



Designation: D 1068 – 9603

Standard Test Methods for Iron 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 iron in water. Procedures are given for determining total iron, dissolved iron, and ferrous iron. Undissolved iron may be calculated from the total iron and dissolved iron determinations. The test methods are given as follows:

| | Range | Sections |
|---|----------------------|----------|
| Test Method A—Atomic Absorption, Direct | 0.1 to 5.0 mg/L | 7 to 15 |
| Test Method C—Atomic Absorption, Graphite Furnace | 5 to 100 μ g/L | 16 to 24 |
| Test Method D—Photometric Bathophenanthroline μ g/L | 40 to 1000 μ g/L | 25 to 36 |

1.2 It is the user's responsibility to ensure the validity of these test methods to waters of untested matrices.

1.3 *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.* Specific hazards statements are given in Note 3, Note 5, and Note X1.1.

1.4 Two former photometric test methods were discontinued. See Appendix X2 for historical information.

2. Referenced Documents

2.1 *ASTM Standards:*

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

- D 858 Test Methods for Manganese in Water²
D 1066 Practice for Sampling Steam²
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 1687 Test Methods for Chromium in 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 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water²
D 3370 Practices for Sampling Water from Closed Conduits²
D 3558 Test Methods for Cobalt in Water²
D 3559 Test Methods for Lead in Water²
D 3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry²
D 4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents²
~~E 60 Practice~~
~~D 5810 Guide for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals Spiking into Aqueous Samples³~~
~~D 5847 Practice for the Writing Quality Control Specifications for Standard Test Methods for Water Analysis³~~
~~E 275 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals³~~
~~E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared Spectrophotometers⁴~~

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 *total recoverable iron*—an arbitrary analytical term relating to the recoverable forms of iron that are determinable by the digestion method which is included in these test methods.

4. Significance and Use

4.1 Iron is the second most abundant metallic element in the earth's crust and is essential in the metabolism of plants and animals. If presented in excessive amounts, however, it forms oxyhydroxide precipitates that stain laundry and porcelain. As a result, the recommended limit for iron in domestic water supplies is 0.3 mg/L. These test methods are useful for determining iron in many natural waters.

5. Purity of Reagents

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁵ 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. Other reagent water types may be used, provided it is first ascertained that the water is of sufficiently high purity to permit its use without adversely affecting the bias and precision of the test method. Type II water was specified at the time of round-robin testing of these test methods. In addition, water used in preparing solutions for the determination of ferrous iron shall be freshly boiled and essentially oxygen free.

6. Sampling

6.1 Collect the sample in accordance with Practice D 1066, Specification D 1192, or Practices D 3370, as applicable.

6.2 Samples should be preserved with HNO₃ or HCl (sp gr 1.42) to a pH of 2 or less immediately at the time of collection. If only dissolved iron is to be determined, the sample shall be filtered through a 0.45-µm membrane filter before acidification. The holding time for samples can be calculated in accordance with Practice D 4841.

6.3 If ferrous iron is to be determined, the sample should be analyzed as soon as possible after collection and contact with atmospheric oxygen should be minimized.

² Annual Book of ASTM Standards, Vol 11.01.

³ Annual Book of ASTM Standards, Vol 03.05.

⁴ Annual Book of ASTM Standards, Vol 03.06.

⁵ 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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

6.4 Additional information on sampling requirements for Test Method D is provided in 324.1.

TEST METHOD A—ATOMIC ABSORPTION, DIRECT

7. Scope

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

7.2 This test method is applicable in the range from 0.1 to 5.0 mg/L of iron. The range may be extended to concentrations greater than 5.0 mg/L by dilution of the sample.

7.3 This test method has been used successfully with reagent water; tap, ground, and surface waters; unspecified wastewaters; and a refinery primary treatment water. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

8. Summary of Test Method

8.1 Iron is determined by atomic absorption spectrophotometry. Dissolved iron is determined by atomizing the filtered sample directly with no pretreatment. Total recoverable iron is determined by atomizing the sample following hydrochloric-nitric acid digestion and filtration. The same digestion procedure may be used to determine total recoverable nickel (Test Methods D 1886), chromium (Test Methods D 1687), cobalt (Test Methods D 3558), copper (Test Methods D 1688), lead (Test Methods D 3559), manganese (Test Methods D 858), and zinc (Test Methods D 1691).

9. Interferences

9.1 Sodium, potassium, barium, chloride and sulfate (5000 mg/L each), calcium, magnesium, chromium, manganese, cobalt, nickel, copper, zinc, palladium, silver, cadmium, tin, lead, lithium, mercury, selenium, aluminum, antimony, arsenic, vanadium, boron, and molybdenum (100 mg/L) do not interfere.

9.2 Background correction (or chelation-extraction) may be necessary to determine low levels of iron in some waters.

NOTE 1—Instrument manufacturers' instructions for use of the specific correction technique should be followed.

10. Apparatus

10.1 *Atomic Absorption Spectrophotometer*, for use at 248.3 nm.

NOTE 2—The manufacturer's instructions should be followed for all instrumental parameters. A wavelength other than 248.3 nm may be used if it has been determined to be equally suitable.

10.1.1 *Iron Hollow-Cathode Lamp*—Multielement hollow-cathode lamps are available and have also been found satisfactory.

10.2 *Pressure-Reducing Valves*—The supplies of fuel and oxidant shall be maintained at pressures somewhat higher than the controlled operating pressure of the instrument by suitable valves.

11. Reagents and Materials

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

NOTE 3—If the reagent blank concentration is greater than the method detection limit, distill the HCl or use a spectrograde acid. **Precaution**—When HCl is distilled an azeotropic mixture is obtained (approximately 6 N HCl). Therefore, when concentrated HCl is specified for the preparation of reagents or in the procedure, use double the volume specified if distilled acid is used.

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

NOTE 4—If the reagent blank concentration is greater than the method detection limit, distill the HNO₃ or use a spectrograde acid.

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

11.4 *Iron Solution, Stock* (1 mL = 1.0 mg Iron)—Dissolve 1.000 g of pure iron in 100 mL of HCL (1 + 1) with the aid of heat. Cool and dilute to 1 L with water.

11.5 *Iron Solution, Standard* (1 mL = 0.1 mg Iron)—Dilute 100.0 mL of the iron stock solution to 1 L with water.

11.6 *Oxidant*:

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

11.7 *Fuel*:

11.7.1 *Acetylene*—Standard, commercially available acetylene is the usual fuel. Acetone, always present in acetylene cylinders can affect analytical results. The cylinder should be replaced at 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 potentially hazardous situation.

12. Standardization

12.1 Prepare 100 mL each of a blank and at least four standard solutions to bracket the expected iron concentration range of the samples to be analyzed by diluting the standard iron solution with HNO₃ (1 + 499). Prepare the standards each time the test is to be performed.

12.2 When determining total recoverable iron add 0.5 mL of HNO₃ (sp gr 1.42) and proceed as directed in 13.1 through 13.5. When determining dissolved iron proceed as directed in Note 6, 13.1.

12.3 Aspirate the blank and standards and record the instrument readings. Aspirate HNO₃ (1 + 499) between each standard.

12.4 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.

13. Procedure

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

NOTE 6—If only dissolved iron is to be determined, start with 13.3.

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

13.3 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 7—When analyzing samples of brines or samples containing appreciable amounts of suspended matter or dissolved solids, the amount of reduction in volume is left to the discretion of the analyst.

13.4 Cool and filter the samples through a suitable filter (such as fine-textured, acid-washed, ashless paper), into 100-mL volumetric flasks. Wash the filter paper two or three times with water and adjust a volume.

13.5 Aspirate each filtered and acidified sample and determine its absorbance or concentration at 248.3 nm. Aspirate HNO₃ (1 + 499) between each sample.

14. Calculation

14.1 Calculate the concentration of iron in the sample, in milligrams per litre, referring to 12.4.

15. Precision and Bias ⁶

15.1 The precision of this test method for 10 laboratories, which include 16 operations within its designated range may be expressed as follows:

Reagent Water Type II:

$$S_T = 0.047 X + 0.053$$

$$S_o = 0.030 X + 0.037$$

Water of Choice:

$$S_T = 0.050 X + 0.114$$

$$S_o = 0.024 X + 0.078$$

where:

S_T = overall precision,

S_o = single-operator precision, and

X = determined concentration of iron, mg/L.

15.2 Recoveries of known amounts of iron in a series of prepared standards were as shown in Table 1.

15.3 The collaborative test data were obtained on reagent water; tap, lake, ground and surface water; unspecified wastewater; and a refinery primary treatment water. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

15.4 This section on precision and bias 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 of interlaboratory studies of Committee D19 test methods.

16. Quality Control

16.1 In order to be certain that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing iron.

16.2 Calibration and Calibration Verification:

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

⁶ Supporting data are available from ASTM Headquarters. Request RR: D19 - 1035.

TABLE 1 Determination of Bias, Atomic Absorption, Direct

| Reagent Water Type II: | | | Bias, % | Statistically Significant (95 % Confidence Level) |
|------------------------|--------------------|------------|---------|---|
| Amount Added, mg/L | Amount Found, mg/L | Bias, mg/L | | |
| 0.2 | 0.2 | ±0.0 | 0.0 | no |
| 2.4 | 2.4 | ±0.0 | 0.0 | no |
| 4.4 | 4.3 | -0.1 | - 2.3 | yes |
| Natural Water: | | | Bias, % | Statistically Significant (95 % Confidence Level) |
| Amount Added, mg/L | Amount Found, mg/L | Bias, mg/L | | |
| 0.2 | 0.2 | ±0.0 | 0 | no |
| 2.4 | 2.3 | - 0.1 | - 4.17 | yes |
| 4.4 | 4.2 | - 0.2 | - 4.55 | yes |

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.

16.2.2 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 $\pm 15\%$ of the known concentration.

16.2.3 If calibration cannot be verified, recalibrate the instrument.

16.3 Initial Demonstration of Laboratory Capability:

16.3.1 If a laboratory has not performed the test before, or if there has been a major change in the measurement system, for example, new analyst, new instrument, etc., a precision and bias study must be performed to demonstrate laboratory capability.

16.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a mid-range concentration of iron. 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. The replicates may be interspersed with samples.

16.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in Table 1. This study should be repeated until the recoveries are within the limits given in Table 1. If a concentration other than the recommended concentration is used, refer to Practice D 5847 for information on applying the F test and t test in evaluating the acceptability of the mean and standard deviation.

16.4 Laboratory Control Sample (LCS) :

16.4.1 To ensure that the test method is in control, analyze a LCS containing a known concentration of iron with each batch or 10 samples. If large numbers of samples are analyzed in the batch, analyze the LCS after every 10 samples. The laboratory control samples for a large batch should cover the analytical range when possible. 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 $\pm 15\%$ of the known concentration.

16.4.2 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.

16.5 Method Blank:

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

16.6 Matrix Spike (MS):

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

16.6.2 The spike known concentration plus the background known concentration of iron must not exceed the high calibration standard. The spike must produce a known concentration in the spiked sample that is 2 to 5 times the analyte known concentration in the unspiked sample, or 10 to 50 times the detection limit of the test method, whichever is greater.

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

$$P = 100 [A(V_s + V) - B V_s] / C V \quad (1)$$

where:

A \equiv analyte known concentration (mg/L) in spiked sample,

B \equiv analyte known concentration (mg/L) in unspiked sample,

C = known concentration (mg/L) of analyte in spiking solution,
 V_s = volume (mL) of sample used, and
 V = volume (mL) added with spike.

16.6.4 The percent recovery of the spike shall fall within the limits, based on the analyte known concentration, listed in Guide D 5810, 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 8—Acceptable spike recoveries are dependent on the known concentration of the component of interest. See Guide D 5810 for additional information.

16.7 Duplicate:

16.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each batch. If the known concentration of the analyte is less than five times the detection limit for the analyte, a matrix spike duplicate (MSD) should be used.

16.7.2 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 D 5847 for information on applying the F test.

16.7.3 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.

16.8 Independent Reference Material (IRM):

16.8.1 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 known concentration of the IRM should be in the known concentration mid-range for the method chosen. The value obtained must fall within the control limits established by the laboratory.

TEST METHOD C—ATOMIC ABSORPTION, GRAPHITE FURNACE

16. Scope

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

16.2 This test method is applicable in the range from 5 to 100 µg/L of iron using a 20-µL injection. 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 (Test Method A).

16.3 This test method has been used successfully with reagent grade water, filtered tap water, well water, demineralized water, boiler blowdown water, and condensate from a medium Btu-coal gasification process. It is the user's responsibility to ensure validity of this test method to waters of untested matrices.

16.4 The analyst is encouraged to consult Practice D 3919 for a general discussion of interferences and sample analysis procedures for graphite furnace atomic absorption spectrophotometry.

17. Summary Scope

17.1 This test method covers the determination of Test Method

17.1 Iron dissolved and total recoverable iron in most waters and wastewaters.

17.2 This test method is applicable in the range from 5 to 100 µg/L of iron using a 20-µL injection. 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 (Test Method A).

17.3 This test method has been used in conjunction successfully with reagent grade water, filtered tap water, well water, demineralized water, boiler blowdown water, and condensate from a graphite furnace. A sample medium Btu-coal gasification process. It is placed in a graphite tube, evaporated the user's responsibility to dryness, charred (pyrolyzed or ashed), and atomized. The absorption signal generated during atomization is recorded and compared ensure validity of this test method to standards. A general guide for the application waters of the graphite furnace untested matrices.

17.4 The analyst is given in encouraged to consult Practice D 3919:

17.2 Dissolved iron is determined on D 3919 for a filtered sample with no pretreatment.

17.3 Total recoverable iron is determined following acid digestion general discussion of interferences and filtration. Because chlorides interfere with furnace sample analysis procedures for some metals, the use of hydrochloric acid in any digestion or solubilization step is to be avoided. If suspended material is not present, this digestion and filtration may be omitted. graphite furnace atomic absorption spectrophotometry.

18. Interferences

18.1 For Summary of Test Method

18.1 Iron 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. The absorption signal generated

during atomization is recorded and compared to standards. A general guide for the application of the graphite furnace is given in Practice D 3919.

~~18.2~~ Dissolved iron is determined on a filtered sample with no pretreatment.

~~18.3~~ Total recoverable iron is determined following acid digestion and filtration. Because chlorides interfere with furnace procedures for some metals, the use of hydrochloric acid in any digestion or solubilization step is referred to Practice D 3919. be avoided. If suspended material is not present, this digestion and filtration may be omitted.

19. Interferences

~~19.1~~ For a complete discussion on general interferences with furnace procedures, the analyst is referred to Practice D 3919.

20. Apparatus

~~19.1~~

~~20.1~~ *Atomic Absorption Spectrophotometer*, for use at 248.3 nm with background correction.

NOTE 89—A wavelength other than 248.3 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 910—The manufacturer's instructions should be followed for all instrumental parameters.

~~19.2~~

~~20.2~~ *Iron Hollow-Cathode Lamp*—A single-element lamp is preferred, but multielement lamps may be used.

~~19.3~~

~~20.3~~ *Graphite Furnace*, capable of reaching temperatures sufficient to atomize the element of interest.

~~19.4~~

~~20.4~~ *Graphite Tubes*, compatible with furnace device. Pyrolytically coated graphite tubes are recommended to eliminate the possible formation of carbides.

~~19.5~~

~~20.5~~ *Pipets*, microlitre with disposable tips. Sizes may range from 1 to 100 μL , as required.

~~19.6~~

~~20.6~~ *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.

~~19.7~~ ~~20.7~~ Automatic sampling should be used if available.

NOTE 101—Manual injection has been reported to cause widely scattered values even on purified waters due to contamination from pipetting technique.

20.1. Reagents and Materials

~~20.1.1~~ *Iron Solution, Stock* (1.0 mL = 1000 μg Fe)—See 11.4.

~~20.1.2~~ *Iron Solution, Intermediate* (1.0 mL = 10 μg Fe)—Dilute 10.0 mL of iron solution, stock (20.1) and 1 mL of HNO_3 (sp gr 1.42) to 1 L with water.

~~20.1.3~~ *Iron Solution, Standard* (1.0 mL = 0.2 μg Fe)—Dilute 20.0 mL of iron solution, intermediate (20.2) and 1 mL of HNO_3 (sp gr 1.42) to 1 L water. This standard is used to prepare working standards at the time of the analysis.

~~20.1.4~~ *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO_3) (see Note 4).

~~20.1.5~~ *Argon, Standard*, welders grade, commercially available. Nitrogen may also be used if recommended by the instrument manufacturer.

21. Standardization

~~21.1~~ Initially, set the instrument according to the manufacturer's specifications. Follow the general instructions as provided in Practice D 3919.

22. Standardization

~~22.1~~ Initially, set the instrument according to the manufacturer's specifications. Follow the general instructions as provided in Practice D 3919.

23. Procedure

~~22.3.1~~ Clean all glassware to be used for preparation of standard solutions or in the solubilization step, or both, by rinsing first with HNO_3 (1 + 1) and then with water.

~~22.3.2~~ Measure 100.0 mL of each standard and well-mixed sample into 125-mL beakers or flasks. For total recoverable iron add HNO_3 (sp gr 1.42) to each standard and sample at a rate of 5 mL/L and proceed as directed in ~~22.3.4~~ through ~~22.3.6~~.

~~22.3.3~~ If only dissolved iron is to be determined, filter the sample through a 0.45- μm membrane filter prior to acidification and proceed to ~~22.3.6~~.

~~22.3.4~~ 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 7).

TABLE 2 Determination of Bias, Atomic Absorption, Graphite Furnace

| Reagent Water: | | S_T | \pm Bias, $\mu\text{g/L}$ | \pm % Bias | Statistically Significant |
|-------------------------------|-------------------------------|-------|-----------------------------|--------------|---------------------------|
| Amount Added, $\mu\text{g/L}$ | Amount Found, $\mu\text{g/L}$ | | | | |
| 8.0 | 11.3 | 6.18 | + 3.3 | + 41.3 | no |
| 20 | 21.1 | 12.35 | + 1.1 | + 5.5 | no |
| 68 | 67.1 | 30.62 | - 0.9 | - 1.3 | no |
| Natural Water: | | S_T | \pm Bias, $\mu\text{g/L}$ | \pm % Bias | Statistically Significant |
| Amount Added, $\mu\text{g/L}$ | Amount Found, $\mu\text{g/L}$ | | | | |
| 8.0 | 6.9 | 3.17 | -1.1 | -13.8 | no |
| 20 | 19.0 | 8.33 | -1.0 | -5.0 | no |
| 68 | 70.1 | 21.63 | + 2.1 | + 3.1 | no |

223.5 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 2 or 3 times with water and bring to volume (Note 1+2). The acid concentration at this point should be 0.5 % HNO_3 .

NOTE 1+2—If suspended material is not present, this filtration may be omitted. The sample must be diluted to 100 mL.

223.6 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.

23. Calculation

23.1 Determine the concentration of iron in each sample by referring to Practice D 3919.

24. Calculation

24.1 Determine the concentration of iron in each sample by referring to Practice D 3919.

25. Precision and Bias ⁷

245.1 The precision for this test method was developed by 13 laboratories using reagent water and 7 laboratories using tap water, filtered tap water, well water, demineralized water, boiler blowdown water, and condensate from a medium Btu coal gasification process. Although multiple injections may have been made, the report sheets provided allowed only for reporting single values. Thus, no single-operator precision data can be calculated. See Table 2 for bias data and overall precision data.

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

25.3 This section on precision and bias 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 of interlaboratory studies of Committee D19 test methods.

26. Quality Control

26.1 In order to be certain that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing iron.

26.2 Calibration and Calibration Verification:

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

26.2.2 Verify instrument calibration after standardization by analyzing a standard at the known concentration of one of the calibration standards. The known concentration of a mid-range standard should fall within $\pm 15\%$ of the known known concentration.

26.2.3 If calibration cannot be verified, recalibrate the instrument.

26.3 Initial Demonstration of Laboratory Capability:

26.3.1 If a laboratory has not performed the test before, or if there has been a major change in the measurement system, for example, new analyst, new instrument, etc., a precision and bias study must be performed to demonstrate laboratory capability.

⁷ Supporting data are available from ASTM Headquarters. Request RR:D19-1102.

26.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a mid-range known concentration of iron. 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. The replicates may be interspersed with samples.

26.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in Table 2. This study should be repeated until the recoveries are within the limits given in Table 2. If a known concentration other than the recommended known concentration is used, refer to Practice D 5847 for information on applying the F test and t test in evaluating the acceptability of the mean and standard deviation.

26.4 *Laboratory Control Sample (LCS)* :

26.4.1 To ensure that the test method is in control, analyze a LCS containing a known concentration of iron with each batch or 10 samples. If large numbers of samples are analyzed in the batch, analyze the LCS after every 10 samples. The laboratory control samples for a large batch should cover the analytical range when possible. 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 $\pm 15\%$ of the known known concentration.

26.4.2 If the result is not within these limits, analysis of samples is halted until the problem is corrected, and either all the samples in the batch must be reanalyzed, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

26.5 *Method Blank*:

26.5.1 Analyze a reagent water test blank with each batch. The known concentration of iron found in the blank should be less than 0.5 times the lowest calibration standard. If the known concentration of iron is found above this level, analysis of samples is halted until the contamination is eliminated, and a blank shows no contamination at or above this level, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

26.6 *Matrix Spike (MS)*:

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

26.6.2 The spike known concentration plus the background known concentration of iron must not exceed the high calibration standard. The spike must produce a known concentration in the spiked sample that is 2 to 5 times the analyte known concentration in the unspiked sample, or 10 to 50 times the detection limit of the test method, whichever is greater.

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

$$P = 100 [A(V_s + V) - B V_s] / C V \quad (2)$$

where:

- A = analyte known concentration (mg/L) in spiked sample,
- B = analyte known concentration (mg/L) in unspiked sample,
- C = known concentration (mg/L) of analyte in spiking solution,
- V_s = volume (mL) of sample used, and
- V = volume (mL) added with spike.

26.6.4 The percent recovery of the spike shall fall within the limits, based on the analyte known concentration, listed in Guide D 5810, Table 2. 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 13—Acceptable spike recoveries are dependent on the known concentration of the component of interest. See Guide D 5810 for additional information.

26.7 *Duplicate*:

26.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each batch. If the known concentration of the analyte is less than five times the detection limit for the analyte, a matrix spike duplicate (MSD) should be used.

26.7.2 Calculate the standard deviation of the duplicate values and compare to the precision in the collaborative study using an F test. Refer to 6.4.4 of Practice D 5847 for information on applying the F test.

26.7.3 If the result exceeds the precision limit, the batch must be reanalyzed or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

26.8 *Independent Reference Material (IRM)*:

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

TEST METHOD D—PHOTOMETRIC BATHOPHENANTHROLINE FOR BPA-REACTIVE AND HCl-REACTIVE FERROUS FORMS**257. Scope**

257.1 This test method is applicable to the determination of two ferrous iron forms, bathophenanthroline (BPA)-reactive and hydrochloric acid (HCl)-reactive, in water having ferrous iron concentrations between 40 and 1000 µg/L. BPA-reactive ferrous iron is essentially ionic Fe(II) and HCl-reactive ferrous iron most likely represents total Fe(II).

257.2 This test method has been used successfully with reagent water and fly ash pond effluent water. It is the user's responsibility to assure the validity of this test method for water of untested matrices.

268. Summary of Test Method

268.1 The analysis for BPA-reactive ferrous iron consists of the addition of BPA to a buffered sample which forms a red-colored complex with ferrous iron. The red ferrous complex is extracted from the aqueous solution with *n*-hexyl or isoamyl alcohol and the intensity of its color is measured. HCl-reactive ferrous iron is determined by the addition of buffer and BPA to a previously acidified sample followed by extraction and measurement of the red ferrous complex. Maximum absorption of the complex occurs at 533 nm, and Beer's law is valid.

279. Significance and Use

279.1 The form of iron most directly toxic to aquatic life is ferrous iron. This test method allows analysis for both ionic and total ferrous iron in water with the sensitivity to detect the trace concentrations normally found (40 µg/L to 300 µg/L).

28.—

30. Interferences

2830.1 The metal ions other than ferrous iron which can form a complex with bathophenanthroline are manganese, cadmium, copper, zinc, cobalt, nickel, chromium, and ruthenium. The complexation/extraction is carried out at pH 4.0 to 4.5 in the presence of excess bathophenanthroline to achieve maximum color development with Fe(II) and also to eliminate interferences of competing ions. In acid solution, all competing ions form colorless complexes except ruthenium and cobalt which are yellow, and none except the colorless copper complex are extractable into an organic solvent. In a natural water sample buffered at pH 4, cuprous copper is the only metal ion that could potentially affect the measurement of ferrous iron; both species compete for the complexing agent. However, excess bathophenanthroline is present to complex both the ferrous iron and cuprous copper in the sample.

29.—

31. Apparatus

29.1—

31.1 *Photometer*, a spectrophotometer or filter photometer suitable for use at 533 nm and equipped with absorption cell providing a light path length of 5 cm. Photometers, and photometric practices prescribed in this test method, shall conform to Practice E 60. Spectrophotometers shall conform to Practice E 275.

302. Reagents

302.1 *Acetate Buffer Solution* (NaC₂H₃O₂) (pH 4.0)—Dissolve 10 g NaC₂H₃O₂ in 100 mL of water. If necessary, add glacial acetic acid or ammonium hydroxide (1 + 1) to adjust pH to 4.0. Purify acetate buffer by adding BPA reagent and extracting any complexed iron-BPA with hexanol. Allow 2 to 5 days for the organic and aqueous (acetate buffer) phases to separate in a separatory funnel. Discard the alcohol layer.

302.2 *Alcohol, n*—hexyl (preferred) or isoamyl (alternative).

302.3 *Alcohol*, methyl or ethyl (95 %).

302.4 *Ammonium Hydroxide Solution* (1 + 1)—Dilute 500 mL of ammonium hydroxide (NH₄OH, sp gr 0.90) with 500 mL of water and mix.

302.5 *Bathophenanthroline (BPA) Solution* (0.668 g/L)—

Dissolve 0.0668 g (4,7 diphenyl-1,10-phenanthroline) in 100 mL of ethyl alcohol (95 %).

302.6 *Hydrochloric Acid* (HCl) (1 + 1)—Cautiously add 1 volume of HCl (sp gr 1.19) to 1 volume of water and mix.

302.7 *Iron Solution, Standard* (1 mL = 10 µg Fe)—Dissolve 0.0702 g ferrous ammonium sulfate [Fe(NH₄)₂(SO₄)₂·6H₂O] into 700 mL of water that has had 20 mL of concentrated H₂SO₄(sp gr 1.84) added to it. Dilute to 1 L with water. Make up fresh every 24 to 48 h. Keep standard solution out of direct sunlight.

302.8 *Sulfuric Acid* (1 + 9)—Cautiously add 1 volume of H₂SO₄(sp gr 1.84) to 9 volumes of water and mix.

313. Sampling

313.1 Sampling shall be done with any device that minimizes the effect of atmospheric oxygen on the sample, for instance, a van-Dorn or hand-held and dipped bottle. Immediate analysis is preferred, but up to 1 h can elapse between sampling and analysis

without significant change to forms of iron if the sample is essentially free of air bubbles, is placed on ice, and held in the dark until analysis. For frequent monitoring of similar water matrices that are held up to 1 h, the analyst should confirm for those particular waters that the holding time used is inconsequential for iron analyses. A holding period up to 24 h can probably occur without significant change to ferrous iron forms by mixing reagents and complexing ferrous iron forms in the field (335.2 to 335.11). Once the color is formed, the complex shall be stable, without contact with air, and out of direct sunlight. The analyst should verify for tested waters that the holding time is inconsequential for iron analyses.

324. Calibration

324.1 Prepare a series of working standards to cover the expected range of ferrous iron concentration by diluting appropriate volumes of standard iron solution (see 302.6). Add 0.25 mL of 1 + 9 sulfuric acid (see 302.8) per 100 mL of solution as a preservative. Make up fresh every 24 h. Keep working standards out of direct sunlight.

324.2 Proceed as directed in 335.1 to 335.14.

324.3 Simultaneously carry out a blank determination to correct for iron in the reagents.

324.4 Prepare a calibration curve by plotting the absorbances of the working standard solutions against the micrograms of ferrous iron. Separate calibration curves must be prepared for the BPA-reactive ferrous iron in HCl-reactive ferrous iron.

335. Procedure

335.1 When testing for BPA-reactive ferrous iron, proceed with 335.2 and 335.3, followed immediately by 335.8. When testing for HCl-reactive ferrous iron, proceed to 335.4.

335.2 Transfer 5 mL of acetate buffer into a clean 125-mL separatory funnel.

335.3 Pipet 50 mL of sample from the sampling device directly into the buffer solution. The pipet tip must be at or slightly beneath the liquid-air interface while the sample is draining from the pipet. Swirl the separatory funnel to mix the contents and then proceed to 335.8.

335.4 When testing for HCl-reactive ferrous iron, place 4 mL of HCl (1 + 1) into a clean 125-mL separatory funnel.

335.5 Pipet 50 mL of sample from the sampling device directly into the acid. The pipet tip must be at or slightly beneath the liquid-air interface while the sample is draining from the pipet. Swirl the separatory funnel to mix the contents and then wait exactly 10 min.

335.6 Add 5 mL of acetate buffer. Swirl to mix.

335.7 Add an adequate volume (approximately 5 mL) of NH_4OH (1 + 1) to bring the pH between 4.0 and 4.5. Swirl to mix.

335.8 Add 10 mL of bathophenanthroline solution to the separatory funnel. Shake vigorously for 30 s.

335.9 Pipet either 10.0 mL of *n*-hexyl alcohol when testing for BPA-reactive ferrous iron or 20.0 mL of *n*-hexyl alcohol when testing for HCl-reactive ferrous iron to the separatory funnel, and shake vigorously for 30 s.

335.10 Allow 3 to 5 min for the organic and water phases to separate in the separatory funnel.

335.11 Open the stopcock of the separatory funnel and drain off the aqueous (bottom) layer.

335.12 Pipet either 5.0 mL of methyl or ethyl alcohol when testing for BPA-reactive ferrous iron or 10.0 mL of methyl or ethyl alcohol when testing for HCl-reactive ferrous iron to the red-colored organic phase.

335.13 Pour the organic phase through a suitable coarse filter into a beaker to remove particulates which could interfere with the absorbance measurement.

335.14 Measure the absorbance of the organic phase by means of any applicable apparatus listed in 29.1 31.1 at 533 nm.

346. Calculation

346.1 Calculate the concentration of ferrous iron, in micrograms per litre as follows:

$$\text{Ferrous Iron, } \mu\text{g/L} = (W \times 1000)/S$$

where:

W = ferrous iron read from the calibration curve, micrograms, and

S = original sample used, millilitres.

357. Precision and Bias ⁸

357.1 The single-operator and overall precision of this test method within its designated range varies with the quantity being tested in accordance with the data given in Table 3.

357.2 The collaborative test was conducted by six laboratories with single operators analyzing reagent water and fly ash pond effluent water containing ferrous iron concentrations of 50, 400, and 800 $\mu\text{g/L}$. In some instances, not all six laboratories analyzed each sample type at every concentration level.

357.3 Recoveries of known amounts of ferrous iron from the same water were as shown in Table 4.

⁸ Supporting data are available from ASTM Headquarters. Request RR: D19-1128.

**TABLE 3 Overall and Single Operator Precision Data-
Photometric Bathophenanthroline**

| Amount Added, $\mu\text{g/L}$ | Overall Precision, S_o , $\mu\text{g/L}$ | Single Operator Precision, S_o , $\mu\text{g/L}$ |
|-------------------------------|--|--|
| Reagent water | | |
| Type 1 (BPA reactive) | | |
| 50 | 16.9 | 4.9 |
| 400 | 47.1 | 6.8 |
| 800 | 33.6 | 13.3 |
| Reagent water | | |
| Type 1 (HCl reactive) | | |
| 50 | 11.8 | 10.8 |
| 400 | 51.9 | 25.6 |
| 800 | 291.6 | 28.9 |
| Water of choice | | |
| (BPA reactive) | | |
| 50 | 29.0 | 27.1 |
| 400 | 32.3 | 25.7 |
| 800 | 33.8 | 37.1 |
| Water of choice | | |
| (HCl reactive) | | |
| 50 | 24.2 | 22.1 |
| 400 | 33.5 | 19.4 |
| 800 | 191.7 | 199.9 |

**TABLE 4 Determination of Bias, Ferrous Iron-Photometric
Bathophenanthroline**

| Amount Added, $\mu\text{g/L}$ | Amount Found, $\mu\text{g/L}$ | \pm Bias | \pm %Bias | Statistically Significant (95 % Confidence Level) |
|-------------------------------|-------------------------------|------------|-------------|---|
| Reagent water | | | | |
| Type 1 (BPA reactive) | | | | |
| 50 | 41.2 | -8.8 | -17.6 | No |
| 400 | 427.8 | +27.6 | +6.9 | No |
| 800 | 801.3 | +1.3 | +0.2 | No |
| Reagent water | | | | |
| Type 1 (HCl reactive) | | | | |
| 50 | 48.3 | -1.7 | -3.4 | No |
| 400 | 413.3 | +13.3 | +3.3 | No |
| 800 | 998.0 | +198.0 | +24.8 | No |
| Water of choice | | | | |
| (BPA reactive) | | | | |
| 50 | 64.0 | +14.0 | +28.0 | No |
| 400 | 399.5 | -0.5 | -0.1 | No |
| 800 | 806.6 | +6.6 | +0.8 | No |
| Water of choice | | | | |
| (HCl reactive) | | | | |
| 50 | 64.1 | +14.1 | +28.0 | No |
| 400 | 422.3 | +22.3 | +5.6 | No |
| 800 | 770.2 | -29.8 | -3.7 | No |

357.4 This data may not apply to waters of untested matrices.

357.5 This section on precision and bias conforms to Practice D 2777 – 77 which was in place at the time of collaborative testing. Under the allowances made in 1.5.1.4 of D 2777 – 86, these precision and bias data do meet existing requirements of interlaboratory studies of Committee D-19 test methods.

38. Quality Control

38.1 In order to be certain that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing iron.

38.2 Calibration and Calibration Verification:

38.2.1 Analyze at least three working standards containing known concentrations of iron that bracket the expected sample known concentration, prior to analysis of samples, to calibrate the instrument. 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.

38.2.2 Verify instrument calibration after standardization by analyzing a standard at the known concentration of one of the

calibration standards. The known concentration of a mid-range standard should fall within $\pm 15\%$ of the known known concentration.

38.2.3 If calibration cannot be verified, recalibrate the instrument.

38.3 *Initial Demonstration of Laboratory Capability:*

38.3.1 If a laboratory has not performed the test before, or if there has been a major change in the measurement system, for example, new analyst, new instrument, etc., a precision and bias study must be performed to demonstrate laboratory capability.

38.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a mid-range known concentration of iron. 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. The replicates may be interspersed with samples.

38.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in Tables 3 and 4. This study should be repeated until the recoveries are within the limits given in Tables 3 and 4. If a known concentration other than the recommended known concentration is used, refer to Practice D 5847 for information on applying the F test and t test in evaluating the acceptability of the mean and standard deviation.

38.4 *Laboratory Control Sample (LCS) :*

38.4.1 To ensure that the test method is in control, analyze a LCS containing a known concentration of iron with each batch or 10 samples. If large numbers of samples are analyzed in the batch, analyze the LCS after every 10 samples. The laboratory control samples for a large batch should cover the analytical range when possible. 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 $\pm 15\%$ of the known known concentration.

38.4.2 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.

38.5 *Method Blank:*

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

38.6 *Matrix Spike (MS):*

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

38.6.2 The spike known concentration plus the background known concentration of iron must not exceed the high calibration standard. The spike must produce a known concentration in the spiked sample that is 2 to 5 times the analyte known concentration in the unspiked sample, or 10 to 50 times the detection limit of the test method, whichever is greater.

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

$$P = 100 [A(V_s + V) - B V_s] / C V \quad (3)$$

where:

A \equiv analyte known concentration (mg/L) in spiked sample,

B \equiv analyte known concentration (mg/L) in unspiked sample,

C \equiv known concentration (mg/L) of analyte in spiking solution,

V_s \equiv volume (mL) of sample used, and

V \equiv volume (mL) added with spike.

38.6.4 The percent recovery of the spike shall fall within the limits, based on the analyte known concentration, listed in Guide D 5810, Tables 3 and 4. 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 14—Acceptable spike recoveries are dependent on the known concentration of the component of interest. See Guide D 5810 for additional information.

38.7 *Duplicate:*

38.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each batch. If the known concentration of the analyte is less than five times the detection limit for the analyte, a matrix spike duplicate (MSD) should be used.

38.7.2 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 D 5847 for information on applying the F test.

38.7.3 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.

38.8 *Independent Reference Material (IRM):*

38.8.1 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 known concentration of the IRM should be in the known concentration mid-range for the method chosen. The value obtained must fall within the control limits established by the laboratory.

39. Keywords

369.1 analysis; atomic absorption; chelation-extraction; colorimetric; flame; graphite furnace; iron; water

APPENDIXES

(Nonmandatory Information)

X1. NOTES ON SOLUBILIZING REFRACTORY IRON COMPOUNDS

X1.1 Some forms of iron oxide are very resistant to the dissolving action of hydrochloric acid. For example, a colloidal form found in high pressure boiler condensate is very refractory. If it is suspected that a portion of the iron is insoluble with the acid treatment given in the method, several techniques can be used to yield the iron in soluble form. Blank determinations should be made with all reagents used in any methods of solubilizing the iron in order to correct for iron contamination. After such treatments the procedure for determination of ferrous iron will no longer apply, since the relative quantities of ferrous and ferric iron in the samples will be altered.

X1.1.1 *Fusion Method*—Evaporate the proper sized sample to dryness in a clean porcelain crucible. Fuse the residue with a minimum of potassium or sodium bisulfate (KHSO_4 or NaHSO_4). Cool and leach in 50 mL of water containing 2 mL of hydrochloric acid (HCl, sp gr 1.19). Continue with filtration, if necessary, and with the steps for color development.

X1.1.2 *Perchloric-Acid Treatment*—After addition of HCl and evaporation to a small volume, add 3 mL of nitric acid (HNO_3 , sp gr 1.42), 3 mL of perchloric acid (70 %) (see X1.1.3), and 3 mL of sulfuric acid (H_2SO_4 , sp gr 1.84). Evaporate to dense white fumes, cool the beaker, and wash the inside of the beaker carefully with water. Add a few drops of formic acid, and fume again to dense clouds of sulfur trioxide to remove the last traces of nitric acid. Cool, add water carefully, and heat for a short time to dissolve easily soluble salts. Cool, filter, if necessary, and continue with the steps for color development.

NOTE X1.1—**Warning:** Warm perchloric acid solutions react explosively with organic matter. The use of nitric acid prevents this vigorous reaction.

X1.1.3 *Thioglycolic Acid Method*—Wilson⁹ has shown that a sample made to 1 % (V/V) with thioglycolic acid and heated for 30 min at 90°C (195°F) will completely dissolve “unreactive” iron. Pocock¹⁰ confirms the finding and also eliminates the use of hydroxylamine hydrochloride. Dilute the proper-sized portion of sample to 75 mL with water and acidify with hydrochloric acid. Add 1 mL of thioglycolic acid and heat just under boiling for 30 min. Cool, filter, if necessary, and continue with the steps for color development.

⁹ Wilson, A. L., *Analyst*, Vol 89, June 1964, pp. 402, 410.

¹⁰ Pocock, F. J., paper presented at the 152nd National Meeting of the American Chemical Society, New York City, Sept. 12, 1966.

X2. RATIONALE FOR DISCONTINUATION OF TEST METHODS

X2.1 Photometric Methods (Orthophenanthroline and Bathophenanthroline):

X2.1.1 These test methods were discontinued in 1988. They were last published in the 1988 *Annual Book of ASTM Standards*, Vol 11.01.

X2.1.2 These test methods cover the determination of iron in water for samples containing 0.05 to 3.0 mg/L (orthophenanthroline) and 0.02 to 0.2 mg/L (bathophenanthroline). Some data relevant to these test methods are filed at ASTM Headquarters as research reports D19 - 52, D19 - 135, and D19 - 148.

X2.1.3 *Summary of Test Methods:*

X2.1.3.1 *Orthophenanthroline*—Undissolved iron and iron oxides are put into solution by treatment with acids. If the iron is not readily soluble in acids, fusion techniques are applied. The iron is determined photometrically with 1,10-phenanthroline (*o*-phenanthroline), which forms an orange-red complex with ferrous iron. The intensity of the color produced is proportional to the amount of ferrous iron in the water. Hydroxylamine hydrochloride is added to reduce ferric iron to the ferrous state when determining total and dissolved iron.

X2.1.3.2 *Bathophenanthroline*—Total iron is determined by this test method. Undissolved iron and iron oxides are put into

solution by treatment with acid. The iron is reduced with hydroxylamine hydrochloride and then reacted with 4,7-diphenyl-1,10-phenanthroline (bathophenanthroline). The red ferrous complex is extracted from the aqueous solution with *n*-hexyl or isoamyl alcohol and the intensity of its color is measured. Maximum absorption of the complex occurs at 533 nm, and Beer's law is valid.

X2.1.4 These test methods were discontinued because there were insufficient laboratories interested in participating in a collaborative study to obtain the necessary precision and bias data as required by Practice D 2777.

SUMMARY OF CHANGES

This section identifies the location of selected changes to these test methods that have been incorporated since the last issue. For the convenience of the user, Committee D19 has highlighted those changes that may impact the use of these test methods. This section may also include descriptions of the changes or reasons for the changes, or both.

- (1) The QC sections were added to the test method.
- (2) Sections 15.4 and 25.3 were added.
- (3) Section references were updated.

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