



Designation: D511 – 14 (Reapproved 2021)^{ε1}

Standard Test Methods for Calcium and Magnesium in Water¹

This standard is issued under the fixed designation D511; 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.

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

^{ε1} NOTE—The WTO caveat was added editorially in December 2021.

1. Scope

1.1 These test methods cover the determination of calcium and magnesium in water by complexometric titration and atomic absorption spectrometric procedures. Two test methods are included, as follows:

Test Method A—Complexometric Titration

Test Method B—Atomic Absorption Spectrometric

Sections

7 – 15

16 – 25

1.2 The values stated in SI units are to be regarded as standard. The values given in parentheses are mathematical conversion to inch-pound units that are provided for information only and are not considered standard.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific hazard statements are given in 12.2.6 and 20.6.

1.4 *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 Recommendations 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

D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water

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

D3370 Practices for Sampling Water from Flowing Process Streams

D4691 Practice for Measuring Elements in Water by Flame Atomic Absorption Spectrophotometry

D4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents

D5810 Guide for Spiking into Aqueous Samples

D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

3. Terminology

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

4. Significance and Use

4.1 Calcium and magnesium salts in water are the primary components of water hardness which can cause pipe or tube scaling.

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.³ 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, II, or III water. Type I is preferred and more commonly used. Type II water was specified at the time of round-robin testing of these test methods.

NOTE 1—The user must ensure the type of reagent water is sufficiently

³ *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 *Annual Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

free of interferences. The water should be analyzed using this test method.

6. Sampling

6.1 Collect the sample in accordance with Practices **D3370**.

6.2 If total recoverable calcium and magnesium concentrations are being determined, acidify the water sample with HNO_3 (sp gr 1.42) to a pH of 2 or less immediately at the time of collection; normally about 2 mL/L are required. The holding time for the samples may be calculated in accordance with Practice **D4841**.

NOTE 2—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 dissolved calcium and magnesium concentrations are being determined, filter the samples through a 0.45- μm membrane filter and acidify with HNO_3 (sp gr 1.42) to a pH of 2 or less immediately at time of collection; normally about 2 mL/L are required.

6.4 A number of sources of calcium contamination have been encountered in laboratories. Among the most common are plastic ware, paper towels, and dust. Rinsing plastic ware with sample prior to use, avoiding contact of apparatus with paper towels, and keeping exposure to the air to a minimum will limit the possibility of contamination.

TEST METHOD A—COMPLEXOMETRIC TITRATION

7. Scope

7.1 This test method is applicable to most waters in a range from 1 to 1000 mg/L of calcium plus magnesium expressed as calcium, but may fail in the analysis of highly colored waters, brines, or waters that contain excessive amounts of metals. The upper and lower limits may be extended by either dilution or use of micro apparatus.

7.2 Data are not available to determine which matrices were used to obtain the precision and bias data, and it is the responsibility of the analyst to determine the acceptability of this test method for the matrix being analyzed.

8. Summary of Test Method

8.1 EDTA (ethylenediamine tetraacetic acid or its salts) is added to a sample containing calcium and magnesium ions after the pH of the solution is adjusted to 10 for the determination of calcium and magnesium or from pH 12 to 13 for the determination of calcium alone. The EDTA initially complexes the calcium and then the magnesium. The end point is observed by the use of a suitable indicator. At a pH of 12 to 13 magnesium is precipitated. Magnesium is determined by the difference between an aliquot titrated at pH 10 and one titrated at pH 12 to 13.

9. Interferences

9.1 EDTA reacts with iron, manganese, copper, zinc, lead, cobalt, nickel, barium, strontium, calcium, magnesium, and several other metals. The interference of heavy metals is

minimized by the addition of hydroxylamine and cyanide, which reduce or complex the metals, or both. Metal concentrations as high as 5 mg/L of iron, 10 mg/L of manganese, 10 mg/L of copper, 10 mg/L of zinc, and 10 mg/L of lead can be tolerated when hydroxylamine and cyanide are added.

9.2 In the titration of calcium plus magnesium, the higher oxidation states of manganese above Mn^{+2} react rapidly with the indicator to form discolored oxidation products. Hydroxylamine hydrochloride reagent is used to reduce manganese to the divalent state. The divalent manganese interference can be eliminated by addition of one or two small crystals of potassium ferrocyanide.

9.2.1 Orthophosphate and sulfate ions interfere at concentrations in excess of 500 and 10 000 mg/L, respectively.

9.2.2 In the presence of aluminum concentrations in excess of 10 mg/L, the blue color that indicates that the end point has been reached will appear and then, on short standing, will revert to red. The reversion should not be confused with the gradual change that normally takes place in the titrated sample several minutes after the titration has been completed.

9.3 In the titration of calcium, ammonium purpurate reacts with strontium but not with magnesium or barium. However, the end point in the presence of strontium is sluggish, and the titration is not strictly stoichiometric. Barium does not titrate as calcium, but affects the indicator in some unknown way so that no end point, or at best a poor end point, is obtained. Barium can be removed by prior precipitation with sulfuric acid, but care must be exercised to prevent precipitation of calcium. Orthophosphate will precipitate calcium at the pH of the test.

9.4 A possible interference from the commonly used polyphosphates, organic phosphonates, and EDTA/NTA compounds in water treatment should be recognized.

10. Apparatus

10.1 *Titration Assembly*—Some analysts prefer to use conventional lighting and hand stirring. Others report better results by using a visual-titration assembly consisting of a motor-driven stirrer, 25-mL burette, white-porcelain-base burette holder, and shaded incandescent lamp. The sample beaker is placed near the front of the porcelain base and the reaction is viewed diagonally downward through the side of the beaker and against the white background. Illumination is from behind the beaker. The capacity of the burette, type lighting, and background color may be varied depending on the ionic concentrations normally encountered and the indicator chosen.

10.2 *pH Meter*, with expanded mV scale.

11. Reagents and Materials

11.1 *Buffer Solution, Ammonium Chloride-Ammonium Hydroxide*—Dissolve 67.6 g of ammonium chloride (NH_4Cl) in 200 mL of water. Add 570 mL of concentrated ammonium hydroxide (NH_4OH , sp gr 0.900). Add 5.00 g of magnesium salt of EDTA and dilute to 1000 mL. Store in a tightly stoppered plastic bottle to prevent the loss of ammonia. Discard the solution when 1 mL added to a neutralized sample fails to produce a pH of 10.0 ± 0.1 at the titration end point. To attain highest accuracy, adjust the magnesium level to exact