



Designation: D8596 – 24

Standard Test Method for Bioavailable Aluminum in Water with Suspended Solids¹

This standard is issued under the fixed designation D8596; 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 determination of bioavailable aluminum in water using an extraction procedure at a pH of 4 and an aging period of 3 h following the addition of an acidic buffer.

1.2 This test method uses existing analytical methods for the determination of aluminum in water and only presents a new extraction procedure designed to recover the bioavailable fraction of aluminum present in a water sample.

1.3 This test method is designed to be used to assess the potential for aluminum in water samples to be toxic to aquatic life.

1.4 This test method is applicable to waters containing dissolved, polymeric, and mineral forms of aluminum and is applicable to concentrations ranging from 0.01 mg/L to 5 mg/L.

1.5 This test method was tested on natural surface waters and wastewaters containing suspended solids. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

1.6 Precision and bias have been obtained on natural waters, wastewaters, and reagent waters. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

1.7 *Units*—The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.8 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.9 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recom-*

mendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

2. Referenced Documents

2.1 ASTM Standards:²

- D1129 Terminology Relating to Water
- D1193 Specification for Reagent Water
- D1293 Test Methods for pH of Water
- D1976 Test Method for Elements in Water by Inductively-Coupled Plasma Atomic Emission Spectroscopy
- D3370 Practices for Sampling Water from Flowing Process Streams
- D5673 Test Method for Elements in Water by Inductively Coupled Plasma—Mass Spectrometry
- E70 Test Method for pH of Aqueous Solutions With the Glass Electrode
- E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods
- E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

2.2 EPA Standards:³

- EPA Method 200.1 Determination of Acid Soluble Metals
- EPA Method 200.7 Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry
- EPA Method 200.8 Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D1129.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *aqueous bioavailable aluminum, n*—an extraction of aluminum in aqueous solution in the presence of suspended solids at pH 4.

¹ This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at www.astm.org/contact. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ Available from United States Environmental Protection Agency (EPA), William Jefferson Clinton Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, <http://www.epa.gov>.

3.2.1.1 *Discussion*—These forms include the metal ions (Al^{+3}) and the aluminum either as monomers or polymers.

3.3 *Acronyms:*

3.3.1 *AAS*—Atomic absorption spectrometry

3.3.2 *DI*—Deionized water

3.3.3 *DOC*—Dissolved organic carbon

3.3.4 *EPA*—U.S. Environmental Protection Agency

3.3.5 *HCl*—Hydrochloric acid

3.3.6 *HDPE*—High-density polyethylene

3.3.7 *ICP-MS*—Inductively coupled plasma-mass spectrometry

3.3.8 *ICP-OES*—Inductively coupled plasma-optical emission spectrometry

3.3.9 *LDPE*—Low-density polyethylene

3.3.10 *QC*—Quality control

4. Summary of Test Method

4.1 Bioavailable aluminum in a water sample is determined by acidifying the sample to a pH of 4 using a buffer for the purpose of converting aluminum hydroxides to their respective ionic forms (Al^{+3}) and keeping them in solution. Natural water and wastewater contain suspended solids often in the range of 25 mg/L to 300 mg/L. The pH adjustment is sufficient to reduce the aluminum polymeric forms to Al^{+3} without dissolving the aluminum that may be present in the suspended solids. Once the sample is adjusted to pH 4 with an acidic buffer to stabilize pH, the sample is allowed to equilibrate for 3 h, followed by filtration.

4.2 The determination of the concentration of aluminum in the pH 4 extracted sample is carried out using one of the following methods according to standard U.S. EPA or ASTM guidance: flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma-optical emission spectrometry (ICP-OES), inductively coupled plasma-mass spectrometry (ICP-MS), or a combination of methods (ICP-OES (Test Method [D1976](#)), ICP-MS (Test Method [D5673](#)), EPA Method 200.8, and EPA Method 200.7). No additional digestion occurs after the filtration (0.45 μm filter) step of the pH 4 method, acid preservation, and before the determination of aluminum concentrations.

4.3 EPA Method 200.1 provides an earlier version of a method designed to be less robust than total recoverable. The method uses a pH adjustment to a pH of 1.65 to 1.85 and a 16 h holding period, followed by filtration.

5. Significance and Use

5.1 Recent research results investigating the relationship between water chemistry and aluminum toxicity to aquatic organisms are available. Toxicity was shown to vary as a function of pH, dissolved organic carbon (DOC), and hardness. Biological responses in toxicity tests do not correlate with dissolved metal because in circumneutral waters (pH 6 to 8.5) aluminum occurs as a hydroxide species or mineral particulate,

both of which are removed by filtration. As such, filtration removes some of the metal species responsible for toxicity.

5.2 The U.S. Environmental Protection Agency (EPA) established water quality criteria for aluminum. Many U.S. states have adopted these criteria and require dischargers to meet water quality standards placed in their discharge permit. No direct relationship between dissolved aluminum and toxicity was shown for a wide variety of aquatic organisms in chronic toxicity studies. Toxicity does, however, correlate with aluminum measurements obtained using the pH 4 extraction method.

5.3 Natural water and wastewater frequently contain significant levels of suspended solids (25 mg/L to 300 mg/L) containing minerals high in aluminum. Regulatory authorities typically recommend measurement of total recoverable aluminum, which uses a strong acid and heat digestion. This digestion procedure results in most or all of the inert non-toxic aluminum present in suspended solids being dissolved and the metal reported as “total or total recoverable.”

5.4 The current method (pH 4 extraction) was developed to provide a method that measures aqueous bioavailable aluminum not associated with suspended solids. The data supporting the use of this method to assess toxicity can be found in the publication by Rodriguez et al.⁴

5.5 The current pH 4 extraction method provides analytical results that are typically greater than the dissolved metal concentration in the same water sample and less than the total recoverable concentration. In water samples with no to very little suspended solids, the pH 4 extracted concentration and the total aluminum concentration are often the same.

5.6 Aluminum salts are frequently used as flocculants in drinking water plants and wastewater treatment plants.

5.7 Aluminum is common in some industrial wastewaters and acid mine (rock) drainage.

6. Apparatus

6.1 *Atomic absorption spectrometer* (FAAS, GFAAS), *Inductively Coupled Plasma–Mass Spectrometer* (ICP-MS), or *Inductively Coupled Plasma–Optical Emission Spectrometer* (ICP-OES).

6.2 See Section 2 and 4.2 for specific methods for use of these instruments. Measurements of aluminum by the selected instrument should follow the manufacturer instructions, calibration procedures, and quality control procedures of the chosen method (see Test Methods [D1976](#) and [D5673](#)).

6.3 *pH Meter and Probe*—Specific methods for the use of pH meters and probes should conform to Test Methods [D1293](#) or [E70](#). Probe will need to be small enough to measure the pH of water in a 50 mL conical tube.

6.4 *Orbital shaker or rotator* capable of 100 rpm.

⁴ Rodriguez, P., Arbildua, J., Villavicencio, G., Urrestarazu, P., Opazo, M., Cardwell, A., Stubblefield, W., Nordheim, E., and Adams, W., Determination of Bioavailable Aluminum in Natural Waters in the Presence of Suspended Solids. *Environmental Toxicology and Chemistry*, 38 (8): 1669–1676 (2019).