



Designation: ~~D1068~~—~~10 D1068~~ – 15

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

This standard is issued under the fixed designation D1068; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reappraisal. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reappraisal.

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

### 1. Scope\*

1.1 These test methods cover the determination of 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:

Test Method	Range	Sections
Test Method A—Atomic Absorption, Direct	0.1 to 5.0 mg/L	<del>7 to 16</del>
Test Method B—Atomic Absorption, Graphite Furnace	5 to 100 $\mu$ g/L	<del>17 to 26</del>
Test Method C—Photometric Bathophenanthroline $\mu$ g/L	40 to 1000 $\mu$ g/L	<del>27 to 38</del>
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1.2 It is the user's responsibility to ensure the validity of these test methods to waters of untested matrices.

1.3 The chelation-extraction and two former photometric test methods were discontinued. See [Appendix X2](#) for historical information.

1.4 The values stated in SI units are to be regarded as standard. ~~No other units of measurement are included in this~~ The values given in parentheses are mathematical conversions to inch-pound units that are provided for information only and are not considered standard.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific hazards statements are given in [Note 34](#), [11.7.1](#), and [X1.1.2](#).

### 2. Referenced Documents

2.1 *ASTM Standards:*<sup>2</sup>

- [D858 Test Methods for Manganese in Water](#)
- [D1066 Practice for Sampling Steam](#)
- [D1129 Terminology Relating to Water](#)
- [D1193 Specification for Reagent Water](#)
- [D1687 Test Methods for Chromium in Water](#)
- [D1688 Test Methods for Copper in Water](#)
- [D1691 Test Methods for Zinc in Water](#)
- [D1886 Test Methods for Nickel in Water](#)
- [D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water](#)

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee [D19](#) on Water and are the direct responsibility of Subcommittee [D19.05](#) on Inorganic Constituents in Water.

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<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

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

[D3370 Practices for Sampling Water from Closed Conduits](#)  
[D3558 Test Methods for Cobalt in Water](#)  
[D3559 Test Methods for Lead in Water](#)  
[D3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry](#)  
[D4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents](#)  
[D5673 Test Method for Elements in Water by Inductively Coupled Plasma—Mass Spectrometry](#)  
[D5810 Guide for Spiking into Aqueous Samples](#)  
[D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis](#)  
[E60 Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry](#)  
[E275 Practice for Describing and Measuring Performance of Ultraviolet and Visible Spectrophotometers](#)

### 3. Terminology

3.1 *Definitions*—For definitions of terms used in these test methods, refer to Terminology [D1129](#).

3.1 *Definitions:*

3.1.1 For definitions of terms used in this standard, refer to Terminology [D1129](#).

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *total recoverable iron, n*—~~an arbitrary analytical a descriptive term relating to the recoverable forms of iron that are determinable by the digestion method which is included~~ iron forms recovered in the acid-digestion procedure specified 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.<sup>3</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification [D1193](#), Type I. Other reagent water types may be used, provided it is first ascertained that the water is of sufficiently high purity to permit its use without adversely affecting the bias and precision of the test method. Type II water was specified at the time of round-robin testing of 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~~Practices [D1066](#) or ~~Practices~~[D3370](#), as applicable.

6.2 Samples should be preserved with HNO<sub>3</sub> 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- $\mu$ m membrane filter before acidification. The holding time for samples can be calculated in accordance with Practice [D4841](#).

NOTE 1—Alternatively, the pH may be adjusted in the laboratory if the sample is returned within 14 days. However, acid must be added at least 24 hours before analysis to dissolve any metals that adsorb to the container walls. This could reduce hazards of working with acids in the field when appropriate.

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.

6.4 Additional information on sampling requirements for Test Method C is provided in [33.1](#).

## 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.

<sup>3</sup> *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

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 [D1886](#)), chromium (Test Methods [D1687](#)), cobalt (Test Methods [D3558](#)), copper (Test Methods [D1688](#)), lead (Test Methods [D3559](#)), manganese (Test Methods [D858](#)), and zinc (Test Methods [D1691](#)).

## 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 2—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 3—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 4—If the reagent blank concentration is greater than the method detection limit, distill the HCl or use a spectrograde acid. **Precaution (Warning—**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.**)**—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 (HNO<sub>3</sub>).

NOTE 5—If the reagent blank concentration is greater than the method detection limit, distill the HNO<sub>3</sub> or use a spectrograde acid.

11.3 *Nitric Acid* (1 + 499)—Add 1 volume of HNO<sub>3</sub> (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. Alternatively, certified iron stock solutions of appropriate known purity are commercially available through chemical supply vendors and may be used.

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); 345 kPa (50 psig). **(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.)

11.8 *Filter Paper*—Purchase suitable filter paper. Typically the filter papers have a pore size of 0.45- $\mu$ m membrane. Material such as fine-textured, acid-washed, ashless paper, or glass fiber paper are acceptable. The user must first ascertain that the filter paper is of sufficient purity to use without adversely affecting the bias and precision of the test method.

## 12. 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 HNO<sub>3</sub> (1 + 499). Prepare the standards each time the test is to be performed-performed or as determined by Practice D4841.

12.2 When determining total recoverable iron add 0.5 mL of HNO<sub>3</sub> (sp gr 1.42) and proceed as directed in 13.1 through 13.5. When determining dissolved iron proceed as directed in Note 56, 13.1.

12.3 Aspirate the blank and standards and record the instrument readings. Aspirate HNO<sub>3</sub> (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 13.5.

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.

NOTE 8—Many laboratories have found block digestion systems a useful way to digest samples for trace metals analysis. Systems typically consist of either a metal or graphite block with wells to hold digestion tubes. The block temperature controller must be able to maintain uniformity of temperature (65°C to 85°C) across all positions of the block. For trace metals analysis, the digestion tubes should be constructed of polypropylene and have a volume accuracy of at least 0.5 %. All lots of tubes should come with a certificate of analysis to demonstrate suitability for their intended purpose.

13.4 Cool and filter the samples through a suitable filter (11.8) (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 Utilize sample from 13.4 acidified sample and determine its absorbance or concentration at 248.3 nm. Aspirate HNO<sub>3</sub> (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<sup>4</sup>

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:

$$S_T = 0.050 X + 0.114$$

$$S_o = 0.024 X + 0.078$$

*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

<sup>4</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1035. Contact ASTM Customer Service at service@astm.org.

**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

$X$  = 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 **D2777 – 77** which was in place at the time of collaborative testing. Under the allowances made in 1.4 of Practice **D2777 – 08, – 13**, 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~~**four** 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 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. Analyze a blank to verify system cleanliness.

16.2.3 If calibration cannot be verified, recalibrate the instrument.

16.2.4 It is recommended to analyze a continuing calibration blank (CCB) and continuing calibration verification (CCV) at a 10 % frequency. The results should fall within the expected precision of the method or  $\pm 15\%$  of the known concentration.

### 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.

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 **D5847** 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, prepare and 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. (laboratory defined or 20 samples). The laboratory control samples for a large batch should cover the analytical range when possible. It is recommended, but not



required to use a second source, if possible and practical for the LCS. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for a mid-range LCS shall fall within  $\pm 15\%$  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 laboratory-defined 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 laboratory-defined 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:

- $A$  = 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) of spiking solution added.

16.6.4 The percent recovery of the spike shall fall within the limits, based on the analyte known concentration, listed in Guide **D5810**, Table 1. If the percent recovery is not within these limits, a matrix interference may be present in the sample selected for spiking. Under these circumstances, one of the following remedies must be employed: the matrix interference must be removed, all samples in the batch must be analyzed by a test method not affected by the matrix interference, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

NOTE 9—Acceptable spike recoveries are dependent on the known concentration of the component of interest. See Guide **D5810** for additional information. <https://standards.iteh.ai/catalog/standards/sist/7da821dc-8db7-4632-add7-3d801aad4b22/astm-d1068-15>

16.7 *Duplicate:*

16.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each laboratory-defined 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 **D5847** 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 B—ATOMIC ABSORPTION,  
GRAPHITE FURNACE**

**17. Scope**

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

17.2 This test method is applicable in the range from 5 to 100  $\mu\text{g/L}$  of iron using a 20- $\mu\text{L}$  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). ICP-MS may also be appropriate but at a higher instrument cost. See Test Method **D5673**.