, and tankage should have provisions for water draining on a scheduled basis. Water promotes corrosion, and microbiological growth may occur at a fuel-water interface. Underground storage is preferred to avoid temperature extremes; above-ground storage tanks should be sheltered or painted with reflective paint. High storage temperatures accelerate fuel degradation. Fixed roof tanks should be kept full to limit oxygen supply and tank breathing.

X3.7.2 Copper and copper-containing alloys should be avoided. Copper can promote fuel degradation and may produce mercaptide gels. Zinc coatings can react with water or organic acids in the fuel to form gels that rapidly plug filters.

X3.7.3 Appendix X2 of Specification D 2880 discusses fuel contaminants **as** a general topic.

X3.8 Fuel Use Conditions

X3.8.1 Many diesel engines are designed so that the diesel fuel is used for heat transfer. In modern heavy-duty diesel engines, for example, only a portion of the fuel that is circulated to the fuel injectors is actually delivered to the combustion chamber. The remainder of the fuel is circulated back to the fuel tank, carrying heat with it. Thus adequate high temperature stability can be a necessary requirement in some severe applications or types of service.

X3.8.2 Inadequate high temperature stability may result in the formation of insoluble degradation products.

X3.9 Use of Degraded Fuels

X3.9.1 Fuels that have undergone mild-to-moderate degradation can often be consumed in a normal way, depending on the fuel system requirements. Filters and other cleanup equipment can require special attention and increased maintenance. Burner nozzle or injector fouling can occur more rapidly.

X3.9.2 Fuels containing very large quantities of fuel degradation products and other contaminants or with runaway microbiological growth require special attention. Consultation with experts in this area is desirable. It can be possible to drain the sediment or draw off most of the fuel above the sediment layer and use it with the precautions described in X3.9.1. However, very high soluble gum levels or corrosion products from microbiological contamination can cause severe operational problems.

X3.10 Thermal Stability Guidelines

X3.10.1 Results from truck fleet experience suggests that Test Method D 6468 can be used to qualitatively indicate whether diesel fuels have satisfactory thermal stability performance properties.[5,6]

X3.10.2 Performance in engines has not been sufficiently correlated with results from Test Method D 6468 to provide definitive specification requirements. However, the following guidelines are suggested.

X3.10.2.1 Fuels giving a Test Method D 6468 reflectance value of 70 % or more in a 90 minute test at the time of manufacture should give satisfactory performance in normal use.

X3.10.2.2 Fuels giving a Test Method D 6468 reflectance value of 80 % or more in a 180 minute test at the time of manufacture should give satisfactory performance in severe use.

X3.10.3 Thermal stability as determined by Test Method D 6468 is known to degrade during storage.[7] The guidance above is for fuels used within six months of manufacture.

X4. DIESEL FUEL LUBRICITY

X4.1 Introduction

X4.1.1 Diesel fuel functions as a lubricant in most components of fuel injection equipment such as pumps and injectors. In limited cases, fuel with specific properties will have insufficient lubricating properties which will lead to a reduction in the normal service life and functional performance of diesel fuel injection systems.

X4.2 Fuel Characteristics Affecting Equipment Wear

X4.2.1 Currently, two fuel characteristics affect equipment wear. These are low viscosity and lack of sufficient quantities of trace components that have an affinity for surfaces. If fuel viscosity meets the requirements of a particular engine, a fuel film is maintained between the moving surfaces of the fuel system components. This prevents excessive meta1-to-metal contact and avoids premature failure due to wear. Similarly, certain surface active molecules in the fuel adhere to, or combine with, surfaces to produce a protective film which also can protect surfaces against excessive wear.

X4.3 Fuel Lubricity

X4.3.1 The concern about fuel lubricity is limited to situations in which fuels with lower viscosities than those specified for a particular engine are used or in which fuels that have been processed in a manner that results in severe reduction of the trace levels of the surface active species that act as surface protecting agents. Presently the only fuels of the latter type shown to have lubricity problems resulted from sufficiently severe processing to reduce aromatics or sulfur.

X4.3.2 Work in the area of diesel fuel lubricity is ongoing by several organizations, such as the International Organization for Standardization (ISO), the ASTM Diesel Fuel Lubricity Task Force, and the Coordinating Research Council (CRC) Diesel Performance Group. These groups include representatives from the fuel injection equipment manufacturers, fuel producers, and additive suppliers. The charge of the ASTM task force has been the recommendation of test methods and fuel lubricity requirements for Specification D 975. Two test methods were proposed and approved. These are Test Method D 6078, a scuffing load ball-on-cylinder lubricity evaluator method, SLBOCLE, and Test Method D 6079, a high frequency reciprocating rig (HFRR) method. Use of these tests raises three issues: 1) The correlation of the data among the two test methods and the fuel injection equipment is not perfect, 2) Both methods in their current form do not apply to all fuel-additive combinations, and 3) The reproducibility values for both test methods are large. In order to protect diesel fuel injection equipment, an HFRR Wear Scar Diameter (WSD) of 520 microns has been placed in Specification D 975.[8]

X4.3.3 Most experts agree that fuels having a SLBOCLE lubricity value below 2000 g might not prevent excessive wear in injection equipment[9] while fuels with values above 3100 g should provide sufficient lubricity in all cases.[10] Experts also agree that if HFFR test at 60°C is used, fuels with values above 600 microns might not prevent excessive wear,[11] while fuels with values below 450 microns should provide sufficient lubricity in all cases.[10] More accurately, an industry-accepted long-term durability pump test, such as Test Method D 6898, can be used to evaluate the lubricity of a diesel fuel. A poor result in such a test indicates that the fuel has low lubricity and may not be able to provide sufficient protection.

NOTE X4.1—Some injection equipment can be fitted with special components that can tolerate low lubricity fuels.

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[5] Bacha, John D., and Lesnini, David G., "Diesel Fuel Thermal Stability at 300°F," *Proceedings of the 6th International Conference on Stability and Handling of Liquid Fuels*, Vancouver, B.C., October 1997.

[6] Schwab, Scott D., Henly, Timothy J., Moxley, Joel F., and Miller, Keith, "Thermal Stability of Diesel Fuel," *Proceedings of the 7th International Conference on Stability and Handling of Liquid Fuels*, Graz, Austria September 2000.

[7] Henry. C. P., "The DuPont F21 149°C (300°F) Accelerated Stability Test," *Distillate Fuel Stability and Cleanliness. ASTM STP 751*, 1981. pp. 22-33.

X5. TENTH PERCENTILE MINIMUM AMBIENT AIR TEMPERATURES FOR THE UNITED STATES (EXCEPT HAWAII)

X5.1 Introduction

X5.1.1 The tenth percentile minimum ambient air temperatures shown on the following maps (Figs. X5.1-X5.12) and in Table X5.1 were derived from an analysis of historical hourly temperature readings recorded over a period of 15 to 21 years from 345 weather stations in the United States. This study was conducted by the U.S. Army Mobility Equipment Research and Development Center (USAMERDC), Coating and Chemical Laboratory, Aberdeen Proving Ground, MD 21005. The tenth percentile minimum ambient air temperature is defined as the lowest ambient air temperature which will not go lower on average more than 10 % of the time. In other words, the daily minimum ambient air temperature would on average not be expected to go below the monthly tenth percentile minimum ambient air temperature more than 3 days for a 30-day month. See Table X5.1.

X5.1.2 These data may be used to estimate low temperature operability requirements. In establishing low temperature operability requirements, consideration should be given to the following. These factors, or any combination, may make low temperature operability more or less severe than normal. As X5.1.2.1 through X5.1.2.12 indicate, field work suggests that cloud point (or wax appearance point) is a fair indication of the low temperature operability limit of fuels without cold flow additives in most vehicles.

X5.1.2.1 Long term weather patterns (Average winter low temperatures will be exceeded on occasion).

X5.1.2.2 Short term local weather conditions (Unusual cold periods do occur).

X5.1.2.3 Elevation (High locations are usually colder than surrounding lower areas).

X5.1.2.4 Specific engine design.

X5.1.2.5 Fuel system design (Recycle rate, filter location, filter capacity, filter porosity, and so forth.)

X5.1.2.6 Fuel viscosity at low temperatures

X5.1.2.7 Equipment add-ons (Engine heaters, radiator covers, fuel line and fuel filter heaters and so forth.)

X5.1.2.8 Types of operation (Extensive idling, engine shutdown, or unusual operation).

X5.1.2.9 Low temperature flow improver additives in fuel.

X5.1.2.10 Geographic area for fuel use and movement between geographical areas.

X5.1.2.11 General housekeeping (Dirt and/or water in fuel or fuel supply system).

X5.1.2.12 Impact failure for engine to start or run (Critical vs. non-critical application).

[8] Mitchell, K., “Diesel Fuel Lubricity—Base Fuel Effects,” SAE Technical Paper 2001–01–1928, 2001.

[9] Westbrook, S.R., “Survey of Low Sulfur Diesel Fuels and Aviation Kerosenes from U.S. Military Installations,” SAE Technical Paper 952369, 1995.

[10] Nikanjam, M., “ISO Diesel Fuel Lubricity Round Robin Program,” SAE Technical Paper 952372, 1995.

[11] Nikanjam, M., “*Diesel Fuel Lubricity: On the Path to Specifications*,” SAE Technical Paper 1999-01-1479, 1999.

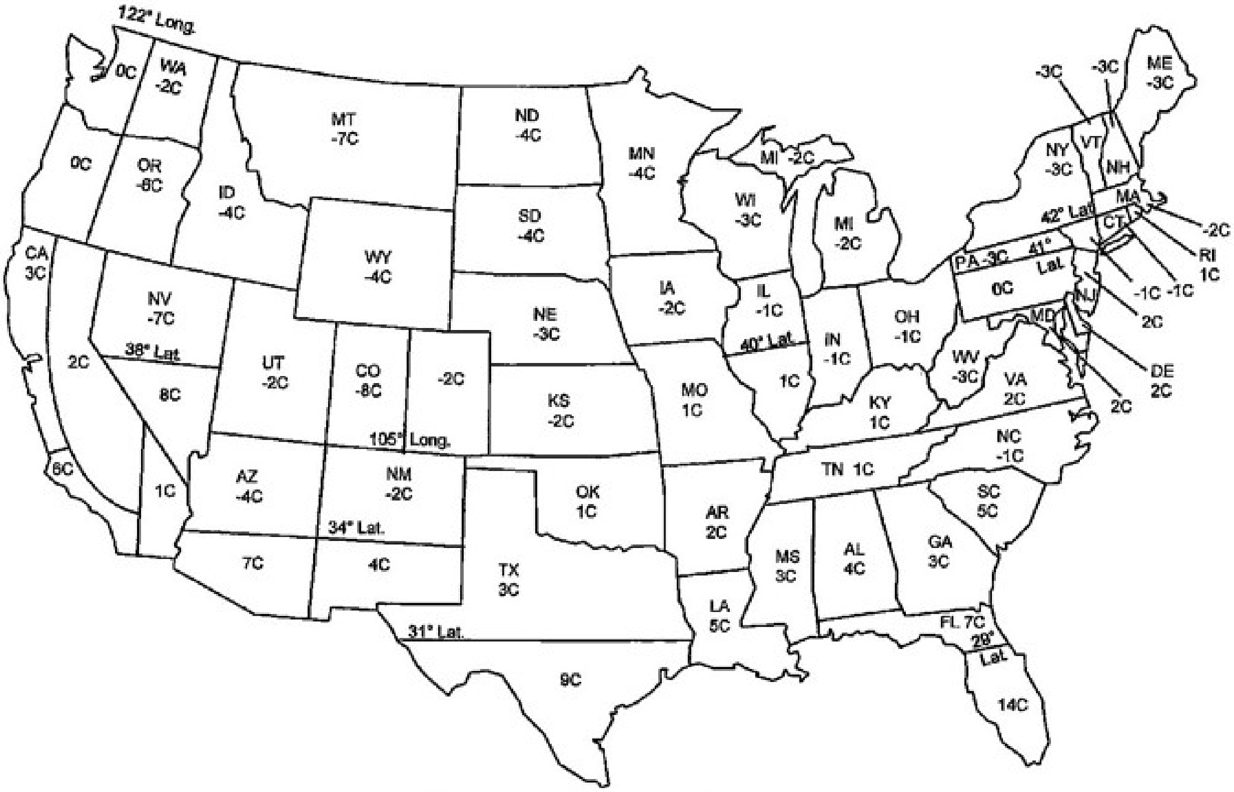

FIG. X5.1 October—10th Percentile Minimum Temperatures

X5.1.3 *Historical Background*—Three test methods have been widely used to estimate or correlate with low temperature vehicle operability. Cloud point. Test Method D 2500, is the oldest of the three and most conservative of the tests. The cloud point test indicates the earliest appearance of wax precipitation that might result in plugging of fuel filters or fuel lines under prescribed cooling conditions. Although not 100 % failsafe, it is the most appropriate test for applications that can not tolerate much risk. The Cold Filter Plugging Point (CFPP) test, Test Method D 6371, was introduced in Europe in 1965. The CFPP was designed to correlate with the majority of European vehicles. Under rapid cooling conditions, 20 cc fuel is drawn through a 45 micron screen then allowed to flow back through the screen for further cooling. This process is continued every 1°C until either the 20 cc fuel fails to be drawn through the screen in 60 s or it fails to return through the screen in 60 s. It was field tested many times in Europe[12] before being widely accepted as a European specification. Field tests have also shown CFPP results more than 10°C below the cloud point should be viewed with caution because those results did not necessarily reflect the true vehicle low temperature operability limits.[13] CFPP has been applied to many areas of the world where similar vehicle designs are used. The Low Temperature Flow Test (LTFT), Test Method D4539, was designed to correlate with the most severe and one of the most common fuel delivery systems used in North American Heavy Duty trucks. Under prescribed slow cool conditions (l°C/h), similar to typical field conditions, several 200 cc fuel specimens in glass containers fitted with 17 µn screen assemblies are cooled. At 1°C intervals one specimen is drawn through die screen under a 20 kPa vacuum. Approximately 90 % of the fuel must come over in 60 s or less for the result to be a pass. This process is continued at lower temperatures (1°C increments) until the fuel fails to come over in the allotted 60 s. The lowest passing temperature is defined as the LTFT for that fuel. In 1981, a CRC program was conducted to evaluate the efficacy of cloud point, CFPP, pour point, and LTFT for protecting the diesel vehicle population in North America and to determine what benefit flow-improvers could provide. The field test consisted of 3 non-flow improved diesel fuels, 5 flow improved diesel fuels, 4 light-duty passenger cars, and 3 heavy-duty trucks. The field trial resulted in two documents[14,15] that provide insight into correlating laboratory tests to North

[12] "Low Temperature Operability of Diesels. A Report by CEC Investigation Group IGF-3," CEC P-171-S2.

[13] "SFPP-A New Laboratory Test for Assessment of Low Temperature Operability of Modern Diesel Fuels," CEC/93/EF 15. 5-7, May 1993.

[14] CRC Report No. 537, "The Relationship Between Vehicle Fuel Temperature and Ambient Temperature, 1981 CRC Kapuskasing Field Test," December 1983.

[15] CRC Report No. 528, "1981 CRC Diesel Fuel Low-Temperature Operability Field Test," September 1983.

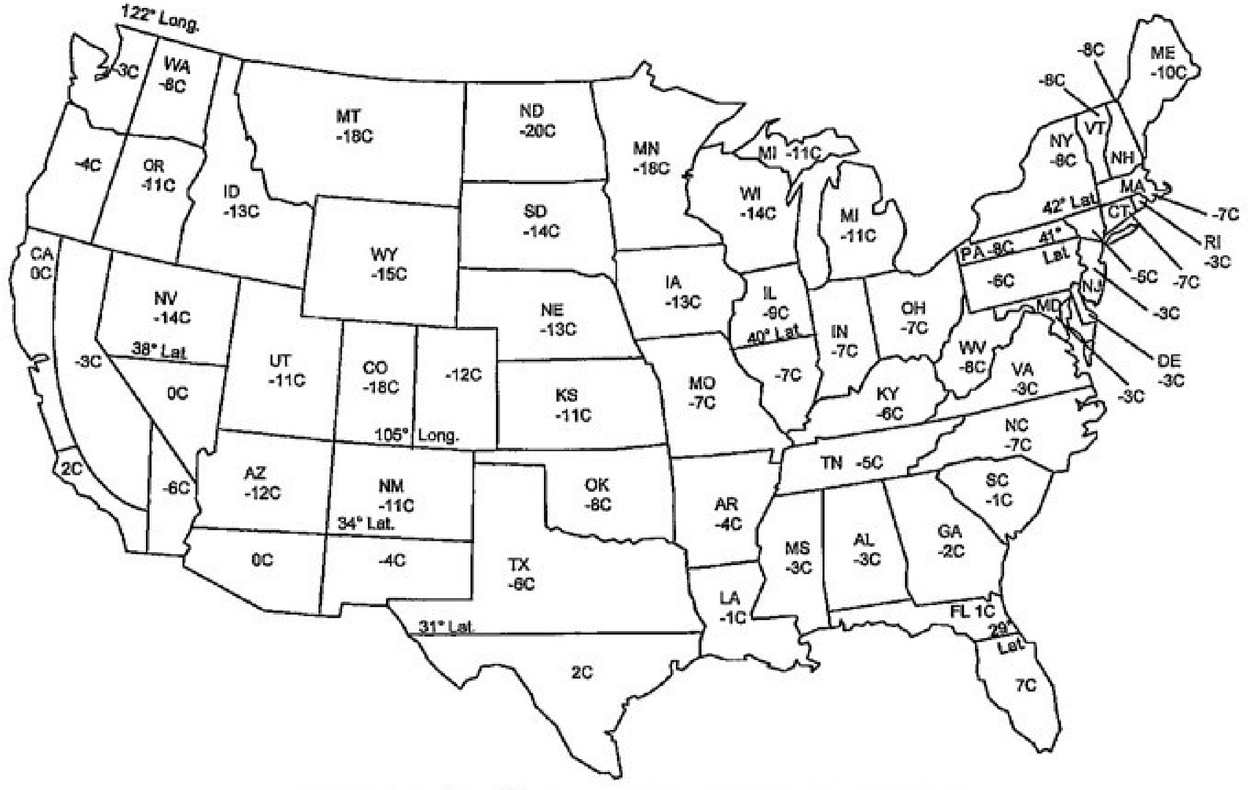

FIG. X5.2 November—10th Percentile Minimum Ambient Air Temperatures

American vehicle performance in the field. The general conclusions of the study were:

(1) In overnight cool down, 30 % of the vehicles tested had a final fuel tank temperature within 2°C of the overnight minimum ambient temperature.

(2) The use of flow-improved diesel fuel permits some vehicles to operate well below the fuel cloud point.

(3) Significant differences exist in the severity of diesel vehicles in terms of low temperature operation.

(4) No single laboratory test was found that adequately predicts the performance of all fuels in all vehicles.

(5) CFPP was a better predictor than pour point, but both methods over-predicted, minimum operating temperatures in many vehicles. For this reason, these tests were judged inadequate predictors of low-temperature performance and dismissed from further consideration.

(6) Cloud point and LTFT showed varying degrees of predictive capability, and offered distinctively different advantages. Both predicted the performance of the base fuels well, but LTFT more accurately predicted the performance of the flow-improved fuels. On the other hand, cloud point came closest to a fail-safe predictor of vehicle performance for all vehicles.

Since the 1981 field test, non-independent studies[16] using newer vehicles verified the suitability of the LTFT for North American heavy-duty trucks. Users are advised to review these and any more recent publications when establishing low temperature operability requirements and deciding upon test methods.

X5.1.3.1 *Current Practices*—It is recognized that fuel distributors, producers, and end users in the United States use cloud point, wax appearance point, CFPP, and LTFT to estimate vehicle low temperature operability limits for diesel fuel. No independent data has been published in recent years to determine test applicability for today's fuels and vehicles.

X5.2 Maps

X5.2.1 The maps in the following figures were derived from CCL Report No. 316, "A Predictive Study for Defining Limiting Temperatures and Their Application in Petroleum Product Specifications," by John P. Doner. This report was published by the U.S. Army Mobility Equipment Research and Development Center (USAMERDC), Coating and Chemical Laboratory, and it is available from the National Technical Information Service, Springfield, VA 22151, by requesting Publication No. AD756-420.

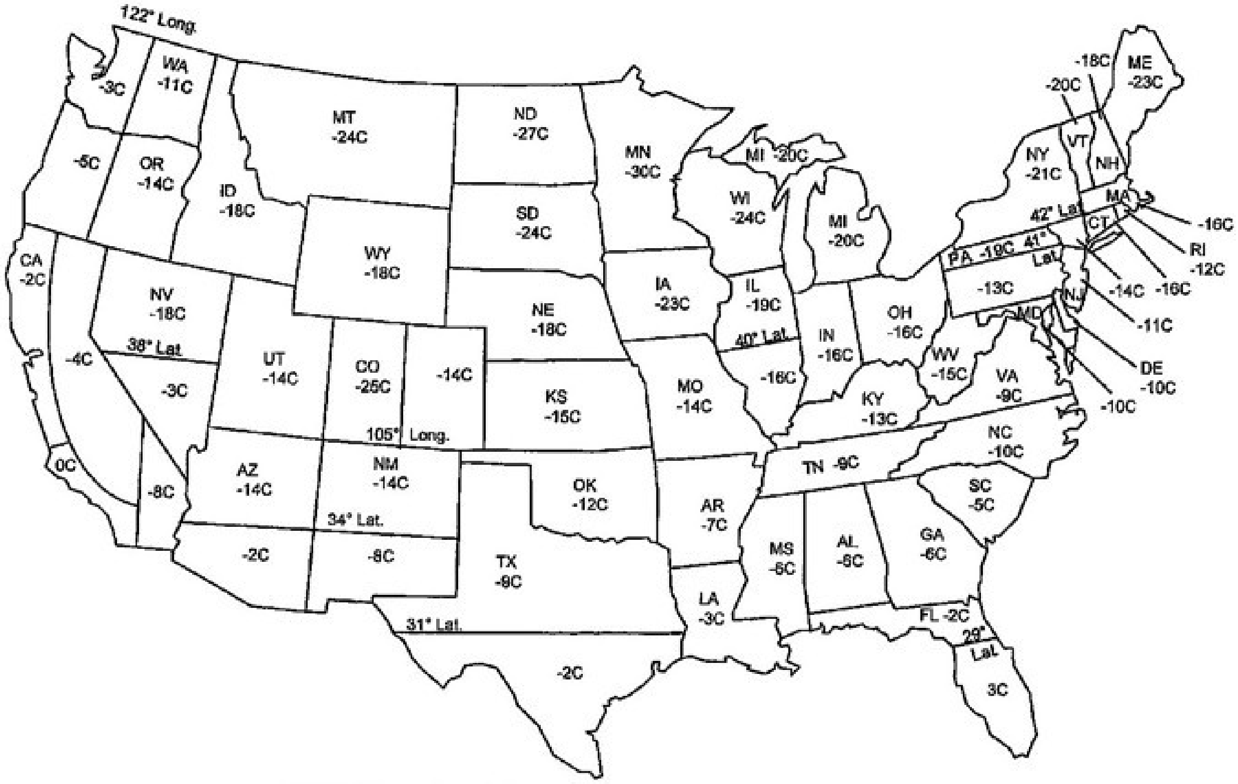

FIG. X5.3 December—10th Percentile Minimum Ambient Air Temperatures

X5.2.2 Where states are divided the divisions are noted on the maps and table with the exception of California, which is divided by counties as follows:

California, North Coast—Alameda, Contra Costa, Del Norte, Humbolt, Lake, Marin, Mendocino, Monterey, Napa, San Benito, San Francisco, San Mateo, Santa Clara, Santa Cruz, Solano, Sonoma, Trinity.

California, Interior—Lassen, Modoc, Plumas, Sierra, Siskiyou, Alpine, Amador, Butte, Calaveras, Colusa, El Dorado, Fresno, Glenn, Kern (except that portion lying east of the Los Angeles County

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[16] SAE 962197, SAE 982576, SAE 2000-01-2883.

Aqueduct), Kings, Madera, Mariposa, Merced, Placer, Sacramento, San Joaquin, Shasta, Stanislaus, Sutter, Tehama, Tulare, Tuolumne, Yolo, Yuba, Nevada.

California, South Coast—Orange, San Diego, San Luis Obispo, Santa Barbara, Ventura, Los Angeles (except that portion north of the San Gabriel Mountain range and east of the Los Angeles County Aqueduct).

California, Southeast—Imperial, Riverside, San Bernardino, Los Angeles (that portion north of the San Gabriel Mountain range and east of the Los Angeles County Aqueduct), Mono, Inyo, Kem (that portion lying east of die Los Angeles County Aqueduct).

X5.2.3 The temperatures in CCL Report No. 316 were in degrees Fahrenheit. The degree Celsius temperatures in Appendix X5 were obtained by converting the original degree Fahrenheit temperatures.

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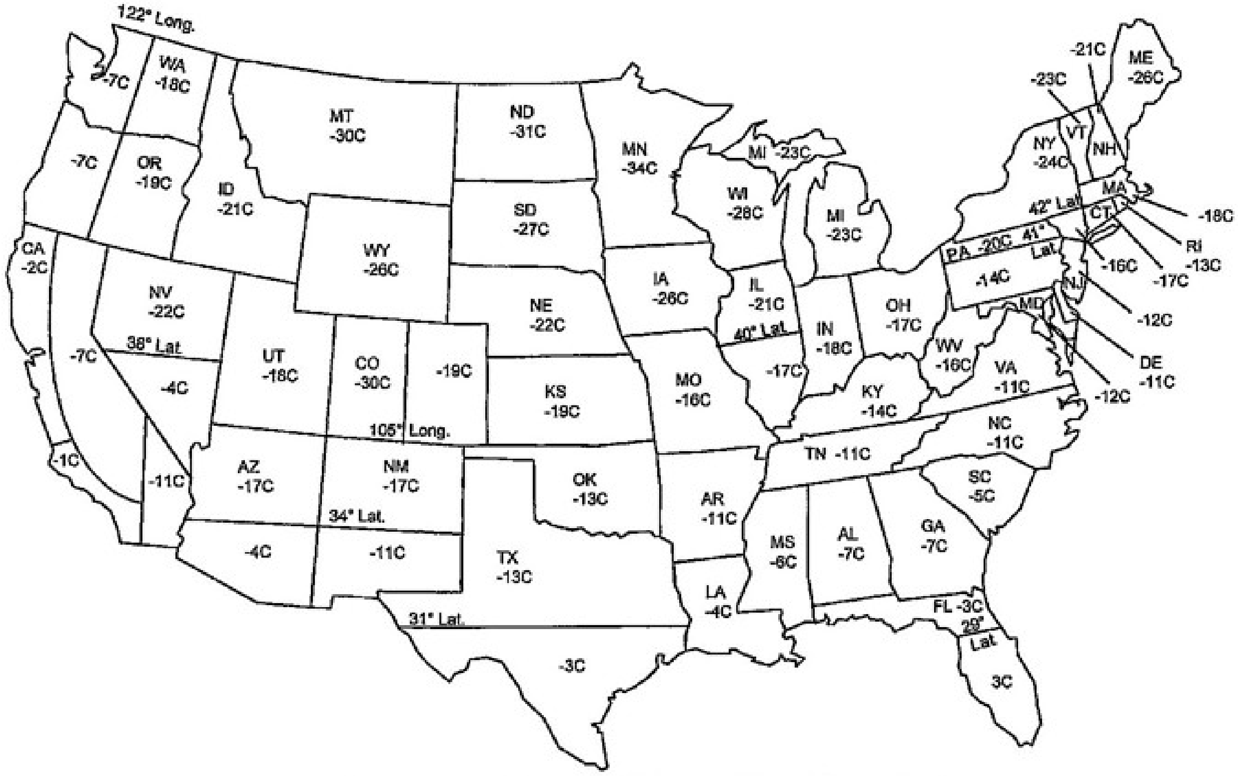

FIG. X5.4 January—10th Percentile Minimum Ambient Air Temperatures

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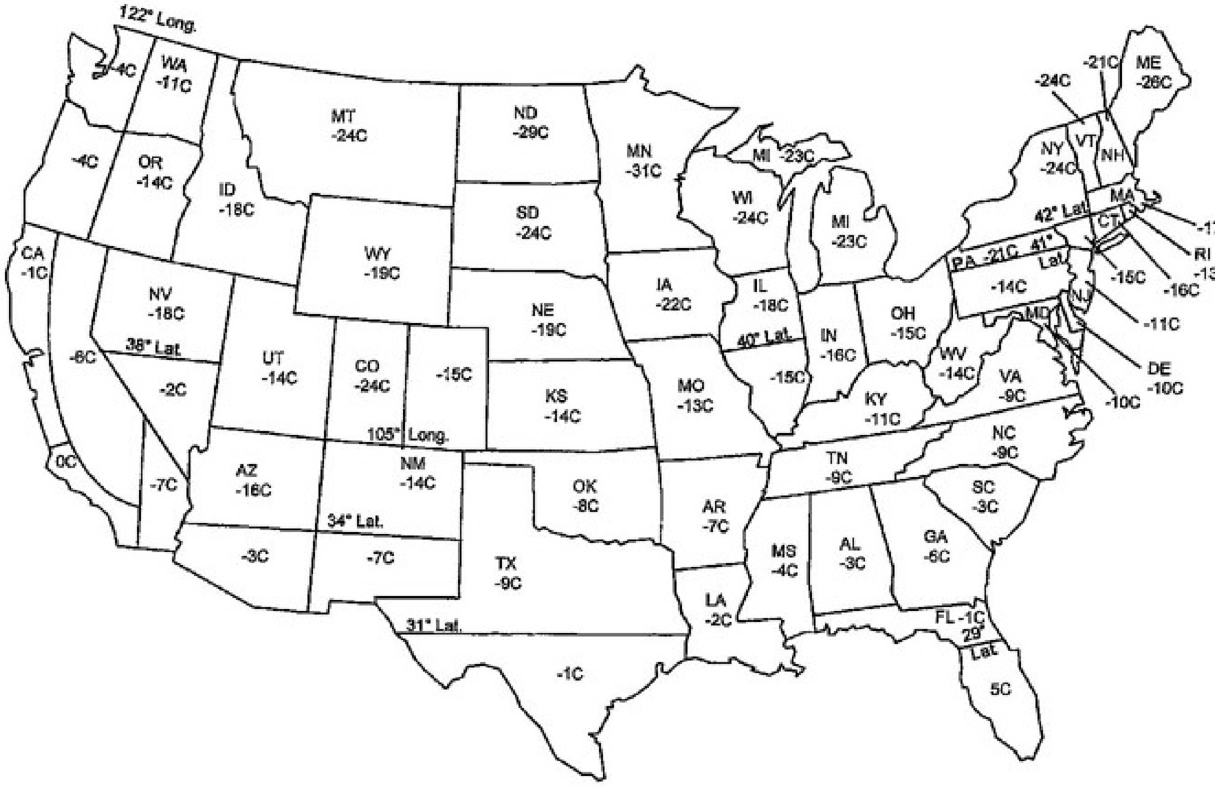

FIG. X5.5 February—10th Percentile Minimum Ambient Air Temperatures

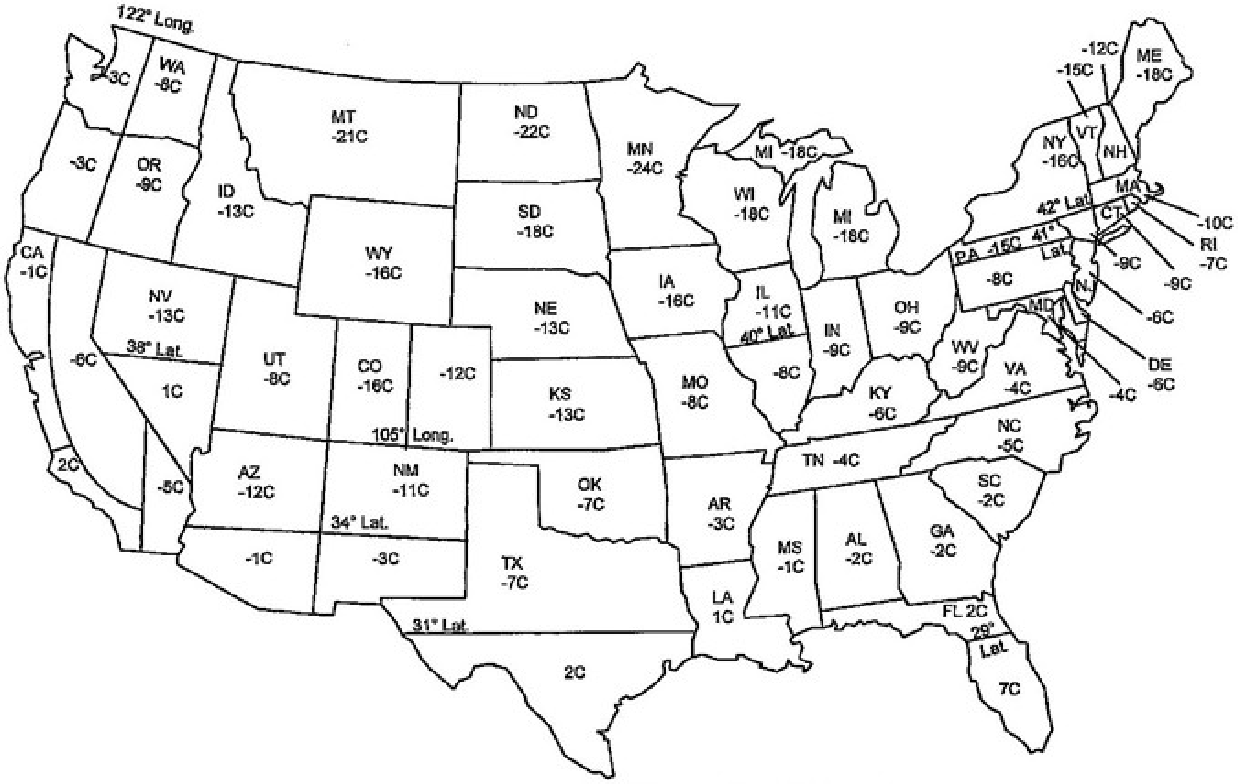

FIG. X5.6 March—10th Percentile Minimum Ambient Air Temperatures

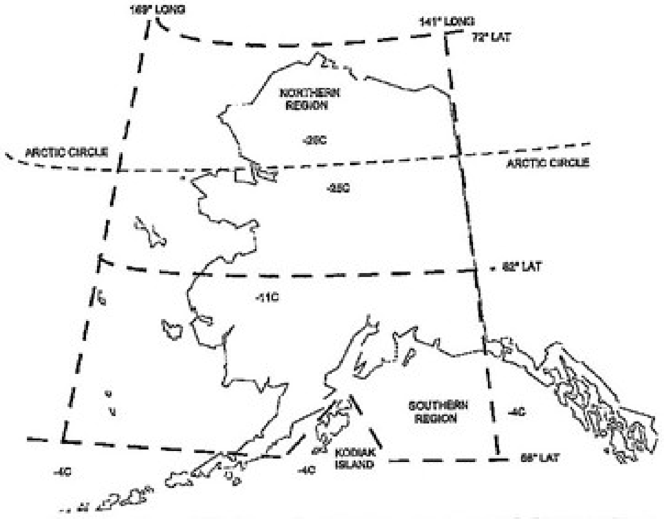

FIG. X5.7 October—10th Percentile Minimum Ambient Air Temperatures

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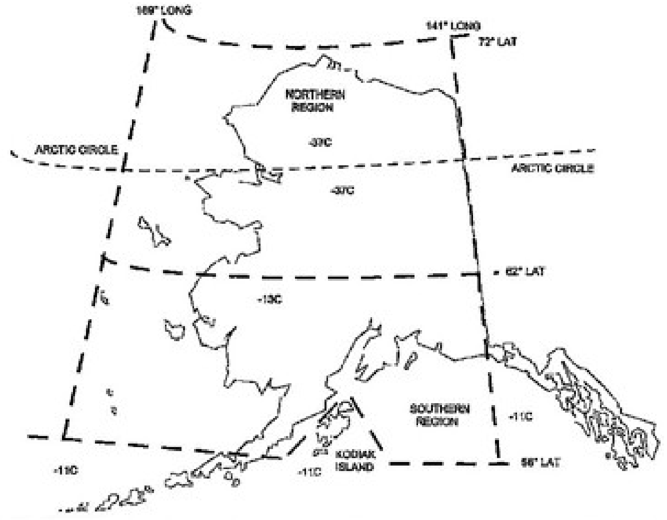

FIG. X5.8 November—10th Percentile Minimum Ambient Air Temperatures

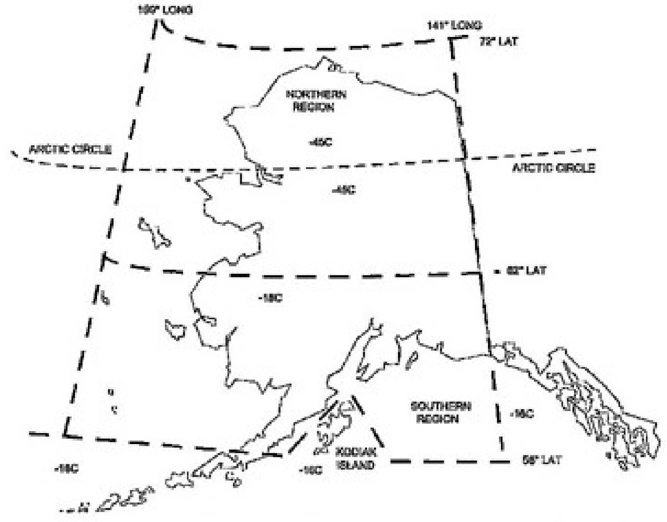

FIG. X5.9 December—10th Percentile Minimum Ambient Air Temperatures

16

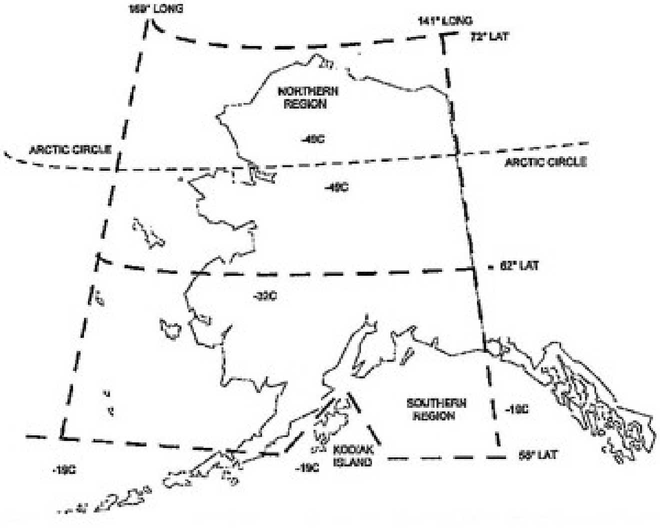

FIG. X5.10 January—10th Percentile Minimum Ambient Air Temperatures

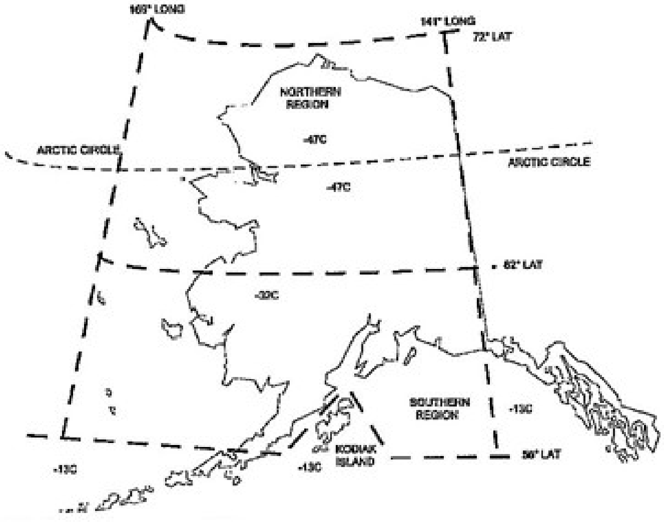

FIG. X5.11 February—10th Percentile Minimum Ambient Air Temperatures

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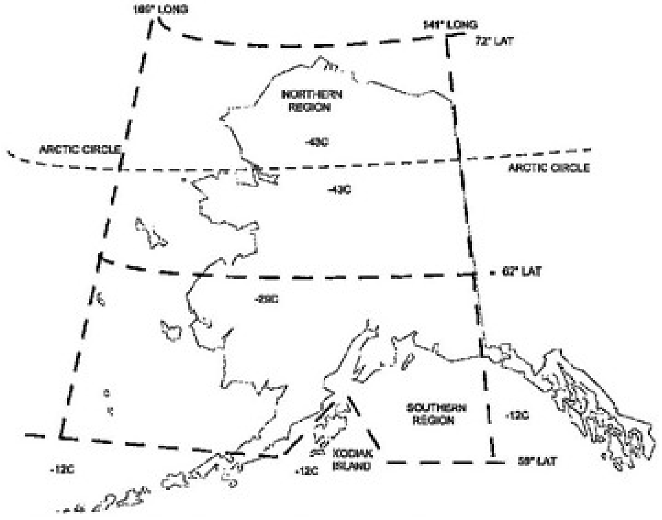

FIG. X5.12 March—10th Percentile Minimum Ambient Air Temperatures

18

TABLE X5.1 Tenth Percentile Minimum Ambient Air Temperatures for the United States (except Hawaii)

State	10th Percentile Temperature°C, min

State		10th Percentile Temperature °C, min					
		Oct.	Nov.	Dec.	Jan.	Feb.	March
Alabama		4	−3	−6	−7	−3	−2
Alaska	Northern	−25	−37	−45	−49	−47	−43
	Southern	−11	−13	−18	−32	−32	−29
	South East	−4	−11	−16	−19	−13	−12
Arizona	North 34° latitude	−4	−12	−14	−17	−16	−12
	South 34° latitude	7	0	−2	−4	−3	−1
Arkansas		2	−4	−7	−11	−7	−3
California	North Coast	3	0	−2	−2	−1	−1
	Interior	2	−3	−4	−7	−6	−6
	South Coast	6	2	0	−1	0	2
	Southeast	1	−6	−8	−11	−7	−5
Colorado	East 105° long	−2	−12	−14	−19	−15	−12
	West 105° long	−8	−18	−25	−30	−24	−16
Connecticut		−1	−7	−16	−17	−16	−9
Delaware		2	−3	−10	−11	−10	−6
Florida	North 29° latitude	7	1	−2	−3	−1	2
	South 29° latitude	14	7	3	3	5	7
Georgia		3	−2	−6	−7	−6	−2
Idaho		−4	−13	−18	−21	−18	−13
Illinois	North 40° latitude	−1	−9	−19	−21	−18	−11
	South 40° latitude	1	−7	−16	−17	−15	−8
Indiana		−1	−7	−16	−18	−16	−9
Iowa		−2	−13	−23	−26	−22	−16
Kansas		−2	−11	−15	−19	−14	−13
Kentucky		1	−6	−13	−14	−11	−6
Louisiana		5	−1	−3	−4	−2	1
Maine		−3	−10	−23	−26	−26	−18
Maryland		2	−3	−10	−12	−10	−4
Massachusetts		−2	−7	−16	−18	−17	−10
Michigan		−2	−11	−20	−23	−23	−18
Minnesota		−4	−18	−30	−34	−31	−24
Mississippi		3	−3	−6	−6	−4	−1
Missouri		1	−7	−14	−16	−13	−8
Montana		−7	−18	−24	−30	−24	−21
Nebraska		−3	−13	−18	−22	−19	−13
Nevada	North 38° latitude	−7	−14	−18	−22	−18	−13
	South 38° latitude	8	0	−3	−4	−2	1
New Hampshire		−3	−8	−18	−21	−21	−12
New Jersey		2	−3	−11	−12	−11	−6

State		10th Percentile Temperature°C, min					
		Oct.	Nov.	Dec.	Jan.	Feb.	March
New Mexico	North 34° latitude	−2	−11	−14	−17	−14	−11
	South 34° latitude	4	−4	−8	−11	−7	−3
New York	North 42° latitude	−3	−8	−21	−24	−24	−16
	South 42° latitude	−1	−5	−14	−16	−15	−9
North Carolina		−1	−7	−10	−11	−9	−5
North Dakota		−4	−20	−27	−31	−29	−22
Ohio		−1	−7	−16	−17	−15	−9
Oklahoma		1	−8	−12	−13	−8	−7
Oregon	East 122° long	−6	−11	−14	−19	−14	−9
	West 122° long	0	−4	−5	−7	−4	−3
Pennsylvania	North 41° latitude	−3	−8	−19	−20	−21	−15
	South 41° latitude	0	−6	−13	−14	−14	−8
Rhode Island		1	−3	−12	−13	−13	−7
South Carolina		5	−1	−5	−5	−3	−2
South Dakota		−4	−14	−24	−27	−24	−18
Tennessee		1	−5	−9	−11	−9	−4
Texas	North 31° latitude	3	−6	−9	−13	−9	−7
	South 31° latitude	9	2	−2	−3	−1	2
Utah		−2	−11	−14	−18	−14	−8
Vermont		−3	−8	−20	−23	−24	−15
Virginia		2	−3	−9	−11	−9	−4
Washington	East 122° long	−2	−8	−11	−18	−11	−8
	West 122° long	0	−3	−3	−7	−4	−3
West Virginia		−3	−8	−15	−16	−14	−9
Wisconsin		−3	−14	−24	−28	−24	−18
Wyoming		−4	−15	−18	−26	−19	−16

19 SUMMARY OF CHANGES

Subcommittee D02.E0.02 has identified the location of selected changes to this standard since the last issue (D 975-06b) that may impact the use of this standard. (Approved Feb. 1, 2007.)

(1) Added standards to the Referenced Documents.

(2) Added Section 4.

(3) Added X2.2.2.

Subcommittee D02.E0.02 has identified the location of selected changes to this standard since the last issue (D 975-06a) that may impact the use of this standard. (Approved Nov. 1, 2006.)

(1) Revised Appendix X4.

Subcommittee D02.E0.02 has identified the location of selected changes to this standard since the last issue (D 975-06) that may impact the use of this standard. (Approved Oct. 1, 2006.)

(1) Added Test Method D 6890.

(2) Revised 5.1.10.

Subcommittee D02.E0.02 has identified the location of selected changes to this standard since the last issue (D 975-05) that may impact the use of this standard. (Approved May 15, 2006.)

(1) Deleted Test Method D 6920 from this standard.

Subcommittee D02.E0.02 has identified the location of selected changes to this standard since the last issue (D 975-04c$^{\epsilon 1}$) that may impact the use of this standard. (Approved June 1, 2005.)

(1) Removed footnote J from Grade No. 4–D in Table 1.

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

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Designation: D 1688 – 95

Standard Test Methods for Copper in Water[1]

This standard is issued under the fixed designation D 1688; 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 (∊) indicates an editorial change since the last revision or reapproval.

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

1. Scope

1.1

These test methods cover the determination of copper in water by atomic absorption spectrophotometry. Three test methods are included as follows:

	Concentration Range	Sections
Test Method A—Atomic Absorption, Direct	0.05 to 5 mg/L	7 to 15
Test Method B—Atomic Absorption, Chelation-Extraction	50 to 500 µg/L	16 to 24
Test Method C—Atomic Absorption, Graphite Furnace	5 to 100 µg/L	25 to 33

1.2

Either dissolved or total recoverable copper may be determined. Determination of dissolved copper requires filtration through a 0.45-μm (No. 325) membrane filter at the time of collection. In-line membrane filtration is preferable.

1.3

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

1.4

This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. For specific hazard statements, see Notes 3, 5, 8, and 13.

1.5

Three former photometric test methods were discontinued. Refer to Appendix X1 for historical information.

2. Referenced Documents

2.1 *ASTM Standards:*

D 858 Test Methods for Manganese in Water[2]

D 1066 Practice for Sampling Steam[2]

D 1068 Test Methods for Iron in Water[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 1687 Test Methods for Chromium in Water[2]

D 1691 Test Methods for Zinc in Water[2]

D 1886 Test Methods for Nickel in Water[2]

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

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

D 3557 Test Methods for Cadmium in Water[2]

D 3558 Test Methods for Cobalt in Water[2]

D 3559 Test Methods for Lead in Water[2]

D 3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry[2]

D 4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents[2]

3. Terminology

3.1

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

4. Significance and Use

4.1

Copper is found in naturally occurring minerals principally as a sulfide, oxide, or carbonate. It makes up approximately 0.01 % of the earth's crust and is obtained commercially from such ores as chalcopyrite ($CuFeS_2$). Copper is also found in biological complexes such as hemocyanin.

4.2

Copper enters water supplies through the natural process of dissolution of minerals, through industrial effluents, through its use, as copper sulfate, to control biological growth in some reservoirs and distribution systems, and through corrosion of copper alloy water pipes. Industries whose wastewaters may contain significant concentrations of copper include mining, ammunition production, and most metal plating and finishing operations. It may occur in simple ionic form or in one of many complexes with such groups as cyanide, chloride, ammonia, or organic ligands.

4.3

Although its salts, particularly copper sulfate, inhibit biological growth such as some algae and bacteria, copper is considered essential to human nutrition and is not considered a toxic chemical at concentrations normally found in water supplies.

5. Purity of Reagents

5.1

Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[3] Other grades may be

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

Current edition approved Feb. 15, 1995. Published April 1995. Originally published as D 1688 – 59 T. Last previous edition D 1688 – 90.

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

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

used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2

Purity of Water—Unless otherwise indicated, 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 lessening the bias and precision of the determination. Type II water was specified at the time of round-robin testing of this test method.

6. Sampling

6.1

Collect the sample in accordance with Practices D 1066, Specification D 1192, and Practices D 3370, as applicable.

6.2

Samples shall be preserved with nitric acid (HNO_3, sp gr 1.42) to a pH of 2 or less immediately at the time of collection, normally about 2 mL/L. If only dissolved copper is to be determined, the sample shall be filtered through a 0.45-µm (No. 325) membrane filter before acidification. The holding time for samples may be calculated in accordance with Practice D 4841.

TEST METHOD A—ATOMIC ABSORPTION, DIRECT

7. Scope

7.1

This test method covers the determination of dissolved and total recoverable copper in most waters and waste waters.

7.2

This test method is applicable in the range from 0.05 to 5 mg/L of copper. The range may be extended to concentrations greater than 5 mg/L by dilution of the sample.

7.3

Collaborative test data were obtained on reagent water, river water, tap water, ground water, lake water, refinery primary treated effluent, and two untreated waste waters. The information on precision and bias may not apply to other waters.

8. Summary of Test Method

8.1

Copper is determined by atomic absorption spectrophotometry. Dissolved copper in the filtered sample is aspirated directly with no pretreatment. Total recoverable copper in the sample is aspirated following hydrochloric-nitric acid digestion and filtration. The same digestion procedure may be used to determine total recoverable cadmium (Test Methods D 3557), chromium (Test Methods D 1687), cobalt (Test Methods D 3558), iron (Test Methods D 1068), lead (Test Methods D 3559), manganese (Test Methods D 858), nickel (Test Methods D 1886), and zinc (Test Methods D 1691).

9. Interferences

9.1

Sodium, potassium, sulfate, and chloride (8000 mg/L each), calcium and magnesium (5000 mg/L each), nitrate (2000 mg/L), iron (1000 mg/L), and cadmium, lead, nickel, zinc, cobalt, manganese, and chromium (10 mg/L each) do not interfere.

9.2

Background correction or a chelation-extraction procedure (see Test Method B) may be necessary to determine low levels of copper in some waters.

Note 1—Instrument manufacturers' instructions for use of the specific correction technique should be followed.

10. Apparatus

10.1

Atomic Absorption Spectrophotometer, for use at 324.7 nm.

Note 2—The manufacturer's instructions should be followed for all instrumental parameters. A wavelength other than 324.7 nm may be used if it has been determined to be equally suitable.

10.1.1

Copper Hollow-Cathode Lamp—Multielement hollow-cathode lamps are available and have been found satisfactory.

10.2

Oxidant—See 11.6.

10.3

Fuel—See 11.7.

10.4

Pressure-Reducing Valves—The supplies of fuel and oxidant shall be maintained at pressures somewhat higher than the controlled operating pressure of the instrument by suitable valves.

11. Reagents and Materials

11.1

Copper Solution, Stock (1.0 mL = 1.0 mg Cu)—Dissolve 1.000 g of electrolytic copper contained in a 250-mL beaker in a mixture of 15 mL of HNO_3 (sp gr 1.42) and 15 mL of water. Slowly add 4 mL of H_2SO_4 (1+1) and heat until SO_3 fumes evolve. Cool, wash down the beaker with water, and dilute to 1 L with water.

11.2

Copper Solution, Standard (1.0 mL = 0.1 mg Cu)—Dilute 100.0 mL of copper stock solution to 1 L with water.

11.3

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

> Note 3—If a high reagent blank is obtained, distill the HCl or use a spectrograde acid. **Caution**—When HCl is distilled an azeotropic mixture is obtained (approximately 6 *N* HCl). Therefore, whenever concentrated HCl is specified for the preparation of a reagent or in the procedure, use double the volume specified if distilled HCl is used.

11.4

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

> Note 4—If a high reagent blank is obtained, distill the HNO_3 or use a spectrograde acid.

11.5

Nitric Acid (1+499)—Add 1 volume of HNO_3 (sp gr 1.42) to 499 volumes of water.

11.6 *Oxidant:*

11.6.1

Air, which has been passed through a suitable filter to remove oil, water, and other foreign substances, is the usual oxidant.

11.7 *Fuel:*

11.7.1

Acetylene—Standard, commercially available acetylene is the usual fuel. Acetone, always present in acetylene cylinders, can affect analytical results. The cylinder should be replaced at 50 psig (345 kPa).

> Note 5: **Precaution**—“Purified” grade acetylene containing a special proprietary solvent rather than acetone should not be used with poly(vinyl chloride) tubing as weakening of the tubing walls can cause a potentially hazardous situation.

12. Standardization

12.1

Prepare 100 mL each of a blank and at least four standard solutions to bracket the expected copper concentration range of the samples to be analyzed by diluting the standard copper solution (11.2) with HNO_3 (1+499). Prepare the standards each time the test is to be performed.

12.2

When determining total recoverable copper add 0.5 mL of HNO_3 (sp gr 1.42) and proceed as directed in 13.2 through 13.4. When determining dissolved copper proceed with 13.5.

12.3

Aspirate the blank and standards and record the instrument readings. Aspirate HNO_3 (1+499) between each standard.

12.4

Prepare an analytical curve by plotting on linear graph paper the absorbance versus standard concentration for each standard. Alternatively, read directly in concentration if this capability is provided with the instrument.

13. Procedure

13.1

Measure 100.0 mL of a well-mixed acidified sample into a 125-mL beaker or flask.

Note 6—If only dissolved copper is to be determined, start with 13.5.

13.2

Add 5 mL of HCl (sp gr 1.19) to each sample.

13.3

Heat the samples on a steam bath or hotplate in a well-ventilated hood until the volume has been reduced to 15 to 20 mL, making certain that the samples do not boil.

Note 7—When analyzing samples containing appreciable amounts of suspended matter, the amount of reduction in volume is left to the discretion of the analyst.

13.4

Cool and filter the samples through a suitable filter, such as fine-textured, acid washed, ashless paper, into 100-mL volumetric flasks. Wash the filter paper two or three times with water and adjust to volume.

13.5

Aspirate each filtered and acidified sample and determine its absorbance or concentration at 324.7 nm. Aspirate HNO_3 (1+499) between each sample.

14. Calculation

14.1

Calculate the concentration of copper in each sample, in milligrams per litre, using an analytical curve or alternatively, read directly in concentration (see 12.4).

15. Precision and Bias[4]

15.1

The collaborative test of this test method was performed by ten laboratories, five of which supplied two operators each. Each of the 15 operators made determinations at three levels on three different days in samples of reagent water and water of choice for a total of 270 determinations.

15.2

These collaborative test data were obtained on reagent grade water, river water, tap water, ground water, lake water, refinery primary treated effluent, and two untreated waste waters. For other matrices, these data may not apply.

15.3

Precision—The single-operator and overall precision of this test method within its designated range may be expressed as follows:

In reagent water, Type II:

$S_O = 0.020X + 0.035$

$S_T = 0.052X + 0.123$

In water or waste water:

TABLE 1 Determination of Bias for Test Method A

Amount Added, mg Cu/L	**Amount Found, mg Cu/L**	**Bias, %**	**Statistically Significant, 95 % Level**
Reagent Water			
4.0	4.11	+2.75	no
2.0	2.06	+3.0	no
0.4	0.46	+15.0	yes
Water or Waste Water			
4.0	4.03	+0.75	no

Amount Added, mg Cu/L	Amount Found, mg Cu/L	Bias, %	Statistically Significant, 95 % Level
2.0	2.02	+1.0	no
0.4	0.41	+2.5	no

$S_O = 0.016X + 0.033$

$S_T = 0.060X + 0.039$

where:

S_o	=	single-operator precision,
S_T	=	overall precision, and
X	=	determined concentration of copper, mg/L.

15.4

Bias—Recoveries of known amounts of copper were as shown in Table 1.

TEST METHOD B—ATOMIC ABSORPTION, CHELATION-EXTRACTION

16. Scope

16.1

This test method covers the determination of dissolved and total recoverable copper in most waters and brines.

16.2

This test method is applicable in the range from 50 to 500 µg/L of copper. The range may be extended to concentrations greater than 500 µg/L by dilution of the sample.

16.3

Collaborative test data were obtained on reagent water, river water, tap water, 50 % artificial sea water, and synthetic NaCl brine (50 000 mg/L). The information on precision and bias may not apply to other waters.

17. Summary of Test Method

17.1

Copper is determined by atomic absorption spectrophotometry. The element, either dissolved or total recoverable, is chelated with pyrrolidine dithiocarbamic acid and extracted with chloroform. The extract is evaporated to dryness, treated with hot nitric acid to destroy organic matter, dissolved in hydrochloric acid, and diluted to a specified volume with water. A portion of the resulting solution is then aspirated into the air-acetylene flame of the spectrophotometer. The digestion procedure summarized in 8.1 is used for total recoverable copper. The same chelation-extraction procedure is used to determine cadmium (Test Methods D 3557), cobalt (Test Methods D 3558), iron (Test Methods D 1068), lead (Test Methods D 3559), nickel (Test Methods D 1886), and zinc (Test Methods D 1691).

18. Interferences

18.1

See Section 9.

19. Apparatus

19.1

All apparatus described in Section 10 are required.

20. Reagents and Materials

20.1

Bromphenol Blue Indicator Solution (1 g/L)—

[4] Supporting data are available from ASTM Headquarters. Request RR: D19-1037.

159 Dissolve 0.1 g of bromphenol blue in 100 mL of 50 % ethanol or isopropanol.

20.2

Chloroform ($CHCl_3$).

20.3

Copper Solution, Stock (1.0 mL = 1.0 mg Cu)—Dissolve 1.000 g of electrolytic copper contained in a 250-mL beaker in a mixture of 15 mL of HNO_3 (sp gr 1.42) and 15 mL of water. Slowly add 4 mL of H_2SO_4 (1+1) and heat until SO_3 fumes evolve. Cool, wash down the beaker with water, and dilute to 1 L with water.

20.4

Copper Solution, Intermediate (1.0 mL = 10 µg Cu)—Dilute 10.0 mL of copper stock solution and 1 mL of HNO_3 (sp gr 1.42) to 1 L with water.

20.5

Copper Solution, Standard (1.0 mL = 1.0 µg Cu)—Immediately before use, dilute 10.0 mL of copper intermediate solution to 100 mL with water. This standard is used to prepare working standards at the time of analysis.

20.6

Hydrochloric Acid (sp gr 1.19)—Concentrated hydrochloric acid (HCl) (see Note 4).

20.7

Hydrochloric Acid (1+2)—Add 1 volume of HCl (sp gr 1.19) to 2 volumes of water.

20.8

Hydrochloric Acid (1+49)—Add 1 volume of HCl (sp gr 1.19) to 49 volumes of water.

20.9

Nitric Acid (sp gr 1.42)—Concentrated nitric acid (HNO_3) (see Note 4).

20.10

Pyrrolidine Dithiocarbamic Acid-Chloroform Reagent—Add 36 mL of pyrrolidine to 1 L of $CHCl_3$. Cool the solution and add 30 mL of CS_2 in small portions, swirling between additions. Dilute to 2 L with $CHCl_3$. The reagent can be used for several months if stored in a cool, dark place.

> Note 8: **Warning**—All components of this reagent are highly toxic. Carbon disulfide is also highly flammable. **Precaution**—Prepare and use in a well-ventilated hood.

20.11

Sodium Hydroxide Solution (100 g/L)—Dissolve 100 g of sodium hydroxide (NaOH) in water and dilute to 1 L.

20.12

Oxidant—See 11.6.

20.13

Fuel—See 11.7.

21. Standardization

21.1

Prepare a blank and sufficient standards containing from 0.0 to 50.0 µg of copper by diluting 0.0 to 50.0-mL portions of standard copper solution (20.5) to 100 mL with water.

21.2

When determining total recoverable copper, use 125-mL beakers or flasks, add 0.5 mL of HNO_3 (sp gr 1.42) and proceed as directed in 22.2 through 22.15. When determining dissolved copper, use 250-mL separatory funnels and proceed as directed in 22.5 through 22.15.

21.3

Construct an analytical curve by plotting the absorbances of standards versus micrograms of copper. Alternatively, read directly in concentration if this capability is provided with the instrument.

22. Procedure

22.1

Measure a volume of a well-mixed acidified sample containing less than 50.0 µg of copper (100 mL maximum) into a 125-mL beaker or flask and adjust the volume to 100 mL with water.

> Note 9—If only dissolved copper is to be determined measure a volume of filtered and acidified sample containing less than 50.0 µg of copper (100-mL maximum) into a 250-mL separatory funnel, and begin with 22.5.

22.2

Add 5 mL of HCl (sp gr 1.19) to each sample.

22.3

Heat the samples on a steam bath or hotplate in a well-ventilated hood until the volume has been reduced to 15 to 20 mL, making certain that the samples do not boil.

> Note 10—When analyzing brine samples and samples containing appreciable amounts of suspended matter, the amount of reduction in volume is left to the discretion of the analyst.

22.4

Cool and filter the samples through a suitable filter, such as fine-textured, acid-washed, ashless paper, into 250-mL separatory funnels. Wash the filter paper two or three times with water and adjust the volume to approximately 100 mL.

22.5

Add 2 drops of bromphenol blue indicator solution and mix.

22.6

Adjust the pH by addition of NaOH (100 g/L) solution until a blue color persists. Add HCl (1+49) by drops until the blue color just disappears; then add 2.5 mL of HCl (1+49) in excess. The pH at this point should be 2.3.

Note 11—The pH adjustment in 22.6 may be made with a pH meter instead of using an indicator.

22.7

Add 10 mL of pyrrolidine dithiocarbamic acid-chloroform reagent and shake vigorously for 2 min. **Warning—**See Note 8.

22.8

Plug the tip of the separatory funnel with cotton, allow the phases to separate, and drain the $CHCl_3$ phase into a 100-mL beaker.

22.9

Repeat the extraction with 10 mL of $CHCl_3$ and drain the $CHCl_3$ layer into the same beaker.

Note 12—If color still remains in the $CHCl_3$ extract, reextract the aqueous phase until the $CHCl_3$ layer is colorless.

22.10

Place the beaker on a hot plate set at low heat or on a steam bath, and evaporate to near dryness. Remove beaker from heat and allow residual solvent to evaporate without further heating.

Note 13: **Precaution**—Perform in a well-ventilated hood.

22.11

Hold the beaker at a 45° angle, and slowly add dropwise 2 mL of HNO_3 (sp gr 1.42), rotating the beaker to effect thorough contact of the acid with the residue.

22.11.1

If acid is added to the beaker in a vertical position, a violent reaction will occur accompanied by high heat and spattering.

22.12

Place the beaker on a hotplate set at low heat or on a steam bath and evaporate to near dryness. Remove beaker from heat and allow residual solvent to evaporate without further heating.

22.13

Add 2 mL of HCl (1+2) to the beaker, and heat, while swirling, for 1 min.

22.14

Cool and quantitatively transfer the solution to a 10-mL volumetric flask and adjust to volume with water.

22.15

Aspirate each sample and record the scale reading or concentration at 324.7 nm.

23. Calculation

23.1

Determine the weight of copper in micrograms in each sample by referring to the analytical curve or, alternatively, by multiplying the direct read-out concentration of copper by 10 mL. (See 21.3.) Calculate the concentration of copper in the original sample in micrograms per litre using Eq 1:

160

TABLE 2 Determination of Bias for Test Method B

Amount Added, μg Cu/L	Amount Found, μg Cu/L	Bias, %	Statistically Significant, 95 % Level
Reagent Water			
300	290	−3.3	no
100	112	+12.0	no
20	65	+225	yes
Water or Brine			
300	234	−22.0	no
100	93	−7.0	no
20	49	+145	no

$$\text{Copper, } \mu g/L = \frac{1000 \times B}{A} \quad (1)$$

where:

A	=	volume of original sample, mL, and
B	=	weight of copper in sample, µg.

24. Precision and Bias[4]

24.1

The collaborative test of this test method was performed by six laboratories, two of which supplied two operators each. Each operator performed the test at three levels. A total of 120 determinations were made.

24.2

These collaborative test data were obtained on reagent grade water, river water, tap water, 50 % artificial seawater, and synthetic NaCl brine (50 000 mg/L). For other matrices, these data may not apply.

24.3

Precision—The single-operator and overall precision of this test method within its designated range may be expressed as follows:

In reagent water, Type II:

$S_O = 0.119X + 9$

$S_T = 0.247X + 47$

In water or brine:

$S_O = 27$

$S_T = 0.270X + 42$

where:

S_O	=	single-operator precision, µg/L,
S_T	=	overall precision, µg/L, and
X	=	concentration of copper, µg/L.

24.4

Bias—Recoveries of known amounts of copper were as shown in Table 2.

TEST METHOD C—ATOMIC ABSORPTION, GRAPHITE FURNACE

25. Scope

25.1

This test method covers the determination of dissolved and total recoverable copper in most waters and wastewaters.

25.2

This test method is applicable in the range from 5 to 100 μg/L of copper. The range can be increased or decreased by varying the volume of sample injected or the instrumental settings. High concentrations may be diluted but preferably should be analyzed by direct aspiration atomic absorption spectrophotometry (see Test Method A).

25.3

This test method has been used successfully with reagent grade water, filtered tap water, condensate from a medium Btu coal gasification process, river water, lake water, well water, and production plant process waters. It is the user's responsibility to assure the validity of this test method in other matrices.

26. Summary of Test Method

26.1

Copper is determined by an atomic absorption spectrophotometer used in conjunction with a graphite furnace. A sample is placed in a graphite tube, evaporated to dryness, charred (pyrolyzed or ashed) and atomized. Since the graphite furnace uses the sample much more efficiently than flame atomization, the detection of low concentrations of elements in small sample volumes is possible. The absorption signal generated during atomization is recorded and compared to standards. A general guide for the application of the graphite furnace is given in Practice D 3919.

26.2

Dissolved copper is determined on a filtered sample with no pretreatment.

26.3

Total recoverable copper is determined following acid digestion and filtration. Because chlorides interfere with furnace procedures for some metals, the use of hydrochloric acid in any digestion or solubilization step is to be avoided. If suspended material is not present, this digestion and filtration may be omitted.

27. Interferences

27.1

For a complete discussion on general interferences with furnace procedures, the analyst is referred to Practice D 3919.

28. Apparatus

28.1

Atomic Absorption Spectrophotometer, for use at 324.7 nm with background correction.

Note 14—A wavelength other than 324.7 nm may be used if it has been determined to be suitable. Greater linearity may be obtained at high concentrations by using a less sensitive wavelength.

Note 15—The manufacturer's instructions should be followed for all instrumental parameters.

28.2

Copper Hollow Cathode Lamp, a single element lamp is preferred, but multielement lamps may be used.

28.3

Graphite Furnace, capable of reaching temperatures sufficient to atomize the element of interest.

28.4

Graphite Tubes, compatible with furnace device. Standard graphite tubes are preferred unless extreme sensitivity is required. In this instance and to eliminate the possible formation of carbides, pyrolytically coated graphite tubes are recommended.

28.5

Pipets, microlitre with disposable tips. Sizes may range from 1 µL to 100 µL, as required.

28.6

Data Storage and Reduction Devices, Computer- and Microprocessor-Controlled Devices, or Strip Chart Recorders shall be utilized for collection, storage, reduction, and problem recognition (such as drift, incomplete atomization, changes in sensitivity, etc.). Strip chart recorders shall have a full scale deflection time of 0.2 s or less to ensure accuracy.

28.7

Automatic Sampling is recommended if available.

29. Reagents and Materials

29.1

Copper Solution, Stock (1.0 mL = 1.0 mg Cu)—See 20.3.

29.2

Copper Solution, Intermediate (1.0 mL = 10 µg Cu)—See 20.4.

29.3

Copper Solution, Standard (1.0 mL = 0.10 µg Cu)—Dilute 10.0 mL of copper intermediate solution (29.2) and 1 mL of HNO_3 (sp gr 1.42) to 1 L with water. This standard is used to prepare working standards at the time of the analysis.

29.4

Nitric Acid (sp gr 1.42)—Concentrated nitric acid (HNO_3). (See Note 5.)

29.5

Argon, standard, welders grade, commercially available. Nitrogen may also be used if recommended by the instrument manufacturer.

30. Standardization

30.1

Initially, set the instrument according to the manufacturer's specifications. Follow the general instructions as provided in Practice D 3919.

31. Procedure

31.1

Clean all glassware to be used for preparation of standard solutions or in the digestion step, or both, by rinsing first with HNO_3 (1+1) and then with water. Alternatively, soaking the glassware overnight in HNO_3 (1+1) is useful for low levels.

31.2

Measure 100.0 mL of each standard and well-mixed sample into 125-mL beakers or flasks.

31.3

For total recoverable copper add HNO_3 (sp gr 1.42) to each standard and sample at a rate of 5 mL/L and proceed as directed in 31.4 through 31.6. If only dissolved copper is to be determined, filter the sample through a 0.45-µm membrane filter prior to acidification, add HNO_3 (sp gr 1.42) to each standard and sample at a rate of 5 mL/L, and proceed to 31.6.

31.4

Heat the samples at 95°C on a steam bath or hotplate in a well-ventilated fume hood until the volume has been reduced to 15 to 20 mL making certain that the samples do not boil. (See Note 7.)

31.5

Cool and filter the sample through a suitable filter (such as fine-textured, acid-washed, ashless paper) into a 100-mL volumetric flask. Wash the filter paper 2 or 3 times with water and bring to volume (see Note 16). The acid concentration at this point should be 0.5 % HNO_3.

Note 16—If suspended material is not present, this filtration may be omitted, but the sample must still be diluted to 100 mL.

31.6

Inject a measured aliquot of sample into the furnace device following the directions as provided by the particular instrument manufacturer. Refer to Practice D 3919.

TABLE 3 Determination of Bias and Overall Precision for Test Method C

Amount Added, µg Cu/L	Amount Found, µg Cu/L	S_T	± Bias	Bias, ± %	Statistically Significant, 95 % Confidence Level
Reagent Water					
32	31.3	4.54	−0.7	−2.2	No
11	11.7	1.33	+0.7	+6.4	No
5	5.6	1.65	+0.6	+12.0	No
Waters of Choice					
32	36.3	9.15	+4.3	+13.4	No
11	12.0	2.57	+1.0	+9.1	No
5	9.0	6.96	+4.0	+80.0	No

32. Calculation

32.1

Determine the concentration of copper in each sample by referring to Practice D 3919.

33. Precision and Bias[5]

33.1

The precision and bias of this test method were tested in reagent water by 16 laboratories. Thirteen laboratories also tested this test method in either boiler blowdown water, lake water, tap water, filtered tap water, condensate, well water, or production plant process waters as a water of choice. One laboratory reported data for two operators. Although multiple injections may have been made, the report sheets provided allowed only for reporting single values. Thus, no single operator precision data can be calculated. Two sets of laboratory data were rejected from both the reagent water series and the water of choice series because of either the laboratory ranking test or the individual outlier test. Bias data and overall precision data are given in Table 3.

33.2

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

34. Keywords

34.1

atomic absorption; chelation; copper; flame; graphite furnace; water

[5] Supporting data are available from ASTM Headquarters. Request RR: D19-1098.

APPENDIX

X1. RATIONALE FOR DISCONTINUATION OF TEST METHODS

(Nonmandatory Information)

X1.1

Colorimetric Test Methods for Determination of Copper in Water:

X1.1.1

These test methods were discontinued in 1988. They were last published in their entirety in the 1988 *Annual Book of ASTM Standards*, Vol 11.01.

X1.1.2

Former Test Method A, Necuproine (for concentrations of copper in the range from 0.05 to 5 mg/L):

X1.1.2.1

This test method is applicable to the determination of copper in water and waste water containing 0.05 mg/L of copper or more.

X1.1.2.2

a. This test method is based on the measurement of the intensity of the yellow color of the cuprous complex of 2,9-dimethyl-1, 10-phenanthroline (neocuproine). Full development of the color takes place over the pH range from 2.3 to 9.0. However, a buffer solution is used to produce an aqueous phase with a pH of 4.0 to 6.0.
b. The copper is reduced with hydroxylamine hydrochloride and the pH of the solution is adjusted with a sodium citrate solution. The cuprous ion is then reacted with 2,9-dimethyl-1, 10-phenanthroline and the yellow complex extracted with chloroform. Any of the usual photometric or visual methods may be used for measuring or comparing the color. The test method follows Beer's law up to a concentration of 5 mg/L of copper. The maximum absorption occurs at 457 nm.

X1.1.3

Former Test Method B, Necuproine (for concentrations of copper in the range from 2 to 100 µg/L):

X1.1.3.1

This test method is applicable to the determination of copper in waters such as steam condensate and deionized water. It is specifically applicable to concentrations of copper from 2 to 1000 µg/L.

X1.1.3.2

This test method is the same as former Test Method A (for high-level neocuproine), except that a choice between chloroform and isoamyl alcohol is given as the organic solvent used for extraction. The maximum absorption occurs at 457 nm when chloroform is the extractant and at 454 nm when isoamyl alcohol is the extractant.

X1.1.4

Former Test Method C, Cuprethol (for concentrations of copper in the range from 0.05 to 4 mg/L):

X1.1.4.1

This test method is applicable to the determination of copper in water containing 0.05 mg/L of copper or more. Former Test Method C is preferred for relatively unpolluted waters since it does not involve an organic extraction step, and allows for a rapid determination.

X1.1.4.2

Cupric ions form a yellow-colored chelate with cuprethol, the trivial name for the reagent, bis(2-hydroxy-ethyl)-dithiocarbamate. The colored compound formed at a pH between 5 and 6 is soluble. The maximum absorption occurs at 435 nm and Beer's law is valid up to a copper concentration of 2 mg/L. Any of the usual photoelectric or visual methods may be used for measuring or comparing the color.

X1.1.5

These test methods were discontinued because there were insufficient laboratories interested in participating in a collaborative study to obtain the necessary precision and bias data as required by Practice D 2777.

Designation: D 2015 - 96

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

This standard is issued under the fixed designation D 2015; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

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

1. Scope

1.1

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

1.2

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

1.3

This standard does not purport to address the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. For specific hazard statements see Section 8.

1.4

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

2. Referenced Documents

2.1

ASTM Standards:

D 121	Terminology of Coal and Coke[2]
D 346	Practice for Collection and Preparation of Coke Samples for Laboratory Analysis[2]
D 1193	Specification for Reagent Water[3]
D 2013	Method of Preparing Coal Samples for Analysis[2]
D 3173	Test Method for Moisture in the Analysis Sample of Coal and Coke[2]
D 3177	Test Methods for Total Sulfur in the Analysis Sample of Coal and Coke[2]
D 3180	Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases[2]
D 4239	Test Method for Sulfur in the Analysis Sample of Coal and Coke Using High Temperature Tube Furnace Combustion Methods[2]
D 4621	Guide for Accountability and Quality Control in the Coal Analysis Laboratory[2]
E 1	Specification for ASTM Thermometers[4]
E 144	Practice for Safe Use of Oxygen Combustion Bombs[5]

3. Terminology

3.1

Definitions:

3.1.1

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

3.1.1.1

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

3.1.2

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

3.1.3

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

3.1.4

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

3.2

Descriptions of Terms Specific to This Standard:

3.2.1

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

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

3.2.2

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

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

4. Summary of Test Method

4.1

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

[1] This test method is under the jurisdiction of ASTM Committee D-5 on Coal and Coke and is the direct responsibility of Subcommittee D05.21 on Methods of Analysis.

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

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

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

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

TABLE 1 Calorific Value

1 Btu = 1055.06 J	1 Btu/lb = 2.326 J/g

[A] International tables calorie.

1 Calorie[A] = 4.1868 J	1.8 Btu/lb = 1.0 cal/g
[A] International tables calorie.	

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

5. Significance and Use

5.1

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

5.2

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

5.3

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

6. Apparatus and Facilities

6.1

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

6.2

Combustion Bomb, shall be constructed of materials that are not affected by the combustion process or products sufficiently to introduce measurable heat input or alteration of end products. The bomb must be designed so that all liquid combustion products can be completely recovered by washing the inner surfaces. There must be no gas leakage during a test. The bomb must be capable of withstanding a hydrostatic pressure test of 20 MPa (3000 psig) at room temperature without stressing any part beyond its elastic limit.

6.3

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

6.4

Calorimeter Vessel, shall be made of metal with a tarnish-resistant coating, and with all outer surfaces highly polished. Its size shall be such that the bomb will be completely immersed in water when the calorimeter is assembled. It shall have a device for stirring the water thoroughly and at a uniform rate, but with minimum heat, input. Continuous stirring for 10 min shall not raise the calorimeter temperature more than 0.01°C (0.02°F) starting with identical temperatures in the calorimeter, room, and jacket. The immersed portion of the stirrer shall be coupled to the outside through a material of low-heat conductivity.

6.5

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

6.6

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

6.6.1

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

6.6.2

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

6.6.3

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

6.7

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

6.8

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

6.9

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

6.10

Ignition Circuit, for ignitipn purposes shall provide 6 to 16 V alternating or direct current to the ignition wire. An ammeter or pilot light is required in the circuit to indicate when current is flowing. A step-down transformer, connected to an alternating current lighting 254 circuit or batteries, may be used.

6.11

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

6.12

Automated Controller and Temperature Measuring Accessories, may be used.

7. Reagents

7.1

Purity of Reagents—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[6] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2

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

7.3

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

7.4

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

7.5

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

7.6

Sodium Carbonate Standard Solution, (Na_2CO_3), should be dried for 24 h at 105°C. Dissolve 20.9 g in water and dilute to 1 L. One millilitre of this solution is equivalent to 10.0 Btu in the nitric acid ($HN0_3$) titration.

8. Hazards

8.1

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

8.2

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

8.3

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

8.4

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

8.5

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

8.6

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

8.7

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

8.8

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

9. Sample

9.1

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

9.2

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

9.3

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

10. Standardization

10.1

The calorimeter is standardized by combustion of benzoic acid.

10.2

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

10.3

Procedure:

10.3.1

Regulate the weights of the pellets of benzoic acid in each series to yield approximately the same temperature rise as that obtained with the coal tested in the same laboratory. The usual range of masses is 0.9 to 1.3 g. Weigh the pellet to the nearest 0.0001 g in the sample holder in which it is to be burned, and record the weight as the mass.

TABLE 2 Standard Deviations for Calorimeter Standardization[A]

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

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

10.3.2

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

10.3.3

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

10.3.4

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

10.3.5

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

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

10.3.6

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

10.3.7

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

10.3.8

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

10.4

Calculations:

10.4.1

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

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

where:

t	=	corrected temperature rise, °C or °F,
t_i	=	initial temperature reading at time of firing, °C or °F,
t_f	=	final temperature reading, °C or °F,
C_e	=	thermometer emergent stem correction, if required (see Note 5 and Annex A1.1.4), and
C_s	=	thermometer setting correction, if required (see Note 5 and Annex A1.1.3).

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

256

10.4.2

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

e_1	=	correction for the heat of formation of HNO_3, Btu. Each millilitre of standard Na_2CO_3 is equivalent to 10.0 Btu, and
e_2	=	correction for heat of combustion of firing wire, Btu (Note 6).
	=	0.41 Btu/mm or 2.6 Btu/mg for No. 34 B & S gage Chromel C wire.
	=	0.49 Btu/mm or 3.2 Btu/mg for No. 34 B & S gage iron wire.

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

10.4.3

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

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

where:

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

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

10.5

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

11. Restandardization

11.1

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

11.1.1

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

11.1.2

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

11.1.3

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

11.1.4

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

TABLE 3 Summary of Numerical Requirements

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

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

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

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

11.1.5

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

11.1.6

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

11.2

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

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

12.1

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

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

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

12.2

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

13. Calculation (Note 2)

13.1

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

13.2

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

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

e_2	=	correction for heat of combustion of ignition wire, Btu,
	=	0.41 Btu/mm or 2.6 Btu/mg for No. 34 B & S gage Chromel C wire,
	=	0.49 Btu/mm or 3.2 Btu/mg for No. 34 B & S gage iron wire, and
e_3	=	correction for difference between heat of formation of H_2SO_4 from the heat of formation of HNO_3, Btu,
	=	23.7 times percent of sulfur in sample times mass of sample, g.

14. Calorific Value (Note 10)

14.1

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

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

where:

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

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

14.2

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

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

where:

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

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

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

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

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

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

$$H_{ar} = 5.37$$

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

15. Report

15.1

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

15.2

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

15.3

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

16. Precision and Bias

16.1

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

16.1.1

Repeatability—The difference in absolute value between two consecutive test results, carried out on the same sample of 250-µm (No. 60) pulp, in the same laboratory, by the same operator, using the same apparatus, should not exceed the repeatability interval for more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the repeatability interval, there is reason to question one, or both, of the test results. The repeatability interval for this test method is 28 cal/g (50 Btu/lb) on a dry basis.

16.1.2

Repeatability—The difference in absolute value between test results, obtained in the same laboratory, by the same operator, using the same riffle, determined on a single test specimen of two separate 2.36-mm (No. 8) test units of coal reduced entirely to 250-µm (No. 60) and prepared from the same bulk sample should not exceed the repeatability limit for more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the repeatability limit, there is reason to question one, or both, of the test results. The repeatability limit for this test method on a dry basis is:

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

16.1.3

Reproducibility—The difference in absolute value of replicate determinations, carried out in different laboratories on representative 250-µm (No. 60) samples, prepared from the same bulk sample after the last stage of reduction, should not exceed the reproducibility interval for more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the reproducibility interval, there is reason to question one, or both, of the test results. The reproducibility interval for this test method is 56 cal/g (100 Btu/lb) on a dry basis.

16.1.4

Reproducibility—The difference in absolute value between test results obtained in different laboratories calculated as the average of determinations on single test specimens of two separate 2.36-mm (No. 8) test units of coal reduced entirely to 250-µm (No. 60) and prepared from the same bulk sample, should not exceed the reproducibility limit for more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the reproducibility limit, there is reason to question one, or both, of the test results. The reproducibility limit for this test method on a dry basis is:

Bituminous coals	60 cal/g (107 Btu/lb)

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

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

258 Note 7—Supporting data for 2.36-mm (No. 8) coal has been filed at ASTM Headquarters and may be obtained by requesting RR:D05-1015.

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

16.2

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

ANNEX
(Mandatory Information)

A1. THERMOMETRIC CORRECTIONS

A1.1 Thermometer Corrections

A 1.1.1

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

A 1.1.2

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

A 1.1.3

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

A 1.1.4

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

A 1.1.4.1

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

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

where:

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

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

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

A 1.1.4.2

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

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

where:

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

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

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

259 **APPENDIXES**
(Nonmandatory Information)

X1. THERMOCHEMICAL CORRECTIONS

X1.1

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

X1.1.1

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

X1.2

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

X1.2.1

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

X1.3

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

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

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

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

260

X2. REPORTING RESULTS IN OTHER UNITS

X2.1

Reporting Results in Joules per Gram:

X2.1.1

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

X2.1.2

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

X2.1.3

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

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

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

E'	=	energy equivalent in units of joules per temperature unit,
H'	=	the heat of combustion of reference material in units of joules per gram weight in air (J/g from the certificate for the NIST benzoic acid), and
e_1' and e_3'	=	corrections in units of joules, (see Table X2.1).

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

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

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

Q_v (gross)	=	gross calorific value with units of joules per gram (weight in air),
E'	=	energy equivalent units, of joules per temperature unit, and
e_1', e_2', and e_3'	=	corrections in units of joules (see Table X2.1).

X2.1.5

Precision:

X2.1.5.1

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

X2.1.5.2

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

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

Correction	Multiplication Factor	Multiply By
$e_1'(HNO_3)$	20 J/mL	mL of 0.34 *N* Na_2CO_3
e_3' (H_2SO_4)	55.2 J/cgS	percent of sulfur in sample times *mass* of sample in grams
e_2' (fuse wire) or	0.95 J/mm	length (mm) of No. 34 B & S gage Chromel C wire
e_2' (fuse wire)	1.14 J/mm	length (mm) of No. 34 B & S gage iron wire
e_2' (fuse wire) or	6.0 J/mg	*mass* (mg) of Chromel C wire
e_2' (fuse wire)	7.4 J/mg	mass (mg) of iron wire
[A] To be used in Eqs X2.1 and X2.2 only.		

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