This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

Designation: D1688 – 17

Standard Test Methods for Copper in Water[1]

This standard is issued under the fixed designation D1688; 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 U.S. Department of Defense.

1. Scope*

1.1 These test methods cover the determination of copper in water by atomic absorption spectrophotometry. Section 34 on Quality Control pertains to these test methods. Three test methods are included as follows:

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

1.2 Either dissolved or total recoverable copper may be determined. Determination of dissolved copper requires filtration through a 0.45-µm (11.10) 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 standard. The values given in parentheses are mathematical conversion to inch-pound units that are provided for information only and are not considered standard.

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

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see 11.3, 11.9.1, 20.10, and 22.11.

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D858 Test Methods for Manganese in Water
D1066 Practice for Sampling Steam
D1068 Test Methods for Iron in Water
D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D1687 Test Methods for Chromium in Water
D1691 Test Methods for Zinc in Water
D1886 Test Methods for Nickel in Water
D1976 Test Method for Elements in Water by Inductively-Coupled Argon Plasma Atomic Emission Spectroscopy
D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
D3370 Practices for Sampling Water from Closed Conduits
D3557 Test Methods for Cadmium in Water
D3558 Test Methods for Cobalt in Water
D3559 Test Methods for Lead in Water
D3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry
D4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents
D5673 Test Method for Elements in Water by Inductively Coupled Plasma—Mass Spectrometry
D5810 Guide for Spiking into Aqueous Samples
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this standard, refer to Terminology D1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *continuing calibration blank, n*—a solution containing no analytes (of interest) which is used to verify blank response and freedom from carryover.

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

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[2] 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**

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3.2.2 *continuing calibration verification, n*—a solution (or set of solutions) of known concentration used to verify freedom from excessive instrumental drift; the concentration is to cover the range of calibration curve.

3.2.3 *total recoverable copper, n*—a descriptive term relating to the forms of copper recovered in the acid-digestion procedure specified in this test standard.

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.

4.4 ICP-MS or ICP-AES may also be appropriate but at a higher instrument cost. See Test Methods D5673 and D1976.

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 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 D1193, 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 D1066 and D3370, 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 (11.10) membrane filter before acidification. The holding time for samples may be calculated in accordance with Practice D4841.

NOTE 1—Alternatively, the pH may be adjusted in the laboratory within 14 days of collection. However, acid must be added at least 24 hours before analysis to dissolve any metals that adsorb to the container walls. This could reduce hazards of working with acids in the field when appropriate.

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 D3557), chromium (Test Methods D1687), cobalt (Test Methods D3558), iron (Test Methods D1068), lead (Test Methods D3559), manganese (Test Methods D858), nickel (Test Methods D1886), and zinc (Test Methods D1691).

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 2—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.

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

NOTE 3—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 *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. A purchased copper stock solution of appropriate known purity is also acceptable.

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

(**Warning—**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 5—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 *Sulfuric Acid*—Concentrated sulfuric acid (H_2SO_4).

11.7 *Sulfuric Acid (1 + 1)*—Cautiously, and with constant stirring and cooling, add 1 volume of concentrated sulfuric acid (H_2SO_4, sp gr 1.84) to 1 volume of water.

11.8 *Oxidant:*

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

11.9 *Fuel:*

11.9.1 *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 345 kPa (50 psi). (**Warning—**"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.)

11.10 *Filter Paper*—Purchase suitable filter paper. Typically the filter papers have a pore size of 0.45-µm membrane. Material such as fine-textured, acid-washed, ashless paper, or glass fiber paper are acceptable. The user must first ascertain that the filter paper is of sufficient purity to use without adversely affecting the bias and precision of the test method.

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 (11.5). Prepare the standards each time the test is to be performed or as determined by Practice D4841.

12.2 When determining total recoverable copper add 0.5 mL of HNO_3 (sp gr 1.42) (11.4)and proceed as directed in 13.3 – 13.5. When determining dissolved copper proceed with 13.6.

12.3 Aspirate the blank and standards and record the instrument readings. Aspirate HNO_3 (1 + 499) (11.5) between each standard.

12.4 Read directly in concentration if this capability is provided with the instrument or prepare an analytical curve by plotting the absorbance versus standard concentration for each standard.

13. Procedure

13.1 An effective way to clean all glassware to be used for preparation of standard solutions or in the digestion step, or both, is by soaking the glassware overnight with HNO_3 (1 + 1) and then rinse with reagent.

13.2 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 13.6.

13.3 Add 5 mL of HCl (sp gr 1.19) (11.3) to each sample.

13.4 Heat the samples (between 65°C and 95°C) on a steam bath or hotplate below boiling 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.

NOTE 8—Many laboratories have found block digestion systems a useful way to digest samples for trace metals analysis. Systems typically consist of either a metal or graphite block with wells to hold digestion tubes. The block temperature controller must be able to maintain uniformity of temperature across all positions of the block. The digestion block must be capable of maintaining a temperature between 65°C and 95°C. For trace metals analysis, the digestion tubes should be constructed of polypropylene and have a volume accuracy of at least 0.5 %. All lots of tubes should come with a certificate of analysis to demonstrate suitability for their intended purpose.

13.5 Cool and filter (11.10) 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.

13.6 Aspirate each filtered and acidified sample and determine its absorbance or concentration at 324.7 nm. Aspirate HNO_3 (1 + 499) (11.5) between each sample.

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
2.0	2.02	+1.0	no
0.4	0.41	+2.5	no

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 and bias for this test method conform to Practice D2777 – 77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of Practice D2777 – 13, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

15.4 *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:

$$S_O = 0.020X + 0.035 \quad (1)$$

$$S_T = 0.052X + 0.123 \quad (2)$$

In water or waste water:

$$S_O = 0.016X + 0.033 \quad (3)$$

$$S_T = 0.060X + 0.039 \quad (4)$$

where:

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

15.5 *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 D3557), cobalt (Test Methods D3558), iron (Test Methods D1068), lead (Test Methods D3559), nickel (Test Methods D1886), and zinc (Test Methods D1691).

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)—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. A purchased copper stock solution of appropriate known purity is acceptable.

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.

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[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1037. Contact ASTM Customer Service at service@astm.org.

20.6 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl) (see Note 5).

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 5).

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. (**Warning—**All components of this reagent are highly toxic. Carbon disulfide is also highly flammable. 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 *Sulfuric Acid*—Concentrated sulfuric acid (H_2SO_4).

20.13 *Sulfuric Acid (1 + 1)*—Cautiously, and with constant stirring and cooling, add 1 volume of concentrated sulfuric acid (H_2SO_4, sp gr 1.84) to 1 volume of water.

20.14 *Oxidant*—See 11.8.

20.15 *Fuel*—See 11.9.

20.16 *Filter Paper*—See 11.10.

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) (20.9) and proceed as directed in 22.3 – 22.16. When determining dissolved copper, use 250-mL separatory funnels and proceed as directed in 22.6 – 22.16.

21.3 Read directly in concentration if this capability is provided with the instrument or construct an analytical curve by plotting the absorbances of standards versus concentration of copper.

22. Procedure

22.1 An effective way to clean all glassware to be used for preparation of standard solutions or in the digestion step, or both, is by soaking the glassware overnight with HNO_3 (1 + 1) and then rinse with reagent.

22.2 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 22.6.

22.3 Add 5 mL of HCl (sp gr 1.19) (20.6) to each sample.

22.4 Heat the samples (between 65°C and 95°C) on a steam bath or hotplate below boiling 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.

NOTE 11—Many laboratories have found block digestion systems a useful way to digest samples for trace metals analysis. Systems typically consist of either a metal or graphite block with wells to hold digestion tubes. The block temperature controller must be able to maintain uniformity of temperature across all positions of the block. The digestion block must be capable of maintaining a temperature between 65°C and 95°C. For trace metals analysis, the digestion tubes should be constructed of polypropylene and have a volume accuracy of at least 0.5 %. All lots of tubes should come with a certificate of analysis to demonstrate suitability for their intended purpose.

22.5 Cool and filter the samples through a suitable filter (20.16), 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.

22.6 Add 2 drops of bromphenol blue indicator solution (20.1) and mix.

22.7 Adjust the pH by addition of NaOH (100 g/L) (20.11) solution until a blue color persists. Add HCl (1 + 49) (20.8) by drops until the blue color just disappears; then add 2.5 mL of HCl (1 + 49) (20.8) in excess. The pH at this point should be 2.3.

NOTE 12—The pH adjustment in 22.7 may be made with a pH meter instead of using an indicator.

22.8 Add 10 mL of pyrrolidine dithiocarbamic acid-chloroform reagent and shake vigorously for 2 min. (**Warning—**See 20.10.)

22.9 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.

22.10 Repeat the extraction with 10 mL of $CHCl_3$ (20.2) and drain the $CHCl_3$ layer into the same beaker.

NOTE 13—If color still remains in the $CHCl_3$extract, reextract the aqueous phase until the $CHCl_3$ layer is colorless.

22.11 Place the beaker on a hot plate set at low heat (between 65°C and 95°C) or on a steam bath below boiling, and evaporate to near dryness. Remove beaker from heat and allow residual solvent to evaporate without further heating. (**Warning—**Perform in a well-ventilated hood.)

NOTE 14—Many laboratories have found block digestion systems a useful way to digest samples for trace metals analysis. Systems typically consist of either a metal or graphite block with wells to hold digestion tubes. The block temperature controller must be able to maintain uniformity of temperature across all positions of the block. The digestion block must be capable of maintaining a temperature between 65°C and 95°C. For trace metals analysis, the digestion tubes should be constructed of polypropylene and have a volume accuracy of at least 0.5 %. All lots of tubes should come with a certificate of analysis to demonstrate suitability for their intended purpose.

22.12 Hold the beaker at a 45° angle, and slowly add dropwise 2 mL of HNO_3 (sp gr 1.42) (20.9), rotating the beaker to effect thorough contact of the acid with the residue.

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

22.13 Place the beaker on a hotplate set at low heat (between 65°C and 95°C) or on a steam bath below boiling and evaporate to near dryness. Remove beaker from heat and allow residual solvent to evaporate without further heating.

22.14 Add 2 mL of HCl (1 + 2) (22.8) to the beaker, and heat, while swirling, for 1 min.

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

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

23. Calculation

23.1 If instrument readout is not in concentration, 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 5:

$$\text{Copper, } \mu g/L = \frac{1000 \times B}{A} \quad (5)$$

where:

1000 = 1000 mL / L,
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 and bias for this test method conform to Practice D2777 – 77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of Practice D2777 – 13, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

24.4 *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:

$$S_O = 0.119X + 9 \quad (6)$$

$$S_T = 0.247X + 47 \quad (7)$$

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

In water or brine:

$$S_O = 27 \quad (8)$$

$$S_T = 0.270X + 42 \quad (9)$$

where:

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

24.5 *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 D3919.

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 D3919.

28. Apparatus

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

NOTE 15—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 16—The manufacturer's instructions should be followed for all instrumental parameters.

28.2 *Copper Hollow Cathode Lamp,* a single element lamp is preferred, but multi-element 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. 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.

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 11.9.1.)

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

29.6 *Filter Paper*—See 11.10.

30. Standardization

30.1 Initially, set the instrument according to the manufacturer's specifications. Follow the general instructions as provided in Practice D3919.

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, 31.5, and31.6. 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 (between 65°C and 95°C) on a steam bath or hot plate below boiling 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.)

NOTE 17—Many laboratories have found block digestion systems a useful way to digest samples for trace metals analysis. Systems typically consist of either a metal or graphite block with wells to hold digestion tubes. The block temperature controller must be able to maintain uniformity of temperature of across all positions of the block. The digestion block must be capable of maintaining a temperature between 65°C and 95°C. For trace metals analysis, the digestion tubes should be constructed of polypropylene and have a volume accuracy of at least 0.5 %. All lots of tubes should come with a certificate of analysis to demonstrate suitability for their intended purpose.

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 18). The acid concentration at this point should be 0.5 % HNO_3.

NOTE 18—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 D3919.

32. Calculation

32.1 Determine the concentration of copper in each sample by referring to Practice D3919.

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

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[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1098. Contact ASTM Customer Service at service@astm.org.

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

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.

33.3 Precision and bias for this test method conform to Practice D2777 – 77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of Practice D2777 – 13, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

34. Quality Control (QC)

34.1 To ensure that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing copper.

34.2 *Calibration and Calibration Verification:*

34.2.1 Analyze at least three working standards containing concentrations of copper that bracket the expected sample concentration prior to analysis of samples to calibrate the instrument. The calibration correlation coefficient shall be equal to or greater than 0.990.

34.2.2 Verify instrument calibration after standardization by analyzing a standard at the concentration of one of the calibration standards. The absorbance shall fall within 4 % of the absorbance from the calibration. Alternately, the concentration of a mid-range standard should fall within ±15 % of the known concentration. Analyze a calibration blank to verify system cleanliness. The blank result should be less than the method reporting limit.

34.2.3 If calibration cannot be verified, recalibrate the instrument.

34.2.4 It is recommended to analyze a continuing calibration blank (CCB) and continuing calibration verification (CCV) at a 10 % frequency. The CCB result should be less than the method reporting limit. The results should fall within the expected precision of the method or ±15 % of the known concentration.

34.3 *Initial Demonstration of Laboratory Capability:*

34.3.1 If a laboratory has not performed the test before, or if there has been a major change in the measurement system, for example, new analyst, new instrument, etc., a precision and bias study must be performed to demonstrate laboratory capability.

34.3.2 Analyze seven replicates of a standard solution prepared from an independent reference material containing a mid-range concentration of copper. The matrix and chemistry of the solution should be equivalent to the solution used in the collaborative study. Each replicate must be taken through the complete analytical test method including any sample preservation and pretreatment steps.

34.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in Tables 1-3. This study should be repeated until the recoveries are within the limits given in Tables 1-3. If a concentration other than the recommended concentration is used, refer to Practice D5847 for information on applying the F test and t test in evaluating the acceptability of the mean and standard deviation.

34.4 *Laboratory Control Sample (LCS):*

34.4.1 To ensure that the test method is in control, prepare and analyze a LCS containing a mid-range concentration of copper with each batch (laboratory-defined or 20 samples). The laboratory control samples for a large batch should cover the analytical range when possible. It is recommended, but not required to use a second source, if possible and practical for the LCS. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for the LCS shall fall within ±15 % of the known concentration.

34.4.2 If the result is not within these limits, analysis of samples is halted until the problem is corrected, and either all the samples in the batch must be reanalyzed, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

34.5 *Method Blank:*

34.5.1 Analyze a reagent water test blank with each laboratory-defined batch. The concentration of copper found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of copper is found above this level, analysis of samples is halted until the contamination is eliminated, and a blank shows no contamination at or above this level, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

34.6 *Matrix Spike (MS):*

34.6.1 To check for interferences in the specific matrix being tested, perform a MS on at least one sample from each laboratory-defined batch by spiking an aliquot of the sample with a known concentration of copper and taking it through the analytical method.

34.6.2 The spike concentration plus the background concentration of copper must not exceed the high calibration standard. The spike must produce a concentration in the spiked sample that is 2 to 5 times the analyte concentration in the unspiked sample, or 10 to 50 times the detection limit of the test method, whichever is greater.

34.6.3 Calculate the percent recovery of the spike (P) using the following formula:

$$P = \frac{100\left[A\left(V_s + V\right) - B\ V_s\right]}{C\ V} \qquad (10)$$

where:

A = analyte known concentration (µg/L) in spiked sample,
B = analyte known concentration (µg/L) in unspiked sample,
C = known concentration (µg/L) of analyte in spiking solution,
V = volume (mL) of sample used, and
V = volume (mL) of spiking solution added.

34.6.4 The percent recovery of the spike shall fall within the limits, based on analyte concentration, listed in Guide D5810, Table 1. If the percent recovery is not within these limits, a matrix interference may be present in the sample selected for spiking. Under these circumstances, one of the following remedies must be employed: the matrix interference must be removed, all samples in the batch must be analyzed by a test method not affected by the matrix interference, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

NOTE 19—Acceptable spike recoveries are dependent on the concentration of the component of interest. See Guide D5810 for additional information.

34.7 *Duplicate:*

34.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each laboratory-defined batch. If the concentration of the analyte is less than five times the detection limit for the analyte, a matrix spike duplicate (MSD) should be used.

34.7.2 Calculate the standard deviation of the duplicate values and compare to the precision in the collaborative study using an F test. Refer to 6.4.4 of Practice D5847 for information on applying the F test.

34.7.3 If the result exceeds the precision limit, the batch must be reanalyzed or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

34.8 *Independent Reference Material (IRM):*

34.8.1 In order to verify the quantitative value produced by the test method, analyze an IRM submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the reference material should be in the concentration mid-range for the method chosen. The value obtained must fall within the control limits established by the laboratory.

35. Keywords

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

APPENDIX

(Nonmandatory Information)

X1. RATIONALE FOR DISCONTINUATION OF TEST METHODS

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.

(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-hydroxyethyl)-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 D2777.

SUMMARY OF CHANGES

Committee D19 has identified the location of selected changes to this standard since the last issue (D1688 – 12) that may impact the use of this standard. (Approved June 1, 2017.)

(1) Revised 1.3 to update the SI statement.
(2) Revised Section 2 to include Test Methods D1976 and D5673.
(3) Revised Section 3 to correct format and add terms.
(4) Added 4.4 to inform the user of the possibility of using an ICP-MS or ICP-AES.
(5) Revised Note 1 to include information on adding acid.
(6) Revised Sections 11, 20, and 29 to include information on filter paper.
(7) Revised 12.1, 12.4, 28.6, 34.2.1, 34.2.2, 34.2.4, and 34.4.1.
(8) Revised Section 13 to include information on cleaning glassware.
(9) Revised 13.4, 22.4, 22.11, 22.13, and 31.4 and Note 8, Note 11, Note 14, and Note 17 to include information on the heating blocks.
(10) Added 22.1 to include information about cleaning glassware and renumbered subsequent sections.

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