



Designation: D 1691 – 02

Standard Test Methods for Zinc in Water¹

This standard is issued under the fixed designation D 1691; 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 approval. 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 zinc in water. Two test methods are given as follows:

Test Method	Concentration	Sections
Test Method A—Atomic Absorption, Direct	0.05 to 2 mg/L	8-16
Test Method B—Atomic Absorption, Chelation-Extraction	20 to 200 μ g/L	17-25

1.2 Either dissolved or total recoverable zinc may be determined.

1.3 These test methods have been used successfully with reagent grade water. See the specific test method for applicability to other matrices. It is the user's responsibility to assure the validity of these test methods in other matrices.

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 Section 6 and Note 5, Note 8, and Note 13.

1.5 Two former colorimetric 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 Water²
- D 1066 Practice for Sampling Steam²
- D 1068 Test Methods for Iron in Water²
- D 1129 Terminology Relating to Water²
- D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits²
- D 1193 Specification for Reagent Water²
- D 1687 Test Methods for Chromium in Water²
- D 1688 Test Methods for Copper in Water²

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.

Current edition approved March 10, 2002. Published May 2002. Originally published as D 1691 – 59 T. Last previous edition D 1691 – 95.

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

D 1886 Test Methods for Nickel in Water²

D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D19 on Water²

D 3370 Practices for Sampling Water from Closed Conduits²

D 3557 Test Methods for Cadmium in Water²

D 3558 Test Methods for Cobalt in Water²

D 3559 Test Methods for Lead in Water²

D 4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents²

D 5810 Guide for Spiking into Aqueous Samples²

D 5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis³

3. Terminology

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

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *total recoverable zinc*—an arbitrary analytical term relating to the recoverable form of zinc that is determinable by the digestion method which is included in the Procedure.

4. Significance and Use

4.1 Zinc is an essential and beneficial element in body growth. Concentrations above 5 mg/L can cause a bitter astringent taste and opalescence in alkaline waters. The zinc concentration of U.S. drinking waters varies between 0.06 and 7.0 mg/L with a mean of 1.33 mg/L. Zinc most commonly enters the domestic water supply from deterioration of galvanized iron and dezincification of brass. Zinc in water also may result from industrial water pollution.⁴

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

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

⁴ "Standard Methods for the Examination of Water and Wastewater," 16th edition, 1985, APHA, AWWA-WPCF.

specifications are available.⁵ 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 adversely affecting the bias and precision of the test method. Type II water was specified at the time of round-robin testing of this test method.

6. Hazards

6.1 Although zinc is nontoxic to man, these test methods require the use of certain other toxic and hazardous reagents and materials. Each should be used with care and exerting proper precautions.

7. Sampling

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

7.2 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 of HNO₃. If only dissolved zinc is to be determined, the sample, shall be filtered through a 0.45- μ m membrane filter before acidification. The holding time for samples may be calculated in accordance with Practice **D 4841**.

TEST METHOD A—ATOMIC ABSORPTION, DIRECT

8. Scope

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

8.2 This test method is applicable in the range from 0.05 to 2.0 mg/L of zinc. The range may be extended to concentrations greater than 2.0 mg/L by dilution of the sample.

8.3 This test method has been used successfully with reagent grade water, river water, wastewater, ground water, tap water, lake water, refinery effluent. The information on precision and bias may not apply to other waters.

9. Summary of Test Method

9.1 Zinc is determined by atomic absorption spectrophotometry. Dissolved zinc is determined by aspirating a portion of the filtered and preserved sample directly with no pretreatment. Total recoverable zinc is determined by aspirating the sample following hydrochloric-nitric acid digestion and filtration. The same digestion procedure is used to determine total recoverable cadmium (Test Methods **D 3557**), chromium, (Test Methods **D 1687**), cobalt (Test Methods **D 3558**), copper (Test

Methods **D 1688**), iron (Test Methods **D 1068**), lead (Test Methods **D 3559**), manganese (Test Methods **D 858**), and nickel (Test Methods **D 1886**).

10. Interferences

10.1 Sodium, potassium, sulfate, and chloride (9000 mg/L each), calcium and magnesium (4000 mg/L each), nitrate (2000 mg/L), and cadmium, lead, copper, nickel, cobalt, and chromium (10 mg/L each) do not interfere.

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

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

11. Apparatus

11.1 *Atomic Absorption Spectrophotometer*, for use at 213.9 nm.

NOTE 2—The manufacturer's instructions should be followed for all instrumental parameters. Wavelengths other than 213.9 nm may be used if they have been determined to be equally suitable.

11.1.1 *Zinc Light Source*—Hollow-cathode lamps or electrodeless discharge lamps have been found satisfactory.

11.2 *Oxidant*—See **12.6**.

11.3 *Fuel*—See **12.7**.

11.4 *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.

12. Reagents and Materials

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

NOTE 3—If the reagent blank concentration is greater than the method detection limit, 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 in the preparation of a reagent or in the procedure, use double the amount specified if a distilled acid is used.

12.2 *Nitric Acid (sp gr 1.42)*—Concentrated nitric acid (HNO₃).

NOTE 4—If the reagent blank concentration is greater than the method detection limit, distill the HNO₃ or use a trace metal grade acid.

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

12.4 *Zinc Solution, Stock (1 mL = 1.0 mg Zn)*—Dissolve 1.245 g of zinc oxide (ZnO) in a mixture of 10 mL of HNO₃(sp gr 1.42) and 10 mL of water. Dilute to 1 L with water. A purchased stock solution of appropriate purity is also acceptable.

12.5 *Zinc Solution, Standard (1 mL = 0.1 mg Zn)*—Dilute 100.0 mL of the zinc stock solution and 1 mL of HNO₃(sp gr 1.42) to 1 L with water.

12.6 *Oxidant*:

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

⁵ *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.

12.7 Fuel:

12.7.1 *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—**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.

13. Standardization

13.1 Prepare 100 mL each of a blank and at least four standard solutions to bracket the expected zinc concentration range of the samples to be analyzed by diluting the standard zinc solution (12.5) with HNO₃(1 +499). Prepare the standards each time the test is to be performed and select so as to give zero, middle, and maximum points for an analytical curve.

13.2 When determining total recoverable zinc, add 0.5 mL of HNO₃(sp gr 1.42) to each blank and standard solution and proceed as directed in 14.2-14.4. After the digestion of the blank and standard solutions has been completed in 14.4, return to 13.3 to complete the standardization for total recoverable determinations. To determine dissolved zinc, proceed with 13.3.

13.3 Aspirate the blank and standards, and record the absorbance of each at 213.9 nm. Aspirate HNO₃(1 +499) between each standard.

13.4 Prepare an analytical curve by plotting the absorbance versus concentration for each standard. Alternatively, read directly in concentration from the instrument.

14. Procedure

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

NOTE 6—If only dissolved zinc is to be determined, start with 14.5.

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

14.3 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—For samples with appreciable amounts of suspended matter or dissolved solids, the amount of reduction in the volume is left to the discretion of the analyst.

14.4 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.

14.5 Aspirate each filtered and acidified sample and standard and determine its absorbance or concentration at 213.9 nm. Atomize HNO₃(1 +499) between each sample and standard.

15. Calculation

15.1 Calculate the concentration of zinc in each sample, in milligrams per litre, using the analytical curve prepared in 13.4 or read directly in concentration.

TABLE 1 Determination of Precision and Bias for Zinc by Atomic Absorption, Direct

Amount Added, mg/L	Amount Found, mg/L	S _T , mg/L	S _O , mg/L	%, Bias	Statistically Significant, 95 % Level
Reagent Water					
0.16	0.172	0.052	0.038	+ 7.5	No
0.80	0.798	0.068	0.034	-0.2	No
1.50	1.459	0.107	0.041	-2.7	Yes
Water of Choice					
0.16	0.172	0.041	0.033	+ 7.5	Yes
0.80	0.796	0.081	0.047	-0.5	No
1.50	1.446	0.098	0.060	-3.6	Yes

16. Precision and Bias ⁶

16.1 The overall precision and bias of this test method, within its designated range, is shown in Table 1.

16.2 These collaborative test data were obtained from eleven laboratories on reagent grade, river, lake, ground and effluent waters. For other waters these data may not apply.

16.3 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.

TEST METHOD B—ATOMIC ABSORPTION, CHELATION-EXTRACTION

17. Scope

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

17.2 This test method is applicable in the range from 20 to 200 µg/L of zinc.

17.3 This test method has been used successfully with reagent grade water, river water, wastewater, ground water, tap water, lake water, refinery effluent. The information on precision and bias may not apply to other waters.

18. Summary of Test Method

18.1 Zinc 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. The resulting solution is then aspirated into the air-acetylene flame of the spectrophotometer. The digestion procedure summarized in 9.1 is used when determining total recoverable zinc. The same chelation-extraction procedure is used to determine total recoverable cadmium (Test Methods D 3557), cobalt (Test Methods D 3558), copper (Test Methods D 1688), iron (Test Methods D 1068), lead (Test Methods D 3559), and nickel (Test Methods D 1886).

⁶ Supporting data are available from ASTM International Headquarters, 100 Barr Harbor Dr., West Conshohocken, PA 19428-2959. Request RR: D19-1039.