



Designation: **D1691—12 D1691 – 17**

Standard Test Methods for Zinc in Water¹

This standard is issued under the fixed designation D1691; 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 reappraisal. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reappraisal.

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 zinc in water. Section 26 on Quality Control pertains to these test methods. Two test methods are given as follows:

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

Test Method	Concentration Range	Sections
A—Atomic Absorption, Direct	0.05 to 2 mg/L	8 – 16
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 The values stated in either SI units or inch-pound units are to be regarded separately as standard. The values stated given 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.

1.5 *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 Section 6 and Note 612.7.1, Note 1021.7, and 23.10 Note 16.

1.6 Two former colorimetric test methods were discontinued. Refer to Appendix XI for historical information.

1.7 *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](#)

[D1688 Test Methods for Copper 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

[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](#)

[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:

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 zinc, *n*—~~an arbitrary~~ descriptive analytical term relating to the recoverable form of zinc that is determinable by the digestion method that is included in ~~the Procedure~~ this test standard.

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.³

4.2 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.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 [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 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~~Practices [D1066](#) and ~~Practices~~Practices [D3370](#), 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 [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

³ “Standard Methods for the Examination of Water and Wastewater,” 16th edition, 1985, APHA, AWWA-WPCF.

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 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.

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

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.~~

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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 **D3557**), chromium, (Test Methods **D1687**), cobalt (Test Methods **D3558**), copper (Test Methods **D1688**), iron (Test Methods **D1068**), lead (Test Methods **D3559**), manganese (Test Methods **D858**), and nickel (Test Methods **D1886**).

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

11. Apparatus

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

NOTE 3—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**.

11.2 *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.

12. Reagents and Materials

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

NOTE 4—If the reagent blank concentration is greater than the method detection limit, 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 in the preparation of a reagent or in the procedure, use double the amount specified if a distilled acid is used.

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

NOTE 5—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 zinc stock solution of appropriate known 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.

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 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—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.

12.8 *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.

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~~ curve or as determined by Practice D4841.

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~~ 14.3 – 14.4 ~~14.5~~. After the digestion of the blank and standard solutions has been completed in ~~14.4~~ 14.5, 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 or concentration of each at 213.9 nm. Aspirate HNO₃ (1 +499) between each standard.

13.4 ~~Prepare~~ Read directly in concentration if this capability is provided with the instrument or 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 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.

14.2 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~~ 14.6.

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

14.4 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—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.

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.

14.5 Cool and filter the samples through a suitable ~~filter~~ filter (12.8), 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.

14.6 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_r , mg/L	S_o , mg/L	%, Bias	Statistically Significant, 95 % Level
Reagent Water					
0.16	0.172	0.052	0.038	+7.5	No
0.16	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
0.16	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 Bias⁵

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 [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.

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.~~

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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 [D3557](#)), cobalt (Test Methods [D3558](#)), copper (Test Methods [D1688](#)), iron (Test Methods [D1068](#)), lead (Test Methods [D3559](#)), and nickel (Test Methods [D1886](#)).

19. Interferences

19.1 See Section [10](#).

20. Apparatus

20.1 Apparatus described in Section [11](#) are required.

⁵ Supporting data are available from ASTM International Headquarters, 100 Barr Harbor Dr., West Conshohocken, PA 19428-2959. Request have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1039. Contact ASTM Customer Service at service@astm.org.

21. Reagents and Materials

21.1 *Bromphenol Blue Indicator Solution* (1 g/L)—Dissolve 0.1 g of bromphenol blue in 100 mL of 50 % ethanol or isopropanol.

21.2 *Chloroform* (CHCl₃).

21.3 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl) (see **Note 3**).

21.4 *Hydrochloric Acid* (1 +2)—Add 1 volume of hydrochloric acid (HCl), sp gr 1.19, to 2 volumes of water.

21.5 *Hydrochloric Acid* (1 +49)—Add 1 volume of hydrochloric acid (HCl) sp gr 1.19, to 49 volumes of water.

21.6 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO₃) (see **Note 5**).

21.7 *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. Avoid inhalation and direct contact.)

NOTE 10—Warning: All components of this reagent are highly toxic. Carbon disulfide is also highly flammable. Prepare and use in a well-ventilated hood. Avoid inhalation and direct contact.

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

21.9 *Zinc Solution, Stock* (1.0 mL = 1.0 mg Zn)—See **12.4**.

21.10 *Zinc Solution, Intermediate* (1.0 mL = 0.1 mg Zn)—See **12.5**.

21.11 *Zinc Solution, Standard* (1.0 mL = 1.0 µg Zn)—Immediately before use, dilute 10.0 mL of zinc intermediate standard solution and 1 mL of HNO₃ (sp gr 1.42) to 1 L with water. This standard is used to prepare working standards at the time of analysis.

21.12 *Oxidant*—See **12.6**.

21.13 *Fuel*—See **12.7**.

21.14 *Filter Paper*—See **12.8**.

22. Standardization

22.1 Prepare a blank and sufficient standards containing from 0.0 to 20.0 µg of zinc by diluting 0.0 to 20.0-mL portions of zinc standard solution (**21.11**) to 100 mL with water.

22.2 When determining total recoverable zinc use 125-mL beakers or flasks, add 0.5 mL of HNO₃ (sp gr 1.42) and proceed as directed in **23.2 – 23.15**. When determining dissolved zinc use 250-mL separatory funnels and proceed as directed in **23.5 + 23.15**.

22.3 ~~Construct~~ 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 zinc. ~~Alternatively, read directly in concentration from the instrument.~~

23. Procedure

23.1 Measure a volume of a well-mixed acidified sample containing less than 20.0 µg of zinc (100-mL maximum) into a 125-mL beaker or flask and adjust the volume to 100 mL with water.

NOTE 9—If only dissolved zinc is to be determined, measure a volume of filtered and acidified sample containing less than 20.0 µg of nickel (100-mL maximum) into a 250-mL separatory funnel, and start with **23.5**.

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

23.3 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—For brines and samples with appreciable amounts of suspended matter or dissolved solids, 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%~~ 0.5 %. All lots of tubes should come with a certificate of analysis to demonstrate suitability for their intended purpose.

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

23.5 Add 2 drops of bromphenol blue indicator (~~21.1~~(21.1)) solution and mix.