



## Standard Test Method for Aluminum in Water<sup>1</sup>

This standard is issued under the fixed designation D 857; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope

1.1 This test method covers the direct flame atomic absorption determination of aluminum in the nitrous oxide-acetylene flame.

1.2 This test method is applicable to waters containing dissolved and total recoverable aluminum in the range from 0.5 to 5.0 mg/L. Aluminum concentrations as high as approximately 50 mg/L can be determined using this test method without dilution. However, no precision and bias data are available for concentrations greater than 5.0 mg/L.

1.3 This test method was tested on reagent, natural, and potable waters. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

1.4 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), iron (Test Methods D 1068), lead (Test Method D 3559), manganese (Test Method D 858), and zinc (Test Methods D 1691).

1.5 Precision and bias data have been obtained on reagent, natural, and potable waters. It is the responsibility of the user to ensure the validity of this test method on untested matrices.

1.6 *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 Note 1, Note 2, and Note 3.

1.7 Former Test Methods A (Fluorometric) and B and C (Spectrophotometric) were discontinued. Refer to Appendix X1 for historical information.

### 2. Referenced Documents

#### 2.1 ASTM Standards:

- D 858 Test Method for Manganese in Water<sup>2</sup>
- D 1066 Practice for Sampling Steam<sup>2</sup>
- D 1068 Test Methods for Iron in Water<sup>2</sup>
- D 1129 Terminology Relating to Water<sup>2</sup>
- D 1193 Specification for Reagent Water<sup>2</sup>

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee D-19 on Water and are the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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

- D 1687 Test Methods for Chromium in Water<sup>2</sup>
- D 1688 Test Methods for Copper in Water<sup>2</sup>
- D 1691 Test Methods for Zinc in Water<sup>2</sup>
- D 1886 Test Methods for Nickel in Water<sup>2</sup>
- D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water<sup>2</sup>
- D 3370 Practices for Sampling Water from Closed Conduits<sup>2</sup>
- D 3558 Test Methods for Cobalt in Water<sup>2</sup>
- D 3559 Test Method for Lead in Water<sup>2</sup>
- D 4841 Practice for Estimation of Holding Times for Water Samples Containing Organic and Inorganic Constituents<sup>2</sup>

### 3. Terminology

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

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *total recoverable aluminum*—an arbitrary term relating to the forms of aluminum recovered in the acid digestion procedure specified in this test method.

### 4. Summary of Test Method

4.1 Aluminum is determined by direct atomic absorption with only the addition of an ionization suppressor and sensitivity enhancer (optional).

### 5. Significance and Use

5.1 Although there is little information available concerning the toxicological significance of aluminum in man, the American Water Works Association has established a water quality guideline or goal of a maximum of 0.05 mg/L. Under the National Pollution Discharge Elimination System, some permits may set aluminum discharge limits. Some evidence does exist to indicate that low levels (5 mg/L) will interfere with activated sludge processes. For the above reasons monitoring of aluminum may be desirable.

5.2 Aluminum is monitored in boiler make-up water, where alum has been used, to determine whether aluminum is present after pretreatment. Residual aluminum may consume ion exchange capacity or consume boiler water treatment chemicals added to stoichiometrically chelate hardness ions (that is, calcium and magnesium) in boiler feed water.

5.3 Aluminum is monitored in cooling water make-up, since its presence may result in deactivation of anionic substances in scale or corrosion inhibitor treatment chemicals, or both. Deactivation may result in decreased performance of inhibitors.

## 6. Interferences

6.1 Aluminum ionizes slightly in the nitrous oxide-acetylene flame, but the addition of sodium chloride described in this test method suppresses this interference. By this technique, a maximum concentration of 9000 mg/L sodium, 9000 mg/L potassium, 4000 mg/L calcium, 4000 mg/L magnesium, 9000 mg/L sulfate, 9000 mg/L chloride, 9000 mg/L nitrate, and 9000 mg/L iron may be tolerated.

## 7. Apparatus

7.1 *Atomic Absorption Spectrophotometer*, for use at 309.3 nm.

7.2 *Aluminum Hollow-Cathode Lamp*—Multielement lamps are not recommended.

7.3 *Oxidant*—See 8.8.

7.4 *Fuel*—See 8.9.

7.5 *Pressure-Reducing Regulators*—The supplies of fuel and oxidant should be reduced by suitable regulators to the levels recommended by the manufacturer of the spectrophotometer.

NOTE 1—**Warning:** The nitrous oxide-acetylene flame is hazardous due to its flash-back potential. Follow the instrument manufacturer's recommended operating procedures closely.

## 8. Reagents and Materials

8.1 *Purity of Reagents*—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.

8.2 *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 lessening the bias and precision of the determination. Type II water was specified at the time of round-robin testing of this test method.

8.3 *Aluminum Solution, Standard (1 mL = 0.1 mg Al)*—Dissolve 1.758 g of aluminum potassium sulfate ( $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ) in water. Add 1 mL of nitric acid and dilute to 1 L.

8.4 *Bis-(2-Ethoxyethyl) Ether*.

NOTE 2—**Warning:** Avoid inhalation. Perform all manipulation in a well-ventilated hood. This ether can form dangerous peroxides and should be inspected regularly for their presence.

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

8.6 *Nitric Acid (sp gr 1.42)*—Concentrated nitric acid ( $\text{HNO}_3$ ).

<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.

8.7 *Sodium Chloride Solution (25.4 g/L)*—Dissolve 25.4 g of sodium chloride (NaCl) in water and dilute to 1 L.

8.8 *Oxidant:*

8.8.1 *Air*, which has been suitably dried and filtered, is used to support combustion before switching to nitrous oxide.

8.8.2 *Nitrous Oxide* is the required oxidant.

8.9 *Fuel:*

8.9.1 Standard commercially available acetylene is the required fuel. The cylinder should be replaced at a gage pressure of 517 kPa (75 psi) to minimize the carry-over of acetone. Since "purified" grades contain a solvent that softens poly(vinyl chloride) tubing, its use constitutes a safety hazard and is not recommended.

## 9. Sampling

9.1 Collect samples in accordance with Practices D 1066 or D 3370, as applicable. For dissolved aluminum, filter the samples at the time of collection through a 0.45- $\mu\text{m}$  filter. Acidify the filtrate to pH 2 or less with nitric acid. For total recoverable aluminum, acidify the unfiltered sample to pH 2 or less at the time of collection. The holding time for samples may be calculated in accordance with Practice D 4841.

9.2 Soak all glassware in hot HCl (1 + 1) for 2 h. Drain and rinse at least five times with water. Drain and flush with methyl alcohol, ethyl alcohol, or isopropyl alcohol.

## 10. Preparation of Apparatus

10.1 Soak all glassware in hot HCl (1 + 1) for 2 h. Drain and rinse at least five times with water. Drain and flush with methyl alcohol, ethyl alcohol, or isopropyl alcohol.

## 11. Calibration and Standardization

11.1 Prepare aluminum standards in the range from 0.0 to 5.0 mg/L by dilution of the aluminum standard solution (see 8.3) with water.

11.2 Add 1.0 mL of NaCl solution to 10.0 mL of standard and mix thoroughly. If very low concentrations of aluminum are anticipated in the samples, 1 mL of *bis*-(2-ethoxyethyl) ether may be added to the blank and each standard, which will act as a sensitivity enhancer. If this sensitivity enhancer is used, it must also be added to each sample (12.6).

11.3 Measure the absorbance of the standards and construct an analytical curve by plotting the absorbance of the standards versus the concentration of aluminum. Alternatively, read directly in concentration if this capability is provided with the spectrophotometer.

## 12. Procedure

12.1 If dissolved aluminum is to be determined proceed to 12.6.

12.2 Measure a volume of well-mixed acidified sample containing less than 0.5 mg of aluminum (100 mL maximum) into a 125-mL beaker.

12.3 Add 0.5 mL of  $\text{HNO}_3$  and 5 mL of HCl.

12.4 Heat the samples on a hot plate in a well-ventilated hood until the volume has been reduced to 10 to 15 mL, making certain the samples do not boil.

NOTE 3—For brines and samples with high levels of suspended matter, the amount of reduction in volume is left to the discretion of the analyst.

12.5 Cool and, if necessary, filter the samples through a filter (fine-texture, acid-washed, ashless paper) into a 100-mL volumetric flask. Wash the paper several times and bring the volume to 100-mL.

12.6 To a 10-mL aliquot of sample add 1.0 mL of NaCl and mix thoroughly. If 1 mL of bis-(2-ethoxyethyl) ether was added to the blank and standards as a sensitivity enhancer (11.2), an equal amount must be added to each sample.

12.7 Atomize each of the standards, samples, and blank and determine its absorbance or concentration. Atomize water between samples.

### 13. Calculation

13.1 Determine the concentration of aluminum in each sample by referring to the calibration curve in 13.3.

13.2 Calculate the concentration of total recoverable aluminum in milligrams per litre using Eq. 1:

$$\text{Aluminum, mg/L} = C \times (100/V) \quad (1)$$

where:

$C$  = concentration from curve, mg/L, and

$V$  = volume of aliquot, mL.

13.3 Calculate the concentration of dissolved aluminum directly from the calibration curve.

### 14. Precision and Bias <sup>4</sup>

14.1 Precision data for this test method were obtained on reagent, natural, and potable waters. It is the user's responsibility to assure the validity of this test method for waters of untested matrices.

14.2 The collaborative test of the direct atomic absorption test method for aluminum in reagent water was performed at three levels by four laboratories (seven operators) making a total of fifteen observations at each level. The test in matrix water at the same levels was performed by three laboratories (six operators) making a total of twelve observations at each level.

<sup>4</sup>Supporting data are available from ASTM Headquarters, 1916 Race St., Philadelphia, PA 19103. Request Research Report RR: D19 - 1064.

**TABLE 1 Overall ( $S_T$ ) and Single-Operator ( $S_o$ ) Interlaboratory Precision for Aluminum by Direct AAS**

Reagent Water:			
Concentration ( $X$ ), mg/L	0.848	2.54	4.11
$S_T$	0.167	0.19	0.19
$S_o$	0.128	0.18	0.23
Natural Water:			
Concentration ( $X$ ), mg/L	0.772	2.48	4.07
$S_T$	0.194	0.19	0.21
$S_o$	0.166	0.16	0.28

**TABLE 2 Recovery by Direct AAS**

Amount Added, mg/L	Amount Found, mg/L	% Bias	Statistically Significant (95 % Confidence Level)
Reagent Water			
0.749	0.848	+ 13.2	yes
2.49	2.54	+ 2.0	no
4.49	4.11	-8.4	yes
Matrix Water			
0.749	0.772	+ 3.1	no
2.49	2.48	-0.4	no
4.49	4.07	-9.4	yes

14.3 Precision and bias for this test method conform to Practice D 2777-77, which was in place at the time of collaborative testing. Under the allowances made in 1.5 of Practice D 2777-86, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D-19 test methods.

14.4 The overall and single-operator precision of this test method ( $S_T$  and  $S_o$  respectively) within its designated range for reagent water and selected water matrices varies with the quantity tested in accordance with Table 1.

14.5 Recoveries of known amounts of aluminum from reagent water, Type II, and selected water matrices were as shown in Table 2.

14.6 The sensitivity enhancer was not used in collaborative tests. It is the user's responsibility to determine its effect on precision and bias.

### 15. Keywords

15.1 aluminum; analysis; atomic absorption flame; water

## APPENDIX

### (Nonmandatory Information)

#### X1. RATIONALE FOR DISCONTINUATION OF TEST METHODS

##### X1.1 Former Test Method A—Fluorometric:

X1.1.1 This test method was discontinued in 1988. The test method may be found in its entirety in the 1988 *Annual Book of ASTM Standards*, Vol 11.01.

X1.1.2 This test method is applicable to the determination of soluble aluminum in water in concentrations below 5 µg/L. The water must be of relatively high purity. Heavy metal ions of the order of 20 µg/L produce interferences.

X1.1.3 The fluorescence of an aluminum-morin complex formed at a pH of 3 is measured and referred to a previously

prepared calibration curve to determine the aluminum concentration.

X1.1.4 This test method was discontinued because there were insufficient laboratories interested in participating in another collaborative study to obtain the necessary precision and bias as required by Practice D 2777.

##### X1.2 Former Test Method B—Spectrophotometric:

X1.2.1 This test method was discontinued in 1988. The test method may be found in its entirety in the 1988 *Annual Book*

of *ASTM Standards*, Vol 11.01.

X1.2.2 This test method is applicable to the determination of total aluminum in water in the range from 0.00 to 0.50 mg/L as Al<sup>3+</sup> (based on a 100-mL sample). The range of the test may be extended by taking a suitable aliquot.

X1.2.3 The aluminum is complexed with sodium fluoride to prevent its reaction with 8-quinolinol while interfering ions are removed by a weak cationic ion exchange resin and an 8-quinolinol-chloroform extraction. The aluminum is then made reactive to the 8-quinolinol by pH adjustment and its chloroform-extracted 8-quinolate is measured spectrophotometrically.

X1.2.4 This test method was discontinued because there were insufficient laboratories interested in participating in another collaborative study to obtain the necessary precision and bias as required by Practice D 2777.

### X1.3 Former Test Method C—Spectrophotometric:

X1.3.1 This test method was discontinued in 1988. The test

method may be found in its entirety in the 1988 *Annual Book of ASTM Standards*, Vol 11.01.

X1.3.2 This test method is applicable to water relatively free of interfering substances. The procedure is simple and rapid, but only soluble aluminum is determined.

X1.3.3 Ferron (8-hydroxy-7-iodo-5-quinoline sulfonic acid) reacts with aluminum to form a soluble complex that absorbs ultraviolet light. The absorbance of the complex is proportional to the soluble aluminum and is measured by a spectrophotometer at a wavelength of 370 nm.

X1.3.3.1 A significant interference from iron is greatly minimized by adding orthophenanthroline. This has the additional advantage that iron may be simultaneously determined, but at a wavelength of 520 nm.

X1.3.4 This test method was discontinued because there were insufficient laboratories interested in participating in another collaborative study to obtain the necessary precision and bias as required by Practice D 2777.

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