



Standard Test Methods for Chromium in Water¹

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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 μ 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.

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. Referenced Documents

2.1 ASTM Standards:

- D 858 Test Methods for Manganese in Water²
- D 1066 Practice for Sampling Steam²
- D 1068 Test Methods for Iron in Water²
- D 1129 Terminology Relating to Water²
- D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits²
- D 1193 Specification for Reagent Water²
- D 1688 Test Methods for Copper in Water²
- D 1691 Test Methods for Zinc in Water²
- D 1886 Test Methods for Nickel in Water²
- D 3370 Practices for Sampling Water from Closed Conduits²
- D 3557 Test Methods for Cadmium in Water²
- D 3558 Test Methods for Cobalt in Water²
- D 3559 Test Methods for Lead in Water²
- D 4691 Practice for Measuring Elements in Water by Flame Atomic Absorption Spectrophotometry²
- D 4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents²
- D 5810 Guide for Spiking into Aqueous Samples²
- D 5847 Practice for the Writing Quality Control Specifications for Standard Test Methods for Water Analysis³
- E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analyses of Metals⁴
- E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared Spectrophotometers⁵

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.

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

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

⁴ *Annual Book of ASTM Standards*, Vol 03.05.

⁵ *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 Society⁶ 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.

⁶ *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 HNO₃ (sp gr 1.42) to pH of 2 or less immediately at the time of collection, normally about 2 mL HNO₃/L. If only dissolved chromium is to be determined, the sample shall be filtered through a 0.45- μ 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 NO₂ 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- μ 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.

TABLE 1 Determination of Bias and Precision, Photometric Diphenylcarbohydrazide

| | Amount Added, mg/L | Mean Recovery (\bar{X}), mg/L | \pm Bias | \pm % 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 |

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 D 3557), nickel (Test Methods D 1886), cobalt (Test Methods D 3558), copper (Test Methods D 1688), iron (Test Methods D 1068), lead (Test Methods D 3559), manganese (Test Methods D 858) and zinc (Test Methods D 1691).

18. Interferences

18.1 Iron, nickel, and cobalt at 100 μ g/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 D 4691.

NOTE 4—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*:

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

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

19.3 *Fuel*:

19.3.1 *Acetylene*—Standard, commercially available acetylene is the usual fuel. Acetone, always present in acetylene cylinders, can affect analytical results. The cylinder should be replaced at 50 psig (345 kPa).

NOTE 5—**Warning:** "Purified" grade acetylene containing a special proprietary solvent rather than acetone should not be used with poly(vinyl chloride) tubing as weakening of the tubing walls can cause a hazardous situation.

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

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.

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. **Caution**—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 (HNO₃).

NOTE 7—If a high reagent blank is obtained, distill the HNO₃ or use a spectrograde acid.

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

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 HNO₃(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 HNO₃(sp gr 1.42) and proceed as directed in 22.2-22.4. 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 HNO₃(1 + 499) between each standard.

21.4 Prepare an analytical curve by plotting the absorbance versus concentration for each standard on linear graph paper. Alternatively, read directly in concentration if this capability is provided with the instrument.

22. Procedure

22.1 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 22.5.

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

22.3 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 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.

22.4 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 to three times with water and bring to volume.

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

22.6 Aspirate each filtered and acidified sample and determine its absorbance or concentration. Aspirate HNO₃(1 + 499) between each sample.

23. Calculation

23.1 Calculate the concentration of chromium in the sample, in milligrams per liter, using the analytical curve prepared in 21.4. Alternatively, read directly in concentration if this capability is provided with the instrument.

TABLE 2 Determination of Bias, Atomic Absorption, Direct

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

24. Precision and Bias ⁷

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.

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 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.

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 D 3919, 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.

⁷ Supporting data are available from ASTM Headquarters. Request RR: D19-1036.

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 D 3919.

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 D 3919.

28. Apparatus and Materials

28.1 *Atomic Absorption Spectrophotometer*, for use at 357.9 nm with background correction. See Note 10 and Note 11.

NOTE 10—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 11—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 Device*—Computer and microprocessor controlled devices, or a strip chart recorder, shall be utilized for data collection, reduction, storage, and problem recognition (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

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).

30. Standardization

30.1 Initially, set the instrument in accordance with the manufacturer's specifications. Follow the general instructions in Practice D 3919.

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 $\text{HNO}_3(1 + 1)$ and then rinsing with water.

NOTE 12—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, acidify, and proceed to 31.6.

31.4 Heat the samples at 95°C on a steam bath or hotplate 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).

31.5 Cool and filter the sample through a suitable filter 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 13.

NOTE 13—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 D 3919.

32. Calculation

32.1 Determine the concentration of chromium in each sample by referring to Practice D 3919.

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

| Amount Added, $\mu\text{g/L}$ | Amount Found, $\mu\text{g/L}$ | s_T , $\mu\text{g/L}$ | Bias, $\mu\text{g/L}$ | 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, $\mu\text{g/L}$ | Amount Found, $\mu\text{g/L}$ | s_T , $\mu\text{g/L}$ | Bias, $\mu\text{g/L}$ | 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 |

33. Precision and Bias ⁸

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 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 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.

34. Quality Control (QC)

34.1 The following quality control information is recommended for the determination of chromium in water.

⁸ Supporting data are available from ASTM Headquarters. Request RR: D19-1103.

34.2 For each method the instrument shall be calibrated using a minimum of four calibration standards and a calibration blank. The calibration correlation coefficient shall be equal to or greater than 0.990. In addition to the initial calibration blank, a calibration blank shall be analyzed at the end of the batch run to ensure contamination was not a problem during the batch analysis.

34.3 An instrument check standard shall be analyzed at a minimum frequency of 10 % throughout the batch analysis. The value of the instrument check standard shall fall between 80 % and 120 % of the true value.

34.4 Two method blanks shall be prepared ensuring that an adequate method blank volume is present for a minimum of seven repetitive analysis. The standard deviation of the method blank is used to determine the minimum detectable concentration of each sample and control in the batch.

34.5 A Laboratory Control Sample shall be analyzed with each batch of samples at a minimum frequency of 10 %.

34.6 If the QC for the sample batch is not within the established control limits, reanalyze the samples or qualify the results with the appropriate flags, or both. (Practice D 5847)

34.7 Blind control samples should be submitted by an outside agency in order to determine the laboratory performance capabilities.

35. Keywords

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

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