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Standard Test Method for Hardness in Water[1]

This standard is issued under the fixed designation D1126; 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 Department of Defense.

ε[1] NOTE—Added acronym to ~~3.1.2~~ 3.2.2 and updated 11.5 editorially in August 2007.

1. Scope*

1.1 This test method covers the determination of hardness in water by titration. This test method is applicable to waters that are clear in appearance and free of chemicals that will complex calcium or magnesium. The lower detection limit of this test method is approximately 2 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 was tested on reagent water only. It is the user's responsibility to ensure the validity of the test method for waters of untested matrices.

~~1.3~~

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

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

3. Terminology

3.1 *Definitions:*

~~3.1.1~~*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 per million (epm), n*—a unit chemical equivalent weight of solute per million unit weights of solution.

~~3.1.2~~*3.2.2 laboratory control sample (LCS), n*—a solution with certified hardness.

~~3.1.3For definitions of other terms used in this test method, refer to Terminology D1129.~~

4. Summary of Test Method

4.1 Calcium and magnesium ions in water are sequestered by the addition of disodium ethylenediamine tetraacetate. The end point of the reaction is detected by means of Chrome Black T[3], which has a red color in the presence of calcium and magnesium and a blue color when they are sequestered.

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

***A Summary of Changes section appears at the end of this standard.**

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 and Mg 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 been found not to interfere with this determination.

6.2 The test method is not suitable for highly colored waters, which obscure the color change of the indicator.

7. Reagents

7.1 *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.[4] 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.

[4] *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.

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.