Designation: D 1126 – 02

An American National Standard

Standard Test Method for Hardness in Water[1]

This standard is issued under the fixed designation D 1126; 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.

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 *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 Steam[2]

D 1129 Terminology Relating to Water[2]

D 1193 Specification for Reagent Water[2]

D 3370 Practices for Sampling Water from Closed Conduits[2]

D 5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis[3]

3. Terminology

3.1 *Definitions:*

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

3.1.2 *laboratory control sample, n*—a solution with certified hardness.

3.1.3 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 T[4], 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.

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[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] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 11.02.

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

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. 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.[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.

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

7.3 *Ammonium Hydroxide Solution* (1 + 4)—Mix 1 volume of NH_4OH (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 ($Na_2B_4O_7 \cdot 10H_2O$) in 800 mL of water.

7.4.2 Dissolve 10 g of sodium hydroxide (NaOH), 10 g of sodium sulfide ($Na_2S \cdot 9H_2O$), and 10 g of potassium sodium tartrate ($KNaC_4O_6 \cdot 4H_2O$) 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 $CaCO_3$)—Dissolve 0.2000 g of $CaCO_3$ in 3 to 5 mL of HCl (1 + 4). Dilute to 1 L with water.

7.6 *Calcium Indicator*—Use powdered hydroxynaphthol blue,[6] 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 T[3] 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 T[3] 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 (Na_2H_2 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. 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 $CaCO_3$. 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 NH_4OH solution or HCl solution. Add 0.5 mL of buffer

[5] *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.

[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 indicator powder or 2 drops of liquid and stir. Add standard Na_2H_2EDTA solution slowly from a burette 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 $CaCO_3$) in accordance with 9.1, but use a 100 mL sample and titrate by means of micro-burette. 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 Na_2H_2EDTA solution slowly from a burette with continuous stirring until the color changes from red to royal blue. Complete the titration within 5 min after the NaOH 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:

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

where:
epm = equivalent parts per million; milliequivalents per liter,
C = standard Na_2H_2EDTA 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 liter,
D = standard Na_2H_2EDTA 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 liter,
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 Na_2H_2EDTA solution added in titrating hardness, mL, and
S_1 = sample taken, mL.

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

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 Na_2H_2EDTA 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:

$$\text{Magnesium hardness, mg/L as } CaCO_3 = G - H \quad (6)$$

where:
G = hardness, mg/L as $CaCO_3$, and
H = calcium hardness, mg/L as $CaCO_3$.

11. Precision and Bias [7]

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:

$$S_o = 0.0047\ X + 0.40$$

$$S_T = 0.0078\ X + 1.80$$

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.

[7] Supporting data are available from ASTM International Headquarters. Request RR: D19-1125.

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.

11.5 Precision and bias for this test method conforms to Practice D 2777 - 77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of D 2777 - 98, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

12. Quality Control (QC)

12.1 The following quality control information is recommended for the determination of hardness in water.

12.2 A check standard shall be analyzed at a minimum frequency of 10 % throughout the batch analysis. The value of the check standard shall fall between 80 % and 120 % of the true value.

12.3 A Laboratory Control Sample shall be analyzed with each batch of samples at a minimum frequency of 10 %.

12.4 If the QC for the sample batch is not within the established control limits, reanalyze the samples or qualify the results with the appropriate flags, or both (Practice D 5847).

12.5 Blind control samples should be submitted by an outside agency in order to determine the laboratory performance capabilities.

13. Keywords

13.1 analysis; calcium carbonate hardness; hardness; titration; water