Designation: D8192 – 23

Standard Test Method for Hardness in Colored and Colorless Water[1]

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 $CaCO_3$; 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–napththyl) azo–7–nitro–1 naphthalenesulfonic acid, sodium salt, Color Index 14645.

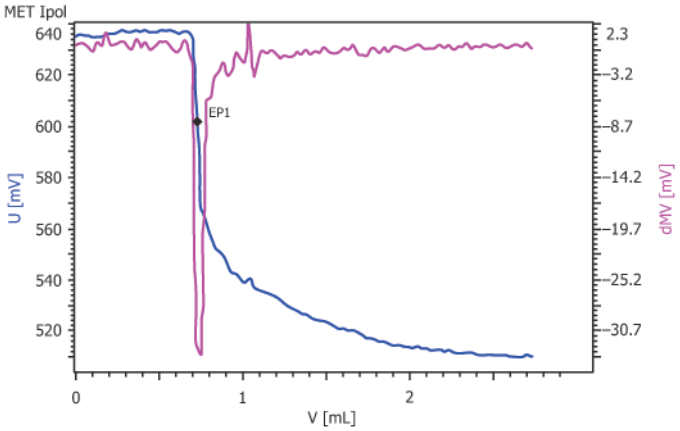

FIG. 1 Titration Curve

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.

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 $K_4Fe(CN)_6 \cdot 3H_2O$ 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. 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.

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.