



Designation: D 1687 – 02

## Standard Test Methods for Chromium in Water<sup>1</sup>

This standard is issued under the fixed designation D 1687; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last approval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

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

### 1. Scope

1.1 These test methods cover the determination of hexavalent and total chromium in water. Three test methods are included as follows:

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

1.2 Test Method A is a photometric method that measures dissolved hexavalent chromium only. 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.

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 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 *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 and Note 5 and Note 6.

<sup>1</sup> 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. Referenced Documents

#### 2.1 ASTM Standards:

- D 858 Test Methods for Manganese in Water<sup>2</sup>
- D 1066 Practice for Sampling Steam<sup>2</sup>
- D 1068 Test Methods for Iron in Water<sup>2</sup>
- D 1129 Terminology Relating to Water<sup>2</sup>
- D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits<sup>2</sup>
- D 1193 Specification for Reagent Water<sup>2</sup>
- D 1688 Test Methods for Copper in Water<sup>2</sup>
- D 1691 Test Methods for Zinc in Water<sup>2</sup>
- D 1886 Test Methods for Nickel in Water<sup>2</sup>
- D 3370 Practices for Sampling Water from Closed Conduits<sup>2</sup>
- D 3557 Test Methods for Cadmium in Water<sup>2</sup>
- D 3558 Test Methods for Cobalt in Water<sup>2</sup>
- D 3559 Test Methods for Lead in Water<sup>2</sup>
- D 4691 Practice for Measuring Elements in Water by Flame Atomic Absorption Spectrophotometry<sup>2</sup>
- D 4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents<sup>2</sup>
- D 5810 Guide for Spiking into Aqueous Samples<sup>2</sup>
- D 5847 Practice for the Writing Quality Control Specifications for Standard Test Methods for Water Analysis<sup>3</sup>
- E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analyses of Metals<sup>4</sup>
- E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared Spectrophotometers<sup>5</sup>

### 3. Terminology

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

#### 3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *Laboratory Control Sample, n*—a solution with the certified concentration(s) of the analytes.

<sup>2</sup> Annual Book of ASTM Standards, Vol 11.01.

<sup>3</sup> Annual Book of ASTM Standards, Vol 11.02.

<sup>4</sup> Annual Book of ASTM Standards, Vol 03.05.

<sup>5</sup> Annual Book of ASTM Standards, Vol 03.06.

#### 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. However, it is not known whether cancer will result from ingestion of chromium in any of its valence states.

#### 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<sup>6</sup> 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 **D 1193**, 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 **D 1066**, Specification **D 1192**, or Practices **D 3370**. The holding time for the samples may be calculated in accordance with Practice **D 4841**.

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.

<sup>6</sup> *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.

6.3 Samples to be analyzed by Test Methods B and C shall be preserved by addition of HNO<sub>3</sub> (sp gr 1.42) to pH of 2 or less immediately at the time of collection, normally about 2 mL HNO<sub>3</sub>/L. If only dissolved chromium is to be determined, the sample shall be filtered through a 0.45- $\mu$ m membrane filter before acidification.

### 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-diphenylcarbazine) 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<sub>2</sub> yield low test results. Sulfamic acid may be added (~10.1 g) prior to the addition of diphenylcarbazine 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 **D 5810**)

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 E 60. Spectrophotometers and spectrophotometric practice shall conform to Practice E 275.

## 11. Reagents

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.

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 2—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.

## 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 A calibration curve must be prepared 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.

## 13. Procedure

13.1 Filter a portion of the sample through a 0.45- $\mu$ m membrane filter 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 3—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 absorbance to the prepared calibration curve (see 12.3).

## 14. Calculation

14.1 Calculate the hexavalent chromium concentration as follows:

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

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 D 2777-77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of D 2777-98, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.