



Standard Test Method for Hardness in Water¹

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This standard has been approved for use by agencies of the Department of Defense. Consult the DoD Index of Specifications and Standards for the specific year of issue which has been adopted by the Department of Defense.

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 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 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 *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:*

D 1066 Practice for Sampling Steam²

D 1129 Terminology Relating to Water²

D 1193 Specification for Reagent Water²

D 3370 Practices for Sampling Water from Closed Conduits²

3. Terminology

3.1 *Definitions:*

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

3.1.2 For definitions of other terms used in this test method, refer to Terminology D 1129.

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

T³, which has a red color in the presence of calcium and magnesium and a blue color when they are sequestered.

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.

7.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Specification D 1193, 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

¹ This test method is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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² *Annual Book of ASTM Standards*, Vol 11.01.

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

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 *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.

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 K₄Fe(CN)₆·3H₂O 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.

affecting the precision and bias of the test method. Type II water was specified at the time of roundrobin testing of this test method.

7.3 Ammonium Hydroxide Solution (1 + 4)—Mix 1 volume of NH₄OH (sp gr 0.90) with 4 volumes of water.

7.4 Buffer Solution—Prepare the buffer solution in three steps as follows:

7.4.1 Dissolve 40 g of sodium tetraborate (Na₂B₄O₇·10H₂O) in 800 mL of water.

7.4.2 Dissolve 10 g of sodium hydroxide (NaOH), 10 g of sodium sulfide (Na₂S·9H₂O), and 10 g of potassium sodium tartrate (KNaC₄O₆·4H₂O) in 100 mL of water.

7.4.3 When cool mix the two solutions and add 1 g of magnesium disodium ethylenediamine tetraacetate, having a magnesium-to-EDTA mole ratio of 1 to 1. Make up to 1 L with water. Keep the solution bottle stoppered when not in use. The reagent will be effective for at least 1 month.

7.5 Calcium Solution, Standard (1 mL = 0.20 mg CaCO₃)—Dissolve 0.2000 g of CaCO₃ in 3 to 5 mL of HCl (1 + 4). Dilute to 1 L with water.

7.6 Calcium Indicator—Use powdered hydroxynaphthol

blue,⁵ or grind solid hydroxynaphthol blue to 40 to 50 mesh size.

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

7.7.1 Hardness Indicator Solution—Dissolve 0.5 g of Chrome Black T³ in 50 mL of diethanolamine or triethanolamine. Store the solution in a dark-colored bottle. This solution has a storage life of several months.

7.7.2 Hardness Indicator Powder—Grind 0.5 g of Chrome Black T³ with 100 g of powdered sodium chloride. Use a dark-colored bottle for storage. The powder has a storage life of at least 1 year.

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

7.9 Disodium Ethylenediamine Tetraacetate (Na₂H₂ EDTA) Solution, Standard (1 mL = 1.0 mg CaCO₃)—Dissolve 3.8 g of disodium ethylenediamine tetraacetate dihydrate in approximately 800 mL of water. Adjust the pH of the solution to 10.5 with NaOH solution (50 g/L). Determine the concentration of this solution using the standard calcium solution, and that procedure in Section 9 that will be used for the sample analysis (9.1, 9.2, or 9.3). Adjust the concentration of the EDTA so that 1 mL will be equivalent to 1.0 mg of CaCO₃. Store the standard EDTA in polyethylene, plastic, or hard rubber bottles and restandardize monthly.

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

8. Sampling

8.1 Collect the sample in accordance with Practice D 1066 or Practices D 3370 as applicable.

9. Procedure

9.1 Hardness—Measure 50 mL of clear sample into an opaque white container or a clear colorless container utilizing a white background. Adjust the pH of the sample to 7 to 10 by adding NH₄OH solution or HCl solution. Add 0.5 mL of buffer solution, and approximately 0.2 g of hardness indicator powder or 2 drops of liquid and stir. Add standard Na₂H₂EDTA solution slowly from a buret with continuous stirring until the color changes from red to blue. Complete the titration within 5 min after the buffer addition. If the titration requires more than 20 mL of the titrating solution, dilute the sample and repeat the test.

9.2 Low Hardness—Determine low-hardness values (0.5 to 5.0 ppm as CaCO₃) in accordance with 9.1, but use a 100 mL sample and titrate by means of microburet. When employing a 100-mL sample, add twice the quantity of the reagents as indicated in 9.1.

9.3 Calcium Hardness—Measure 50 mL of the sample into an opaque white container, or a clear colorless container utilizing a white background. Add 2 mL of NaOH solution and stir. Add approximately 0.2 g of calcium indicator and stir. Add standard Na₂H₂EDTA solution slowly from a buret with continuous stirring until the color changes from red to royal blue. Complete the titration within 5 min after the NaOH

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

addition. If the titration requires more than 15 mL of the titrating solution, dilute the sample and repeat the test.

10. Calculations

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

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

where:

epm = equivalent parts per million; milliequivalents per litre,

C = standard $\text{Na}_2\text{H}_2\text{EDTA}$ solution added in titrating hardness, mL, and

S = sample taken, mL.

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

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

where:

epm = equivalent parts per million; milliequivalents per litre,

D = standard $\text{Na}_2\text{H}_2\text{EDTA}$ solution added in titrating calcium hardness, mL, and

S = sample taken for test, mL.

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

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

where:

epm = equivalent parts per million; milliequivalents per litre,

E = hardness, epm, and

F = calcium hardness, epm.

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

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

where:

C_1 = standard $\text{Na}_2\text{H}_2\text{EDTA}$ solution added in titrating hardness, mL, and

S_1 = sample taken, mL.

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

$$\text{Calcium hardness, mg/L as CaCO}_3 = 1000 D_1/S_1 \quad (5)$$

where:

D_1 = standard $\text{Na}_2\text{H}_2\text{EDTA}$ solution added in titrating calcium hardness, mL, and

S_1 = sample taken, mL.

10.2.2 Calculate the magnesium hardness as calcium carbonate of the sample as follows:

$$\text{Magnesium hardness, mg/L as CaCO}_3 = G - H \quad (6)$$

TABLE 2 Statistical Information, Total Hardness

Amount Added, mg/L	Amount Found, mg/L	Bias	% Bias	Statistically Significant
11.0	11.4	+ 0.4	+ 3.6	No
45.0	46.3	+ 1.3	+ 2.9	No
206.	206.	0.0	0.0	No
450.	453.	+ 3.	+ 0.7	No
Calcium Hardness				
6.2	6.1	-0.1	-1.6	No
25.0	24.9	-0.1	-0.4	No
125.	126.	+ 1.0	+ 0.8	No
250.	250.	0.0	0.0	No

where:

G = hardness, mg/L as CaCO_3 , and

H = calcium hardness, mg/L as CaCO_3 .

11. Precision and Bias ⁶

11.1 The single operation and overall precision of the total hardness test method within its designated range for 6 laboratories, which include a total of 6 operators analyzing each sample on 3 different days may be expressed as follows:

$$S_o = 0.0047 X + 0.40 \quad (7)$$

$$S_T = 0.0078 X + 1.80$$

where:

S_o = pooled single-operator precision, mg/L,

S_T = overall precision, mg/L, and

X = hardness concentration, mg/L.

11.2 The single operator and overall precision of the calcium hardness test method within its designated range for 6 laboratories, which include a total of 6 operators analyzing each sample on 3 different days may be expressed as follows:

$$S_o = 0.0052 X + 0.37$$

$$S_T = 0.025 X + 0.61$$

where:

S_o = pooled single-operator precision, mg/L

S_T = overall precision, mg/L, and

X = calcium hardness concentration, mg/L.

11.3 Recoveries of known amounts of hardness and calcium hardness in a series of prepared standards for the same laboratories and operators are as shown in Table 2.

11.4 These data apply to reagent water only. It is the analyst's responsibility to ensure the validity of this test method for waters of untested matrices.

12. Keywords

12.1 analysis; calcium carbonate hardness; hardness; titration; water

⁶ Supporting data are available from ASTM Headquarters. Request RR: D19-1125.

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