Designation: D 857 – ~~95~~02

Standard Test Method for Aluminum in Water[1]

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 (ϵ) 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:*

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[1] 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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D 858 Test Method for Manganese in Water[2]
D 1066 Practice for Sampling Steam[2]
D 1068 Test Methods for Iron in Water[2]
D 1129 Terminology Relating to Water[2]
D 1193 Specification for Reagent Water[2]
D 1687 Test Methods for Chromium in Water[2]
D 1688 Test Methods for Copper in Water[2]
D 1691 Test Methods for Zinc in Water[2]
D 1886 Test Methods for Nickel in Water[2]
D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water[2]
D 3370 Practices for Sampling Water from Closed Conduits[2]
D 3558 Test Methods for Cobalt in Water[2]
D 3559 Test Method for Lead in Water[2]
D 4841 Practice for Estimation of Holding Times for Water Samples Containing Organic and Inorganic Constituents[2]
D 5810 Guide for Spiking into Aqueous Samples[2]
D 5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis[3]

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.

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

[3] ~~*Reagent Chemicals, American Chemical Society Specifications* , American Chemical Society, Washington, DC. For suggestions on the testing~~Annual Book of~~ reagents not listed by the American Chemical Society, see *Analar*~~ *ASTM 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.~~ Vol 11.02.

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. [4] 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 ($AlK(SO_4)_2 \cdot 12H_2O$) in water. Add 1 mL of nitric acid and dilute to 1 L. A purchased stock solution of appropriate purity is also acceptable.

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 (HNO_3).

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-µm 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, ehtyl 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~~ from 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 HNO_3 and 5 mL of HCl.

~~[4] Supporting data are available from ASTM Headquarters, 1916 Race St., Philadelphia, PA 19103. Request Research Report RR: D19 – 1064.~~

[4] *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.

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:

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

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 [5]

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.

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~~ 1.4 of Practice D 2777–98~~6~~, 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. Quality Control

15.1 In order to be certain that analytical values obtained using this test method are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing aluminum by this test method.

15.2 *Calibration and Calibration Verification*:

15.2.1 Analyze at least three working standards containing concentrations of aluminum that bracket the expected sample concentration prior to analysis of samples to calibrate the instrument.

15.2.2 Verify instrument calibration after standardization by analyzing a standard at the concentration of one of the calibration standards. The absorbance shall fall within 4% of the absorbance from the calibration. Alternately, the concentration of a mid-range standard should fall within ± 10% of the known concentration.

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[5] Supporting data are available from ASTM International Headquarters, 100 Barr Harbor Dr., West Conshohocken, PA 19428. 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

15.2.3 If calibration cannot be verified, recalibrate the instrument.

15.3 *Initial Demonstration of Laboratory Capability*:

15.3.1 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.

15.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing 2.5 mg/L of aluminum. 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.

15.3.3 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.

15.4 *Laboratory Control Sample (LCS)*:

15.4.1 To ensure that the test method is in control, analyze a LCS containing a mid-range concentration of aluminum with each batch or 10 samples. If large numbers of samples are analyzed in the batch, analyze the LCS after every 10 samples. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for the LCS shall fall within ± 15 % of the known concentration.

15.4.2 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.

15.5 *Method Blank*:

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

15.6 *Matrix Spike (MS)*:

15.6.1 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 aluminum and taking it through the analytical method.

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

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

$$P = \frac{100\,[A(V_s + V) - B\,V_s]}{C\,V} \qquad (2)$$

where

A= Analyte Concentration (µg/L) in Spiked Sample

B= Analyte Concentration (µg/L) in Unspiked Sample

C= Concentration (µg/L) of Analyte in Spiking Solution

V_s= Volume (mL) of Sample Used

V= Volume (mL) added with Spike

15.6.4 The percent recovery of the spike shall fall within the limits, based on the analyte 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: acceptable spike recoveries are dependent on the concentration of the component of interest. See Guide 5810 for additional information.

15.7 *Duplicate*:

15.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each batch. If the concentration of the analyte is less than five times the detection limit for the analyte, an MSD should be used.

15.7.2 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.

15.7.3 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.

15.8 *Independent Reference Material (IRM)*:

15.8.1 In order to verify the quantitative value produced by the test method, analyze an IRM submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the reference material should be in the range of 2-3 mg/L aluminum. The value obtained must fall within the control limits established by the laboratory.

16. Keywords

1~~5~~6.1 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^{3+}(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-quinolinate is measured spectrohotometrically.

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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