



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 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 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 CaCO₃; 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](#)

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.

Current edition approved April 15, 2023. Published May 2023. DOI: 10.1520/D8192-23.

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.

[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

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.

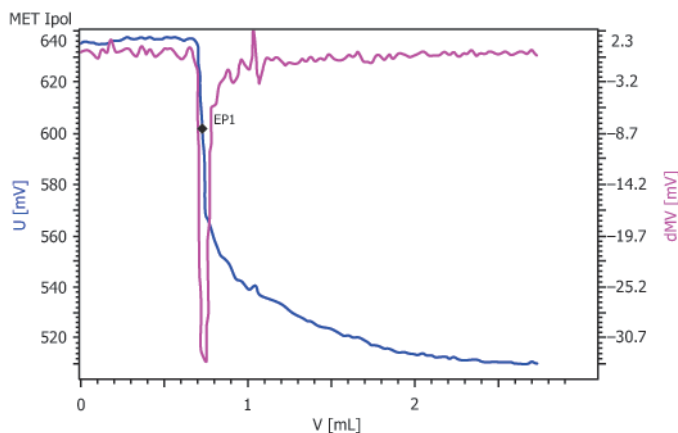


FIG. 1 Titration Curve

titrant added to achieve this equivalence point is then used to calculate the calcium and magnesium ions in water.

5. Significance and Use

5.1 Hardness salts in water, notably calcium and magnesium, are the primary cause of tube and pipe scaling, which frequently causes failures and loss of process efficiency due to clogging or loss of heat transfer, or both.

5.2 Hardness is caused by any polyvalent cations, but those other than Ca^{+2} and Mg^{+2} are seldom present in more than trace amounts. The term hardness was originally applied to water in which it was hard to wash; it referred to the soap-wasting properties of water. With most normal alkaline water, these soap-wasting properties are directly related to the calcium and magnesium content.

6. Interferences

6.1 The substances shown in Table 1 represent the highest concentrations that have not been found to interfere with this determination.

7. Apparatus

7.1 Automatic Titrator:

7.1.1 Automatic Titrator, consisting of a control unit, optical sensing electrode, and stirrer. An automatic titrator must be capable of adding fixed increments of titrant (monotonic) with endpoint seeking capabilities as prescribed in this test method. Titrant increment additions of 0.1 mL are recommended for this test method. At the very least, the automatic titration system shall meet the performance and specification requirements as warranted by the manufacturer.

7.1.1.1 The optical sensor must produce light between 500 nm to 700 nm wavelength to detect color change of Eriochrome Black T^{3, 4} hardness indicator and hydroxyl naphthol blue. It shall interface with the automatic titrator in such a way that the optical signal received from the change in color in the sample beaker is converted to millivolts and an end point volume of EDTA to equivalence can be determined. This end point volume shall be used to calculate hardness. Refer to the optical sensor manufacturer for ideal wavelength settings for each indicator color change or determine the ideal wavelength experimentally.

TABLE 1 Freedom of Reaction from Interferences

Substance	Maximum Concentration Without Interference in the Total Hardness Test, mg/L	Maximum Concentration Without Interference in the Calcium Hardness Test, mg/L
Aluminum, Al^{+++}	20	5
Ammonium, NH_4^+	^A	2 000
Bicarbonate, HCO_3^-	...	500
Bromine, Br	...	2
Cadmium, Cd^{++}	20	...
Carbonate, CO_3^{--}	1 000	50
Chloride, Cl^-	10 000	...
Chlorine, Cl	...	2
Chromate, CrO_4^{--}	500	500
Cobalt, Co^{++}	0.3	...
Copper, Cu^{++}	20	2
Iron, ferric, Fe^{+++}	10^B	20
Iron, ferrous, Fe^{++}	10^B	20
Lead, Pb^{++}	20	5
Manganese, Mn^{++}	1^C	10^C
Nickel, Ni^{++}	0.5^D	...
Nitrate, NO_3^-	500	500
Nitrite, NO_2^-	500	500
Phosphate, PO_4^{--}	100	...
Silicate, SiO_3^{--}	200	100
Strontium, Sr^{++}	^E	^E
Sulfate, SO_4^{--}	10 000	10 000
Sulfite, SO_3^{--}	500	500
Tannin, Quebracho	200	50
Tin, stannic, Sn^{++++}	10	5
Tin, stannous, Sn^{++}	10	5
Zinc, Zn^{++}	20	5

^A No data are available.

^B Iron will not interfere in concentrations up to 200 mg/L. However, the red color of the end point may return in about 30 s.

^C Manganese will not interfere in concentrations up to 10 mg/L if a few crystals of $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ are added to the buffer immediately before use.

^D Accurate results can be obtained in the presence of 1 mg/L nickel, but the end point is slow under these conditions.

^E If strontium is present, it will be titrated with calcium and magnesium.

7.2 Analytical Balance capable of weighing at least to the nearest 0.01 g.

8. Reagents

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.⁵ 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, reference to water shall be understood to mean reagent water conforming to Specification D1193, 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 adversely affecting the precision and bias of the test method.

⁵ ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, 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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

8.3 Buffer Solution pH 10—Commonly used buffers like ammonium hydroxide/ammonium chloride or odorless buffer solution.

NOTE 1—Once buffer is added to the sample, it will be able to maintain the pH of 10 ± 0.25 through the entirety of the titration.

8.4 Calcium Solution, Standard (1 mL = 0.20 mg CaCO_3)—Dissolve 0.2000 g of CaCO_3 in 3 mL to 5 mL of HCl (1 + 4). Dilute to 1 L with water.

8.5 Calcium Indicator—Use powdered hydroxynaphthol blue,⁶ or grind solid hydroxynaphthol blue to 40 to 50 mesh size. Alternately, calcon carboxylic acid, xylenol orange, or murexide can be used.

8.6 Hardness Indicator—The hardness indicator can be prepared, stored, and used in liquid or powder form.

8.6.1 Hardness Indicator Solution—Dissolve 0.5 g of Eriochrome Black T^{3, 4} in 50 mL of diethanolamine, triethanolamine, ethanol, or methoxyethanol. Store the solution in a dark-colored bottle. This solution has a storage life of several months.

8.6.2 Hardness Indicator Powder—Grind 0.5 g of Eriochrome Black T^{3, 4} with 100 g of powdered sodium chloride. Use a dark-colored bottle for storage. The powder has a storage life of at least 2 years.

8.7 Hydrochloric Acid (1 + 4)—Mix 1 volume of concentrated hydrochloric acid (sp gr 1.19) with 4 volumes of water.

8.8 Disodium Ethylenediamine Tetraacetate (EDTA) Solution, Standard (1 mL = 1.0 mg CaCO_3)—Dissolve 3.8 g of disodium ethylenediamine tetraacetate dihydrate in approximately 800 mL of water. Determine the concentration of this solution using the standard calcium (8.5) solution, and the procedure in Section 10 that will be used for the sample analysis (10.1, 10.2, or 10.3) or confirm strength with a standard sample if purchased. Adjust the concentration of the EDTA so that 1 mL will be equivalent to 1.0 mg of CaCO_3 . Store the standard EDTA in polyethylene, plastic, or hard rubber bottles and standardize monthly.

NOTE 2—Commercially available disodium EDTA solution may be used.

8.9 Sodium Hydroxide Solution (50 g/L)—Dissolve 50 g of sodium hydroxide in water and dilute to 1 L.

9. Sampling

9.1 Collect the sample in accordance with Practice D1066 or Practices D3370 as applicable.

10. Procedure

10.1 Hardness—Prepare the dispensing burette and any tubing of the autotitrator to ensure dispensed quantities are accurately measured. Care should be taken to ensure air bubbles are not dispensed during the titration. Verify that the optical sensor is set to the ideal wavelength for the indicator used between 500 nm to 700 nm wavelength. Measure 50 mL of sample into a sample container. Add 10 mL of buffer (8.3)

⁶ 3-Hydroxy-4 (2-hydroxy-4 sulfo-1 naphthyl) azo-2, 7-naphthalenedisulfonic acid, trisodium salt.

solution, and approximately 0.2 g of hardness (8.7) indicator powder or 2 drops (0.05 mL) of liquid and place the beaker onto the stirrer of the automatic titrator. Begin the titration according to the manufacturer's instructions. Standard EDTA (8.8) solution should be added from the burette of the autotitrator with continuous stirring until the color changes from red to blue. The end point is detected automatically and the hardness is calculated based on the sample volume. If the titration requires more than 20 mL of the titrating solution, dilute the sample and repeat the test.

10.2 Low Hardness—Determine low-hardness values (1.0 ppm to 5.0 ppm as CaCO_3) in accordance with 10.1, but use a 100 mL sample. The monotonic titrant additions should be adjusted according to manufacturer instructions.

10.3 Calcium Hardness—Measure 50 mL of sample into a sample container. Add 2 mL of NaOH (8.9) solution and stir, confirming the pH of the solution is 12 to 13 before adding indicator or titrating. Add approximately 0.2 g of calcium (8.5) indicator and stir. Begin the titration according to the manufacturer's instructions. Standard EDTA (8.8) solution should be added from the burette of the autotitrator with continuous stirring until the color changes from red to blue. The end point is detected automatically and the hardness is calculated based on the sample volume.

11. Calculations

11.1 The calculations below are used by autotitrator software to calculate the results.

11.2 Calculate the hardness, epm, of the sample as follows:

$$\text{Hardness, epm} = 20 C/S \quad (1)$$

where:

e_{pm} = equivalent parts per million; milliequivalents per liter,
 C = standard EDTA solution added in titrating hardness, mL, and
 S = sample taken, mL.

11.2.1 Calculate the calcium hardness, epm, of the sample as follows:

$$\text{Calcium hardness, epm} = 20 D/S \quad (2)$$

where:

e_{pm} = equivalent parts per million; milliequivalents per liter,
 D = standard EDTA solution added in titrating calcium hardness, mL, and
 S = sample taken for test, mL.

11.2.2 Calculate the magnesium hardness, epm, of the sample as follows:

$$\text{Magnesium hardness, epm} = E - F \quad (3)$$

where:

e_{pm} = equivalent parts per million; milliequivalents per liter,
 E = hardness, epm, and
 F = calcium hardness, epm.

11.3 Calculate the hardness as calcium carbonate of the sample as follows:

$$\text{Hardness, mg/L as CaCO}_3 = 1000 C_1/S_1 \quad (4)$$