Standard Test Methods for Zinc in Water[1]

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 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 zinc in water. Two test methods are given as follows:

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 µg/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 in each system are mathematical conversions and may not be exact equivalents; therefore, each system shall be used independently of the other.

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 6, *Note 10, and Note 16.*

1.6 Two former colorimetric test methods were discontinued. Refer to Appendix X1 for historical information.

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
D1886 Test Methods for Nickel in Water
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
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*—For definitions of terms used in these test methods, refer to Terminology D1129.

3.2 *Definitions:*

3.2.1 *total recoverable zinc, n*—an arbitrary analytical term relating to the recoverable form of zinc that is determinable by the digestion method that 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.[3]

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

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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.

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

***A Summary of Changes section appears at the end of this standard**

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 D1066 and Practices D3370, as applicable.

7.2 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 of HNO_3. If only dissolved zinc is to be determined, the sample, shall be filtered through a 0.45-µm 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. 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.

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* , 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.

11.4 *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 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.

12.2 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO_3).

NOTE 5—If the reagent blank concentration is greater than the method detection limit, distill the HNO_3 or use a trace metal grade acid.

12.3 *Nitric Acid* (1 +499)—Add 1 volume of HNO_3 (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 HNO_3 (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.

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[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.

12.5 *Zinc Solution, Standard* (1 mL = 0.1 mg Zn)—Dilute 100.0 mL of the zinc stock solution and 1 mL of HNO_3 (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).

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.

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 HNO_3 (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 HNO_3 (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 HNO_3 (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 7—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 8—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 9—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. 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.

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

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 HNO_3 (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.

16. Precision and Bias[5]

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

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.

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 isopropranol.

21.2 *Chloroform* ($CHCl_3$).

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 (HNO_3) (see Note 5).

21.7 *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.

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 HNO_3 (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.

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 HNO_3 (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 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 11—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 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 12—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 13—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. 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.

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) solution and mix.

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

NOTE 14—The pH adjustment in 23.6 may be made with a pH meter instead of using indicator.

23.7 Add 10 mL of pyrrolidine dithiocarbamic acid-chloroform reagent (21.7) and shake vigorously for 2 min. (**Warning—**See Note 10.)

23.8 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.

TABLE 2 Determination of Precision and Bias for Zinc by Atomic Absorption, Chelation-Extraction

Amount Added, µg/L	Amount Found, µg/L	S_T, µg/L	S_O, µg/L	%, Bias	Statistically Significant, 95 % Level
		Reagent Water			
10	24.1	16.2	6.0	+ 141.0	Yes
70	78.1	19.2	11.0	+ 11.6	No
160	171.8	24.2	13.5	+ 7.4	No
		Water of Choice			
10	17.2	11.7	5.9	+ 72.0	Yes
70	82.3	26.8	12.5	+ 17.5	No
160	165.2	28.7	10.2	+ 3.3	No

23.9 Repeat the extraction with 10 mL of $CHCl_3$ (21.2) and drain the $CHCl_3$ layer into the same beaker.

NOTE 15—If color still remains in the $CHCl_3$ extract, reextract the aqueous phase until the $CHCl_3$ layer is colorless.

23.10 Place the beaker on a hotplate set at a low heat or on a steam bath, and evaporate to near dryness. Remove beaker from heat and allow residual solvent to evaporate without futher heating.

NOTE 16—**Precaution:** Perform in a well-ventilated hood.

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

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

23.12 Place the beaker on a hotplate set at low heat or on a steam bath, and evaporate to near dryness. Remove beaker from heat and allow residual solvent to evaporate without further heating.

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

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

23.15 Aspirate each sample and record the scale reading or concentration at 213.9 nm.

24. Calculation

24.1 Determine the weight of zinc in each sample by referring to the analytical curve. Calculate the concentration of zinc in micrograms per litre using Eq 1:

$$\text{Zinc, µg/L} = 1000/A \times B \tag{1}$$

where:

1000 = 1000 mL / Liter
A = volume of original sample, mL and
B = weight of zinc in sample, µg.

25. Precision and Bias

25.1 These collaborative test data were obtained from six laboratories on reagent grade, river, and potable waters. A synthetic brine was also analyzed. This data may not apply for other waters. Precision and bias data are shown in Table 2.

25.2 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, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

26. Quality Control

26.1 In order to be certain 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 zinc.

26.2 *Calibration and Calibration Verification:*

26.2.1 Analyze at least three working standards containing concentrations of zinc that bracket the expected sample concentration prior to analysis of samples to calibrate the instrument.

26.2.2 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 ±10% of the known concentration.

26.2.3 If calibration cannot be verified, recalibrate the instrument.

26.3 *Initial Demonstration of Laboratory Capability:*

26.3.1 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.

26.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a mid-range concentration of zinc. 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.

26.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in Table 1. This study should be repeated until the recoveries are within the limits given in Table 1. 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.

26.4 *Laboratory Control Sample (LCS):*

26.4.1 To ensure that the test method is in control, analyze a LCS containing a mid-range concentration of zinc with each batch or 10 samples. If large numbers of samples are analyzed in the batch, analyze the LCS after every 10 samples. 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.

26.4.2 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.

26.5 *Method Blank:*

26.5.1 Analyze a reagent water test blank with each batch. The concentration of zinc found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of zinc 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.

26.6 *Matrix Spike (MS):*

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

26.6.2 The spike concentration plus the background concentration of zinc 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.

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

$$P = \frac{100\left[A\left(V_s + V\right) - B\ V_s\right]}{C\ V} \qquad (2)$$

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_s= volume (mL) of sample used

V= volume (mL) of spiking solution added

26.6.4 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: acceptable spike recoveries are dependent on the concentration of the component of interest. See Guide D5810 for additional information.

26.7 *Duplicate:*

26.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each 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.

26.7.2 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.

26.7.3 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.

26.8 *Independent Reference Material (IRM):*

26.8.1 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.

27. Keywords

27.1 atomic absorption; chelation; flame; water; zinc

APPENDIX

(Nonmandatory Information)

X1. RATIONALE FOR DISCONTINUATION OF TEST METHODS

X1.1 Colorimetric with Zincon (High and Low Ranges):

X1.1.1 These test methods were discontinued in 1988. They were last published in the 1988 *Annual Book of ASTM Standards*, Vol 11.01.

X1.1.2 These test methods cover the determination of zinc in water for samples containing 0.02 to 5.0 mg/L (high range) and 0.002 to 0.25 mg/L (low range) of zinc. Relevant data has been filed at ASTM International Headquarters as Research Report RR:D–19–160.

X1.1.3 The chemistry of both test methods is the same; they differ only with respect to sample size and reagent concentration of the treated aliquot.

(a) Zinc forms a blue-colored complex with 2-carboxy-2'-hydroxy-5'-sulfoformazyl benzene (zircon) in a solution buffered to a pH of 9.0.

(b) The blue-colored zinc-zircon complex is masked at the low zinc concentration range of the test methods by the intense brick-red color of the zincon indicator solution. The color obeys Beer's law up to a concentration of 5 mg/L of zinc.

X1.1.4 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 (D1691–02(2007)) that may impact the use of this standard.

(1) The SI statement was added to section 1.
(2) D1192 was removed from section 2 and section 7.1.
(3) Section 7 was modified to allow for pH of the samples in the laboratory.
(4) Sections 14 and 23 were modified to include note about the use of block digestion systems.
(5) Reagent references were added to section 23.
(6) Sections 26.3.2 and 26.6.3 were modified.

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