



Designation: D 1688 – 02

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 (ε) indicates an editorial change since the last revision or reapproval.

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

1. Scope

1.1 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	7-15
Test Method B—Atomic Absorption, Chelation-Extraction	50 to 500 µg/L	16-24
Test Method 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 (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 [Note 3](#), [Note 5](#), [Note 8](#), and [Note 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

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 *Annual Book of ASTM Standards*, Vol 11.01.

- [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
- [D 4841](#) Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents ²
- [D 5810](#) Guide for Spiking into Aqueous Samples ²
- [D 5847](#) Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis ³

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 (CuFeS₂). 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

³ *Annual Book of ASTM Standards*, Vol 11.02.



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.⁴ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

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 (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-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 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 stock solution of adequate 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 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 (HNO₃).

NOTE 4—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.

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



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 HNO₃ (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 HNO₃ (sp gr 1.42) and proceed as directed in 13.2–13.4. When determining dissolved copper proceed with 13.5.

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

12.4 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 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 HNO₃(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).

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

15. Precision and Bias ⁵

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 D 2777-77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of Practice D 2777-98, 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:

$$S_O = 0.020X + 0.035$$

$$S_T = 0.052X + 0.123$$

In water or waste water:

$$S_O = 0.016X + 0.033$$

$$S_T = 0.060X + 0.039$$

where:

S_O = single-operator precision,

S_T = overall precision, and

X = determined concentration of copper, mg/L.

15.5 *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.

⁵ Supporting data are available from ASTM International Headquarters. Request RR: D19-1037.

