



Designation: D8192 – 23

Standard Test Method for Hardness in Colored and Colorless Water¹

This standard is issued under the fixed designation D8192; 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 (ϵ) indicates an editorial change since the last revision or reappraisal.

1. Scope

1.1 This test method covers the determination of hardness in water by titration with potentiometric detection via optical sensor. This test method is applicable to waters that are free of chemicals that will complex calcium or magnesium. The lower detection limit of this test method is approximately 2 mg/L to 5 mg/L as CaCO_3 ; the upper limit can be extended to all concentrations by sample dilution. It is possible to differentiate between hardness due to calcium ions and that due to magnesium ions by this test method.

1.2 This test method is applicable to both colorless and colored water samples including groundwater, surface water, wastewater, and drinking water.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *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.*

1.5 *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

D1066 Practice for Sampling Steam

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
D3370 Practices for Sampling Water from Flowing Process Streams
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 this test method, refer to Terminology D1129.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *equivalent parts per million (epm), n*—unit chemical equivalent weight of solute per million unit weights of solution.

3.2.2 *laboratory control sample (LCS), n*—solution with certified hardness.

3.2.3 *optical sensor, n*—potentiometric sensor for titration with photometric endpoint recognition.

4. Summary of Test Method

4.1 Calcium and magnesium ions in water are sequestered by the addition of disodium ethylenediamine tetraacetate (EDTA). The equivalence point of the reaction is detected by means of Eriochrome Black T,^{3, 4} which has a red color in the presence of calcium and magnesium and a blue color when they are sequestered. This can be determined by both manual colorimetric titration with visual detection or by automatic titration using an optical sensor. During a manual titration the titrant is added by the operator and color change is determined by visual inspection. This can lead to subjective and inaccurate results. This method describes the use of an automatic titrator equipped with an optical sensor to accurately add known volumes of titrant and accurately determine the titration equivalence or end point. During an automatic titration, the optical sensor measures absorbance at a particular wavelength that is converted to a millivolt signal and plotted versus titrant volume. See Fig. 1. At the equivalence point, where the color change from red to blue occurs, there will be a corresponding inflection or break point on the titration curve. The volume of

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 service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ Eriochrome is a registered trademark of Huntsman Petrochemical, LLC.

⁴ 3-Hydroxy-4-(1-hydroxy-2-naphthyl) azo-7-nitro-1 naphthalenesulfonic acid, sodium salt, Color Index 14645.