



Designation: ~~D1688~~—~~12~~ **D1688** – 17

Standard Test Methods for Copper in Water¹

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 μ g/L	16 – 24
C—Atomic Absorption, Graphite Furnace	5 to 100 μ g/L	25 – 33

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1.2 Either dissolved or total recoverable copper may be determined. Determination of dissolved copper requires filtration through a 0.45- μ m (~~No. (11.10-325)~~) membrane filter at the time of collection. In-line membrane filtration is preferable.

1.3 The values stated in either SI units or inch-pound units are to be regarded separately as standard. The values stated in each system are mathematical conversions and may not be exact equivalents; therefore, each system shall be used independently of the other. 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 [Note 411.3](#), [Note 611.9.1](#), [Note 1020.10](#), and [Note 1622.11](#).

1.5 Three former photometric test methods were discontinued. Refer to [Appendix X1](#) for historical information.

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](#)

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

[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—Definitions:* For definitions of terms used in these test methods, refer to Terminology [D1129](#).

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.

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.

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.

6.2 Samples shall be preserved with nitric acid (HNO₃, 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- μ m (No. ~~(11.10 325)~~) 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 ~~if the sample is returned within 14 days.~~ 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.~~

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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.

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 Oxidant—See 11.8.~~

~~10.3 Fuel—See 11.9.~~

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 HNO₃ (sp gr 1.42) and 15 mL of water. Slowly add 4 mL of H₂SO₄ (1 + 1) and heat until SO₃ 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. ~~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.~~

(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 (HNO₃).

NOTE 5—If a high reagent blank is obtained, distill the HNO₃ or use a spectrograde acid.

11.5 *Nitric Acid* (1 + 499)—Add 1 volume of HNO₃ (sp gr 1.42) to 499 volumes of water.

11.6 *Sulfuric Acid*—Concentrated sulfuric acid (H₂SO₄).

11.7 *Sulfuric Acid* (1 + 1)—Cautiously, and with constant stirring and cooling, add 1 volume of concentrated sulfuric acid (H₂SO₄, 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.)

~~NOTE 6—**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.~~

11.10 *Filter Paper*—Purchase suitable filter paper. Typically the filter papers have a pore size of 0.45- μ m 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 HNO₃ (1 + 499) (11.5). Prepare the standards each time the test is to be ~~performed~~ performed or as determined by Practice D4841.

12.2 When determining total recoverable copper add 0.5 mL of HNO₃ (sp gr 1.42) (11.4) and proceed as directed in ~~13.2~~ 13.3 – ~~13.4~~ 13.5. When determining dissolved copper proceed with ~~13.5~~ 13.6.

12.3 Aspirate the blank and standards and record the instrument readings. Aspirate HNO₃ (1 + 499) (11.5) between each standard.

12.4 ~~Prepare~~ 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. ~~Alternatively, read directly in concentration from the instrument.~~

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 HNO₃ (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 ~~13.5~~ 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%~~ 0.5%. All lots of tubes should come with a certificate of analysis to demonstrate suitability for their intended purpose.

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
4.0	4.11	+2.75	no
2.0	2.06	+3.0	no
2.0	2.06	+3.0	no
0.4	0.46	+15.0	yes
0.4	0.46	+15.0	yes
Water or Waste Water			
4.0	4.03	+0.75	no
4.0	4.03	+0.75	no
2.0	2.02	+1.0	no
2.0	2.02	+1.0	no
0.4	0.44	+2.5	no
0.4	0.41	+2.5	no

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 HNO₃ (1 + 499) (11.5) between each sample.

14. Calculation

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

15. Precision and Bias⁴

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 D2777-08, – 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.

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.

~~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.~~

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* (CHCl₃).

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 HNO₃ (sp gr 1.42) and 15 mL of water. Slowly add 4 mL of H₂SO₄ (1 + 1) and heat until SO₃ 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 HNO₃ (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 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 (HNO₃) (see Note 5).

20.10 *Pyrrolidine Dithiocarbamic Acid-Chloroform Reagent*—Add 36 mL of pyrrolidine to 1 L of CHCl₃. Cool the solution and add 30 mL of CS₂ in small portions, swirling between additions. Dilute to 2 L with CHCl₃. 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.)

~~NOTE 10—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 *Sulfuric Acid*—Concentrated sulfuric acid (H₂SO₄).

20.13 *Sulfuric Acid* (1 + 1)—Cautiously, and with constant stirring and cooling, add 1 volume of concentrated sulfuric acid (H₂SO₄, sp gr 1.84) to 1 volume of water.