Designation: D1687 − 17

Standard Test Methods for Chromium in Water[1]

This standard is issued under the fixed designation D1687; 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 hexavalent and total chromium in water. Section 34 on Quality Control pertains to these test methods. Three test methods are included as follows:

Test Method	Concentration Range	Sections
A—Photometric Diphenylcarbohydrazide	0.01 to 0.5 mg/L	7 – 15
B—Atomic Absorption, Direct	0.1 to 10 mg/L	16 – 24
C—Atomic Absorption, Graphite Furnace	5 to 100 µg/L	25 – 33

1.2 Test Method A is a photometric method that measures dissolved hexavalent chromium only. Hexavalent chromium can also be determined by ion chromatography, see Test Method D5257. Test Methods B and C are atomic absorption methods that are generally applicable to the determination of dissolved or total recoverable chromium in water without regard to valence state. ICP-MS or ICP-AES may also be appropriate but at a higher instrument cost. See Test Methods D5673 and D1976.

1.3 Test Method A has been used successfully with reagent grade water Types I, II, and III, tap water, 10 % NaCl solution, treated water from a synthetic organic industrial plant that meets National Pollution Discharge Elimination System (NPDES) permit requirements, and EPA-extraction procedure leachate water, process water, lake water, effluent treatment, that is, lime neutralization and precipitation of spent pickle liquor and associated rinse water from stainless steel pickling. Test Method C has been used successfully with reagent water, stock scrubber water, lake water, filtered tap water, river water, well water, production plant water, and a condensate from a medium BTU coal gasification process. Matrices used, except for reagent water, are not available for Test Method B. It is the user's responsibility to ensure the validity of these test methods for waters of untested matrices.

1.4 The values stated in SI units are to be regarded as standard. The values given in 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 4.2, 20.3, and 20.8.1.

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
D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D1688 Test Methods for Copper 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

[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**

D4691 Practice for Measuring Elements in Water by Flame Atomic Absorption Spectrophotometry
D4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents
D5257 Test Method for Dissolved Hexavalent Chromium in Water by Ion Chromatography
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
E60 Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry
E275 Practice for Describing and Measuring Performance of Ultraviolet and Visible Spectrophotometers

3. Terminology

3.1 *Definitions:*

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 *laboratory control sample, n*—a solution with the certified concentration(s) of the analytes.

3.2.4 *total recoverable chromium, n*—a descriptive term relating to the forms of chromium recovered in the acid-digestion procedure specified in this test standard.

4. Significance and Use

4.1 Hexavalent chromium salts are used extensively in metal finishing and plating applications, in anodizing aluminum, and in the manufacture of paints, dyes, explosives, and ceramics. Trivalent chromium salts are used as mordants in textile dyeing, in the ceramic and glass industry, in the leather industry as a tanning agent, and in photography. Chromium may be present in wastewater from these industries and may also be discharged from chromate-treated cooling waters.

4.2 The hexavalent state of chromium is toxic to humans, animals, and aquatic life. It can produce lung tumors when inhaled and readily induces skin sensitization.

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[3] where such specifications are available. 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, II, or III water. Type I is preferred and more commonly used. Type II water was specified at the time of round robin testing of these test methods.

NOTE 1—The user must ensure the type of reagent water chosen is sufficiently free of interferences. The water should be analyzed using the test method.

6. Sampling

6.1 Collect the sample in accordance with the applicable ASTM standard as follows: Practice D1066, or Practices D3370. The holding time for the samples may be calculated in accordance with Practice D4841.

6.2 Samples to be analyzed by Test Method A should be stabilized upon collection by addition of sodium hydroxide solution to a pH greater than or equal to 8, or analyzed immediately. Minor delays in stabilization or analyses of samples containing sulfur reduction compounds can produce significant loss in hexavalent chromium. Acidic samples containing hypobromite, persulfate, or chlorine could oxidize trivalent chromium, if present, to hexavalent form upon preservation, resulting in a positive interference. When the presence of these oxidizing compounds is suspected, samples should not be preserved but analyzed immediately. It will be evident that in this case, the simultaneous presence of reducing compounds could not be anticipated.

6.3 Samples to be analyzed by Test Methods B and C shall be preserved by addition of HNO_3 (sp gr 1.42) to pH of 2 or less immediately at the time of collection, normally about 2 mL HNO_3/L. If only dissolved chromium is to be determined, the sample shall be filtered through a 0.45-µm membrane filter (11.8) before acidification.

NOTE 2—Alternatively, the pH may be adjusted in the laboratory 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

[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 *Analar 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.

TEST METHOD A—PHOTOMETRIC DIPHENYLCARBOHYDRAZIDE

7. Scope

7.1 This test method covers the determination of dissolved hexavalent chromium in water.

7.2 The test method is applicable in the range from 0.01 to 0.5 mg/L chromium. The range may be extended by appropriate sample dilution.

7.3 This test method has been used successfully with reagent grade water Types I, II, and III, tap water, 10 % NaCl solution, treated water from a synthetic organic industrial plant that meets NPDES permit requirements, EPA-extraction procedure leachate water, process water, lake water, effluent from treatment that is, lime neutralization and precipitation of spent pickle liquor and associated rinse water from stainless steel pickling. It is the responsibility of the user to ensure the validity of the test method to waters of untested matrices.

8. Summary of Test Method

8.1 Hexavalent chromium reacts with 1.5-diphenylcarbohydrazide (s-diphenylcarbazide) in an acid medium to produce a reddish-purple color. The intensity of the color formed is proportional to the hexavalent chromium concentration.

9. Interferences

9.1 Vanadium, titanium, or iron present at concentrations of 5 mg/L yield a 10 to 30 % reduction in recovery of chromium. Copper at 100 mg/L yields a 20 to 30 % reduction in recovery in the presence of sulfate. Mercury gives a blue-purple color, but the reaction is not very sensitive at the pH employed for the test.

9.2 Nitrite concentrations in excess of 10 mg/L as NO_2 yield low test results. Sulfamic acid may be added (~10.1 g) prior to the addition of diphenylcarbazide solution to minimize nitrite interference. Add sulfamic acid only when the presence of nitrite has been positively established. Excess sulfamic acid itself creates a slightly positive interference.

9.3 Sulfide and sulfite reduce chromate in an acid medium to give low results.

9.4 Several sample matrices have been identified which produce a yellow-orange complex that interferes with this quantification. When this occurs, it may be remedied by inverting the indicator-buffer sequence. In these cases the analyst should evaluate the matrix effect with the additions of spikes (Guide D5810).

9.5 Although each interferent has been reported, most of the common interferences are eliminated by the preservation procedure at the time of collection. The potentially interfering metals are precipitated and the reducing effect of sulfur compounds has been overcome.

10. Apparatus

10.1 *Photometer*—Spectrophotometer or filter photometer suitable for use at 540 nm and equipped with a cell having a minimum path length of 10 mm. The photometers and photometric practice prescribed in this test method shall conform to Practice E60. Spectrophotometers and spectrophotometric practice shall conform to Practice E275.

11. Reagents and Materials

11.1 *Chromium Solution, Stock* (1 mL = 0.10 mg Cr)—Dissolve 0.2828 g of potassium dichromate ($K_2Cr_2O_7$ that has been oven dried at 105°C for 1 h) in water. Dilute to 1 L with water. Alternatively, certified stock solutions are commercially available through chemical supply vendors and may be used.

11.2 *Chromium Solution, Standard* (1 mL = 0.001 mg Cr)—Dilute 10.0 mL of chromium stock solution (see 11.1) to 1 L with water.

11.3 *Diphenylcarbazide Indicator Solution*—Dissolve 0.25 g of powdered 1,5-diphenylcarbohydrazide in 100 mL of acetone. Store in an amber glass-stoppered flask at 4°C when not in use. This solution is stable for about one week when kept refrigerated. Prepare fresh reagent when the solution becomes discolored.

NOTE 3—Allow the indicator solution to warm to room temperature before use.

11.4 *Phosphoric Acid* (1 + 1)—Dilute 500 mL of concentrated phosphoric acid (sp gr 1.69) to 1 L with water.

11.5 *Phosphoric Acid* (1 + 19)—Dilute 50 mL of concentrated phosphoric acid (sp gr 1.69) to 1 L with water.

11.6 *Sodium Hydroxide Solution* (40 mg/L)—Dissolve 40 mg of sodium hydroxide (NaOH) in water. Cool and dilute to 1 L. This solution is used for sample preservation.

11.7 *Sulfamic Acid*(NH_2SO_3H)—Crystals.

11.8 *Filter Paper*—Purchase suitable filter paper. Typically the filter papers have a pore size of 0.45-µm 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. Calibration

12.1 Prepare a series of at least four standard solutions containing from 0 to 0.50 mg/L of chromium by diluting measured volumes of the standard chromium solution (see 11.2) to 100 mL with water in separate volumetric flasks.

12.2 Transfer 50 mL of each prepared standard solution to separate 125-mL Erlenmeyer flasks and proceed with 13.3 – 13.6.

12.3 Prepare a calibration curve by plotting milligrams per liter of chromium versus absorbance on linear graph paper.

12.4 Read directly in concentration if this capability is provided with the instrument or prepare a calibration curve for each photometer. A recalibration must be made if any alterations of the instrument are made or if new reagents are prepared. At the least, a blank and three chromium standard solutions must be analyzed to verify the original test calibration each time the test is performed.

TABLE 1 Determination of Bias and Precision, Photometric Diphenylcarbohydrazide

	Amount Added, mg/L	Mean Recovery ($\bar{X}$), mg/L	± Bias	± % Bias	Statistically Significant at 5 % Level	S_T	S_o
Reagent water:							
	0.010	0.0125	+0.0025	+25.0	yes	0.006	0.0031
	0.050	0.0502	+0.0002	+0.40	no	0.007	0.0053
	0.350	0.3484	−0.0016	−0.46	no	0.022	0.0130
	0.500	0.4964	−0.0036	−0.72	no	0.022	0.0139
Water of choice:							
	0.010	0.0112	+0.0012	+12.0	no	0.005	0.0025
	0.050	0.0468	−0.0032	−6.40	yes	0.007	0.0042
	0.350	0.3378	−0.0122	−3.49	yes	0.026	0.0159
	0.500	0.4776	−0.0224	−4.48	yes	0.038	0.0204
Leachate:							
	0.010	0.0148	+0.0048	+48.0	yes	0.008	0.0037
	0.050	0.0513	+0.0013	+2.60	no	0.009	0.0062
	0.350	0.3422	−0.0078	−2.23	yes	0.015	0.0093
	0.500	0.4887	−0.0113	−2.26	yes	0.025	0.0130

13. Procedure

13.1 Filter a portion of the sample through a 0.45-µm membrane filter (11.8) and adjust the pH into the 8 to 8.5 range if it is greater than 8.5 with a few drops of the phosphoric acid solution (1 + 19).

13.2 Transfer 50.0 mL of the filtered sample, or a smaller aliquot of sample diluted to 50.0 mL, to a 125-mL Erlenmeyer flask.

13.3 Add 2.0 mL of the diphenylcarbazide solution to each solution and swirl to mix.

NOTE 4—If the sample is colored, prepare a separate aliquot as described in 13.1 and 13.2. Add 2.0 mL of acetone instead of diphenylcarbazide solution and proceed with 13.4 and 13.5. Use this solution as the sample blank.

13.4 Immediately add 5.0 mL of phosphoric acid solution (1 + 1) to each solution and swirl to mix.

13.5 Permit the solutions to stand 15 min for full color development. Measure the absorbance within 30 min after the addition of the diphenylcarbazide solution at 540 nm with a cell having a minimum path length of 10 mm.

13.6 Determine milligrams per liter of chromium as Cr^{+6} in the test sample by referring the direct instrument reading or the absorbance to the prepared calibration curve (see 12.3).

14. Calculation

14.1 Calculate the hexavalent chromium concentration as follows:

$$Cr^{+6}, \text{mg/L} = (W_S - W_B)(50/S) \quad (1)$$

where:

W_S = chromium found in the sample, mg/L (see 13.6),
W_B = chromium found in the sample blank, mg/L (see 13.6), and
S = volume of sample used, mL (see 13.2).

15. Precision and Bias

15.1 The collaborative test data were obtained on reagent grade water Types I, II, and III, tap water, 10 % NaCl solution, treated water from a synthetic organic industrial plant which meets NPDES permit requirements, EPA-extraction procedure leachate water, process water, lake water, effluent from treatment, that is, lime neutralization and precipitation of spent pickle liquor and associated rinse water from stainless steel pickling.

15.2 Single-operator and overall precision of this test method within its designated range and recovery data for the above waters for 16 laboratories, which include a total of 16 operators analyzing each sample on three different days, is given in Table 1.

15.3 Single-operator and overall precision of this test method within its designated range and recovery data for a prepared leachate water for 8 laboratories, which include a total of 8 operators analyzing each sample on three different days, is also given in Table 1.

15.4 It is the user's responsibility to ensure the validity of the test method for waters of untested matrices.

15.5 Precision and bias for this test method conforms to Practice D2777 – 77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of Practice D2777 – 13, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

TEST METHOD B—ATOMIC ABSORPTION, DIRECT

16. Scope

16.1 This test method covers the determination of dissolved and total recoverable chromium in most waters, wastewaters, and brines.

16.2 The test method is applicable in the range from 0.1 to 10 mg/L of chromium. The range may be extended to concentrations greater than 10 mg/L by dilution of the sample.

16.3 It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

17. Summary of Test Method

17.1 Chromium is determined by atomic absorption spectrophotometry. Dissolved chromium is determined by aspirating a portion of the filtered sample directly with no pretreatment. Total recoverable chromium 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), nickel (Test Methods D1886), cobalt (Test Methods D3558), copper (Test Methods D1688), iron (Test Methods D1068), lead (Test Methods D3559), manganese (Test Methods D858) and zinc (Test Methods D1691).

18. Interferences

18.1 Iron, nickel, and cobalt at 100 µg/L and magnesium at 30 mg/L interfere by depressing the absorption of chromium. These interferences are eliminated in solutions containing 10,000 mg/L of 8-hydroxyquinoline. Samples adjusted to this concentration show no interference from 700 mg/L of iron and 10 mg/L each of nickel and cobalt, or from 1000 mg/L of magnesium.

18.2 Potassium above 500 mg/L enhances the chromium absorption.

18.3 Sodium, sulfate, and chloride (9000 mg/L each), calcium and magnesium (4000 mg/L each), nitrate (2000 mg/L), and cadmium, lead, copper, and zinc, (10 mg/L each) do not interfere.

19. Apparatus and Materials

19.1 *Atomic Absorption Spectrophotometer,* for use at 357.9 nm. A general guide for the use of flame atomic absorption applications is given in Practice D4691.

NOTE 5—The manufacturer's instructions should be followed for all instrumental parameters. Wavelengths other than 357.9 nm may be used if they have been determined to be equally suitable.

19.1.1 *Chromium Hollow Cathode Lamp,* multielement hollow-cathode lamps.

19.2 *Oxidant*—See 20.7.

19.3 *Fuel*—See 20.8.

19.4 *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.

20. Reagents and Materials

20.1 *Chromium Solution, Stock* (1 mL = 1.0 mg Cr)—Dissolve 2.828 g of primary standard potassium dichromate ($K_2Cr_2O_7$) in 200 mL of water and dilute to 1 L. Alternatively, certified stock solutions are commercially available through chemical supply vendors and may be used.

20.2 *Chromium Solution, Standard* (1 mL = 0.1 mg Cr)—Dilute 100.0 mL of the chromium stock solution and 1 mL of HNO_3 (sp gr 1.42) to 1 L with water.

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

NOTE 6—If a high reagent blank is obtained, 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 for the preparation of a reagent or in the procedure, use double the amount specified if a distilled acid is used.)

20.4 *8-Hydroxyquinoline Solution* (100 g/L)—Dissolve 50 g of 8-hydroxyquinoline in 35 mL of HCl (sp gr 1.19). Warm the mixture gently on a hot plate to facilitate dissolution. Transfer to a 500-mL volumetric flask and bring to volume with the careful addition of water. Use a hood.

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

NOTE 7—If a high reagent blank is obtained, distill the HNO_3 or use a spectrograde acid.

20.6 Nitric Acid (1 + 499)—Add 1 volume of HNO_3 (sp gr 1.42) to 499 volumes of water.

20.7 *Oxidant:*

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

20.7.2 *Nitrous Oxide,* medical grade, is satisfactory.

20.8 *Fuel:*

20.8.1 *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 hazardous situation.)

20.9 *Filter Paper*—See 11.8.

21. Standardization

21.1 Prepare 100 mL each of a blank and at least four standard solutions, containing 1 mL of 8-hydroxyquinoline solution (100 g/L)/10 mL of standard, to bracket the expected chromium concentration range of the samples to be analyzed, by diluting the standard chromium solution (see 20.2) with HNO_3 (1 + 499). Prepare the standards each time the test is to be performed.

21.2 To determine the total recoverable chromium, add 0.5 mL of HNO_3 (sp gr 1.42) and proceed as directed in 22.3 – 22.5. To determine dissolved chromium, proceed with 21.3.

21.3 Aspirate the blank and standards and record the absorbance or concentration at 357.9 nm. Aspirate HNO_3 (1 + 499) between each standard.

21.4 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 on linear graph paper.

22. Procedure

22.1 Clean all glassware to be used for preparation of standard solutions or in the digestion step, or both, by soaking the glassware overnight in HNO_3 (1 + 1) and then rinsing with reagent.

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

NOTE 8—If only dissolved chromium is to be determined, start with 22.6.

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

22.4 Heat the samples (between 65°C to 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 9—When analyzing brines and samples containing appreciable amounts of suspended matter or dissolved solids, the amount of reduction in the volume is left to the discretion of the analyst.

NOTE 10—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 to 95°C. 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.

22.5 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 to three times with water and bring to volume.

22.6 Pipette 10.0 mL of sample into a 50-mL beaker and add 1.0 mL of 8-hydroxyquinoline solution.

22.7 Aspirate each filtered and acidified sample and determine its absorbance or concentration. Aspirate HNO_3 (1 + 499) between each sample.

23. Calculation

23.1 Read directly in concentration or calculate the concentration of chromium in the sample, in milligrams per liter, using the analytical curve prepared in 21.4.

24. Precision and Bias[4]

24.1 The overall precision (S_T) of this test method within its designated range for six laboratories, which include a total of nine operators analyzing each sample on three different days, varies linearly with the chromium concentration, X, in milligrams per liter.

24.1.1 For reagent water:

$$S_T = 0.097X + 0.010 \quad (2)$$

24.1.2 For selected water matrices:

$$S_T = 0.079X + 0.019 \quad (3)$$

where:

S_T = overall precision, mg/L, and
X = concentration of chromium, mg/L.

24.2 Single-operator precision did not differ significantly from overall precision.

24.3 Recoveries of known amounts of chromium from reagent water and selected water matrices are given in Table 2.

[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1036. Contact ASTM Customer Service at service@astm.org.

TABLE 2 Determination of Bias, Atomic Absorption, Direct

	Amount Added, mg/L	Amount Found, mg/L	Bias	Bias, %	Statistically Significant (95 % confidence level)
Reagent water:					
	0.4	0.399	−0.001	−0.25	no
	3.0	2.89	−0.11	−3.7	no
	7.0	6.99	−0.01	−0.14	no
Selected water matrices:					
	0.4	0.425	+0.025	+6.2	yes
	3.0	3.095	+0.095	+3.2	no
	7.0	7.180	+0.180	+2.6	no

24.4 The selected waters used in this study are not available. It is the user's responsibility to ensure the validity of the test method for waters of untested matrices.

24.5 Precision and bias for this test method conforms to Practice D2777 – 77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of Practice D2777 – 13, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

TEST METHOD C—ATOMIC ABSORPTION, GRAPHITE FURNACE

25. Scope

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

25.2 This test method is applicable in the range from 5 to 100 µg/L of chromium (Refer to Practice D3919, Footnote in Table 1) based on a 20-µL sample size. The range can be increased or decreased by varying the volume of sample injected or the instrumental settings. High concentrations may be diluted but preferably should be analyzed by direct aspiration atomic absorption spectrophotometry.

25.3 This test method has been used successfully with reagent water, stack scrubber water, lake water, filtered tap water, river water, condensate from medium BTU coal gasification process, well water, and production plant water. It is the user's responsibility to ensure the validity of the test method for waters of untested matrices.

26. Summary of Test Method

26.1 Chromium is determined by an atomic absorption spectrophotometer used in conjunction with a graphite furnace. A sample is placed in a graphite tube, evaporated to dryness, charred (pyrolyzed or ashed), and atomized. Since the graphite furnace uses the sample much more efficiently than flame atomization, the detection of low concentrations of elements in small sample volumes is possible. Finally, the absorption signal during atomization is recorded and compared to standards. A general guide for the application of the graphite furnace is given in Practice D3919.

26.2 Dissolved chromium is determined on a filtered sample with no pretreatment.

26.3 Total recoverable chromium is determined acid digestion and filtration. Because chlorides interfere with furnace procedures for some metals, the use of hydrochloric acid in any digestion or solubilization step shall be avoided. If suspended material is not present, this digestion and filtration may be omitted.

27. Interferences

27.1 For a complete discussion on general interferences with furnace procedures, refer to Practice D3919.

28. Apparatus and Materials

28.1 *Atomic Absorption Spectrophotometer,* for use at 357.9 nm with background correction. See Note 11 and Note 12.

NOTE 11—A wavelength other than 357.9 nm may be used if it has been determined to be suitable. Greater linearity may be obtained at high concentrations by using a less sensitive wavelength.

NOTE 12—The manufacturer's instructions should be followed for all instrumental parameters.

28.2 *Chromium Light Source,* chromium hollow-cathode lamp. A single-element lamp is preferred, but multielement lamps may be used.

28.3 *Graphite Furnace,* capable of reaching temperatures sufficient to atomize the element of interest.

28.4 *Graphite Tubes,* compatible with furnace device. In this instance and to eliminate the possible formation of carbides, pyrolytically coated graphite tubes are recommended.

28.5 *Pipettes,* microlitre with disposable tips. Sizes may range from 1 µL to 100 µL, as required.

28.6 *Argon,* standard, welders grade, commercially available. Hydrogen may also be used if recommended by the instrument manufacturer.

28.7 *Data Storage and Reduction Devices, Computer- and Microprocessor-Controlled Devices, or Strip Chart Recorders* shall be utilized for collection, storage, reduction, and problem recognition (such as drift, incomplete atomization, changes in sensitivity, etc.). Strip chart recorders shall have a full scale deflection time of 0.2 s or less to ensure accuracy.

28.8 *Automatic Sampling,* may be used if available.

29. Reagents and Materials

29.1 *Chromium Solution, Stock* (1.0 mL = 1.0 mg Cr)—See 20.1.

29.2 *Chromium Intermediate Solution,* (1.0 mL = 10 µg Cr)—Dilute 10.0 mL of chromium stock solution (20.1) and 1 mL of HNO_3 (sp gr 1.42) to 1 L with water.

29.3 *Chromium Solution, Standard* (1.0 mL = 0.10 µg Cr)—Dilute 10.0 mL of chromium intermediate solution (29.2) 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 the analysis.

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

29.5 *Filter Paper*—See 11.8.

30. Standardization

30.1 Initially, set the instrument in accordance with the manufacturer's specifications. Follow the general instructions in Practice D3919.

31. Procedure

31.1 Clean all glassware to be used for preparation of standard solutions or in the digestion step, or both, by soaking the glassware overnight in HNO_3 (1 + 1) and then rinsing with water.

NOTE 13—Traces of chromium may be sometimes found in laboratory distilled water. It is the responsibility of the analyst to make certain, through analysis of appropriate blanks, that water used for diluting and rinsing is free from detectable amounts of chromium.

31.2 Measure 100.0 mL of each standard and well-mixed sample into 125-mL beakers or flasks.

31.3 For total recoverable chromium, add 5 mL HNO_3 (sp gr 1.42) to each standard and sample and proceed as directed in 31.4 – 31.6. If only dissolved chromium is to be determined, filter the unacidified sample through a 0.45-µm membrane filter (29.5), acidify, and proceed to 31.6.

31.4 Heat the samples (between 65°C to 95°C) on a steam bath or hotplate below boiling in a well-ventilated fume hood until the volume has been reduced to 15 to 20 mL, making certain that the samples do not boil (see Note 9).

NOTE 14—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 to 95°C. 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.

31.5 Cool and filter the sample through a suitable filter (29.5) such as fine-textured, acid washed, ashless paper, into a 100-mL volumetric flask. Wash the filter paper two or three times with water and bring to volume. See Note 15.

NOTE 15—If suspended material is not present, this filtration may be omitted. However, the sample must still be diluted to 100 mL.

31.6 Inject a measured aliquot of sample into the furnace device following the directions as provided by the particular instrument manufacturer. Refer to Practice D3919.

32. Calculation

32.1 Determine the concentration of chromium in each sample by referring to Practice D3919.

33. Precision and Bias[5]

33.1 The precision of this test method was tested by 15 laboratories in reagent water, stack scrubber water, lake water, filtered tap water, river water, tap water, condensate from a

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1103. Contact ASTM Customer Service at service@astm.org.

TABLE 3 Determination of Bias and Overall Precision in Reagent Water, Atomic Absorption, Graphite Furnace

Amount Added, µg/L	Amount Found, µg/L	s_T, µg/L	Bias, µg/L	Bias, %	Statistically Significant
8.0	8.1	1.78	+0.1	+1.25	no
10.0	9.5	2.28	−0.5	−5.0	no
28.0	27.9	3.93	−0.1	−0.36	no

TABLE 4 Determination of Bias and Overall Precision in Water of Choice, Atomic Absorption, Graphite Furnace

Amount Added, µg/L	Amount Found, µg/L	s_T, µg/L	Bias, µg/L	Bias, %	Statistically Significant
8.0	6.67	1.85	−1.33	−16.6	yes
10.0	10.83	3.42	+0.83	+8.3	no
28.0	28.2	5.0	+0.2	+0.7	no

medium BTU coal gasification process, well water, and production plant water. The round-robin study upon which these precision data are based involved the determination of numerous other metals. Replicate determinations were not requested in order to simplify the study and ensure generation of data for all metals. Thus, no single-operator precision data can be calculated. Bias data and overall precision data are given in Table 3 and Table 4.

33.2 These data may not apply to waters of other matrices, therefore, it is the responsibility of the analyst to ensure the validity of the test method in a particular matrix.

33.3 Precision and bias for this test method conforms to Practice D2777 – 77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of Practice D2777 – 13, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

34. Quality Control (QC)

34.1 To ensure 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 for the determination of chromium in water for the test methods in this standard.

34.2 *Calibration and Calibration Verification:*

34.2.1 Analyze at least three working standards containing concentrations of chromium that bracket the expected sample concentration, prior to analysis of samples, to calibrate the instrument. The calibration correlation coefficient shall be equal to or greater than 0.990.

34.2.2 Verify instrument calibration after standardization by analyzing a standard at the concentration of one of the calibration standards. The concentration of a mid-range standard should fall within ±15 % of the known concentration. Analyze a calibration blank to verify system cleanliness. The blank result should be less than the method reporting limit.

34.2.3 If calibration cannot be verified, recalibrate the instrument.

34.2.4 It is recommended to analyze a continuing calibration blank (CCB) and continuing calibration verification (CCV) at a 10 % frequency. The CCB result should be less than the method reporting limit. The CCV results should fall within the expected precision of the method or ±15 % of the known concentration.

34.3 *Initial Demonstration of Laboratory Capability:*

34.3.1 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, and so forth, a precision and bias study must be performed to demonstrate laboratory capability.

34.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a midrange concentration of chromium. 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.

34.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in Tables 1-4. This study should be repeated until the recoveries are within the limits given in Tables 1-4. 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.

34.4 *Laboratory Control Sample (LCS):*

34.4.1 To ensure that the test method is in control, prepare and analyze a LCS containing a known concentration of chromium with each batch (laboratory-defined or 20 samples). The laboratory control samples for a large batch should cover the analytical range when possible. It is recommended, but not required to use a second source, if possible and practical for the LCS. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for a mid-range LCS shall fall within ±15 % of the known concentration.

34.4.2 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.

34.5 *Method Blank:*

34.5.1 Analyze a reagent water test blank with each laboratory-defined batch. The concentration of chromium found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of chromium 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.

34.6 *Matrix Spike (MS):*

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

34.6.2 The spike concentration plus the background concentration of chromium 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.

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

$$P = [A\ (V_s + V) - BV_s]/CV \quad (4)$$

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, and
V = volume (mL) of spiking solution added.

34.6.4 The percent recovery of the spike shall fall within the limits, based on the 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 16—Acceptable spike recoveries are dependent on the concentration of the component of interest. See Guide D5810 for additional information.

34.7 *Duplicate:*

34.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each laboratory-defined 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.

34.7.2 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.

34.7.3 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.

34.8 *Independent Reference Material (IRM):*

34.8.1 In order to verify the quantitative value produced by the test method, analyze an independent reference material (IRM) submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the IRM should be in the concentration mid-range for the method chosen. The value obtained must fall within the control limits established by the laboratory.

35. Keywords

35.1 atomic absorption; chromium; graphite furnace; hexavalent chromium; photometric; water

SUMMARY OF CHANGES

Committee D19 has identified the location of selected changes to this standard since the last issue (D1687 – 12) that may impact the use of this standard. (Approved June 1, 2017.)

(1) Revised 1.2 to allow the option of using ion chromatography or ICP-MS or ICP-AES.
(2) Revised 1.4 to update the SI statement.
(3) Revised Section 2 to include Test Methods D1976, D5257, and D5673.
(4) Revised Section 3 to update and add terms.
(5) Revised Note 2 to include information to clarify the addition of acid.
(6) Added 11.8 and 20.9 to include information on filter paper.
(7) Revised 12.4, 13.6, 21.4, and 23.1 to include direct reading instruments.
(8) Revised Sections 13 and 22 to include information on cleaning glassware.
(9) Revised Sections 19 and 20 for the oxidant and fuel locations and Note numbering was updated as needed.
(10) Revised 22.4 and 31.4 and Note 10 and Note 14 were updated with information on the block digestion requirements.
(11) Revised 28.7.
(12) Revised and expanded Section 34.