Designation: D 2022 – 89 (Reapproved 1995)ε1

Standard Test Methods of Sampling and Chemical Analysis of Chlorine-Containing Bleaches[1]

This standard is issued under the fixed designation D 2022; 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—Keywords were added editorially in February 1995.

1. Scope

1.1 These test methods cover the sampling and chemical analysis of chlorine-containing bleaches. The methods appear in the following order:

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Sodium Hypochlorite (Soda Bleach) Solutions:	
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Available Chlorine	6-9
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Sodium Chloride	19 and 20
Total Alkalinity as Sodium Oxide (Na_2O)	21-24
Free Alkali as Sodium Hydroxide (NaOH)	25-28
Calcium Hypochlorite:	
Sampling	30
Available Chlorine	31-34
Water	35-40
Chloroisocyanuric Acids and Their Derived Salts:	
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1.2 *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.* Material Safety Data Sheets are available for reagents and materials. Review them for hazards prior to usage.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

3. Terminology

3.1 *Definitions:*

3.1.1 *available chlorine*—the measure of the oxidizing powder of the chlorine present as hypochlorite. It is expressed in terms of chlorine with a gram-equivalent weight of 35.46.

4. Reagents

4.1 *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, where such specifications are available.[3] 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.

4.2 Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193.

[1] These test methods are under the jurisdiction of ASTM Committee D-12 on Soaps and Other Detergents and are the direct responsibility of Subcommittee D12.12on Analysis of Soaps and Synthetic Detergents.

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

[3] *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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

SODIUM HYPOCHLORITE (SODA BLEACH) SOLUTIONS

5. Sampling

5.1 The stability of soda bleach is influenced to a considerable degree by the purity of the alkali used in its preparation, by the excess of alkali remaining, and by the kind and amount of metal contamination from equipment. Owing to the relatively unstable nature of bleach solutions, special attention shall be given to the collection and preservation of the sample. Exposure to heat and sunlight promotes decomposition, and shall be avoided. Samples shall be kept cool in a dark place (or in dark-colored bottles) until analyzed, which shall be done without unnecessary delay.

5.2 Strong solutions of bleach shall be accurately diluted and aliquots taken for determination of available chlorine, chlorate, and total chlorine. The size of aliquots shall be such that approximately 40 mL of the 0.1 *N* reagent is required. The alkali determinations shall be made directly on the sample received and sample sizes to require about 10 mL of 0.1 *N* reagent are recommended.

5.3 Precision results will require sampling at a standard temperature such as 20°C. Results expressed in terms of weight percent will require determination of the density or specific gravity. This may be determined with a hydrometer or by weighing the sample, after pipetting the amount to be diluted for analysis into a tared weighing bottle. The weighed sample may be transferred to a volumetric flask and used for subsequent analysis.

AVAILABLE CHLORINE

6. Summary of Test Method

6.1 The sample is added to an acidified solution of potassium iodide and the released iodine is titrated with standard sodium thiosulfate solution to the usual starch end point.

7. Reagents

7.1 *Acetic Acid*, glacial.

7.2 *Potassium Iodide* (KI), crystals, iodate-free.

7.3 *Sodium Thiosulfate Solution Standard*, (0.1 *N*)—Dissolve 25 g of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) crystals in freshly boiled and cooled water and dilute to 1 L. The solution is more stable if the glassware is cleaned with sulfuric-chromic acid and thoroughly rinsed with water. Standardize against potassium iodate as follows: Weigh out accurately 3.567 g of dry potassium iodate (KIO_3) and transfer to a 1-L volumetric flask. Dissolve with water, make up to the mark, and mix thoroughly. This solution will be exactly 0.1000 *N*. To standardize the $Na_2S_2O_3$ solution, carefully pipet a 50-mL aliquot of the KIO_3 solution into a 250-mL Erlenmeyer flask and dilute to 100 mL with water. Add 1 g of KI crystals. When it is dissolved, add 15 mL of 1.0 *N* hydrochloric acid and titrate immediately with the $Na_2S_2O_3$solution. When the solution becomes light yellow, add 1 mL of starch indicator solution and complete the titration to the disappearance of the blue color. Standardize at least monthly. Calculate the normality of the $Na_2S_2O_3$solution as follows:

$$\text{Normality} = (50 \times 0.1)/A \quad (1)$$

where:

A = $Na_2S_2O_3$ solution required for titration of the KIO_3solution, mL.

7.4 *Starch Indicator Solution* (0.5 %)—Mix 0.5 g of soluble starch with 5 mL of cold water and add to 95 mL of boiling water. Mix, cool, and store in a sterilized bottle. Replace frequently or add 0.1 % salicylic acid to minimize deterioration.

8. Procedure

8.1 Dissolve 2 to 3 g of KI crystals in 50 mL of water in a 250-mL Erlenmeyer flask. Add 10 mL of acetic acid, then pipet the aliquot of sample into the solution, keeping the tip of the pipet beneath the surface of the solution until drained. Titrate at once with 0.1 *N* $Na_2S_2O_3$solution until the iodine color is nearly gone, then add 1 mL of starch indicator solution and complete the titration to the disappearance of the blue color. Record the titration as *A* (see Section 14).

9. Calculation

9.1 Calculate the available chlorine as follows:

$$\text{Available chlorine as Cl, g/L} = (AN \times 35.46)/V \quad (2)$$

$$\text{Available chlorine as Cl, weight \%} = [(AN \times 0.03546)/VS] \times 100$$

9.2 Calculate the sodium hypochlorite content as follows:

$$\text{Sodium hypochlorite (NaOCl), g/L} = (AN \times 37.22)/V \quad (3)$$

$$\text{Sodium hypochlorite (NaOCl), weight \%} = [(AN \times 0.03722)/VS] \times 100$$

where:

A = $Na_2S_2O_3$ solution required for titration of the sample, mL

N = normality of the $Na_2S_2O_3$solution,

V = original sample in aliquot used, mL, and

S = specific gravity of the sample.

SODIUM CHLORATE

10. Summary of Test Method

10.1 Sodium chlorate is reduced with sodium bromide in 8 *N* hydrochloric acid.[4,5] After dilution and addition of potassium iodide, the released iodine (equivalent to the hypochlorite plus chlorate) is titrated with standard sodium thiosulfate solution and starch indicator.

11. Apparatus

11.1 The apparatus (Fig. 1) consists of 1-L wide-mouth reaction vessel, *A* (a 1-qt fruit jar will serve), fitted with a 2-hole rubber stopper carrying a separatory funnel, *B*, conveniently graduated or marked at the 10, 20, and 100-mL levels,

[4] Ditz, Hugo, "Determination of Chlorates in Electrolytic Bleaching Lyes and in Lyes Obtained from Absorption Vessels During the Production of Potassium Chlorate," *Chemiker Zeitung*, Vol 25, 1901 p. 727.

[5] White, J. F., "Determination of Available Chlorine in Solutions Containing Textone ($NaClO_2$)," *American Dye-stuff Reporter*, Vol 31, 1942 pp. 484–7.

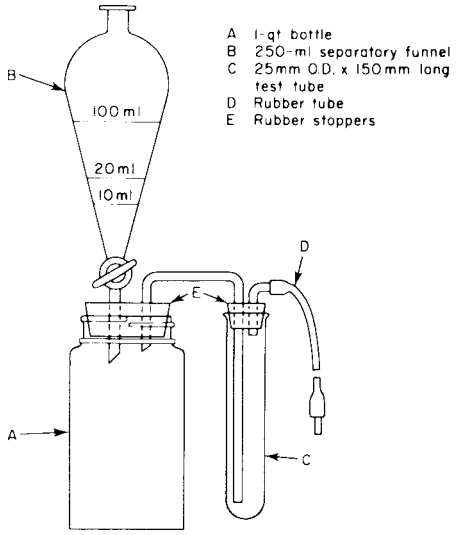

FIG. 1 Apparatus for Determination of Sodium Chlorate in Sodium Hypochlorite (Soda Bleach) Solutions

and a delivery tube leading to a 50-mL test-tube gas trap, *C*, which is fitted with rubber tubing and a glass mouthpiece, *D*.

12. Reagents

12.1 *Hydrochloric Acid* (sp gr 1.42)—Concentrated hydrochloric acid (HCl). For highest accuracy, it should be checked for the presence of oxidizing or reducing matter. When used for an analysis of pure potassium chlorate ($KClO_3$) by this method, there should be no fading or return of the end point, and the assay error should not exceed ±0.5 %.

12.2 *Sodium Bromide Solution* (10 %)—Prepare a 10 % solution of sodium bromide (NaBr).

12.3 *Potassium Iodide Solution* (10 %)—Prepare a 10 % solution of potassium iodide (KI). Decolorize with $Na_2S_2O_3$when necessary.

12.4 *Sodium Thiosulfate Solution Standard*, (0.1 *N*)—See 7.3.

12.5 *Starch Indicator Solution* (0.5 %)—See 7.4.

13. Procedure

13.1 Pipet an aliquot of the sample (same amount as used for available chlorine determination, Sections 6-9) into the reaction vessel. Assemble the apparatus and put 25 mL of KI solution in the gas trap. Close the funnel stopcock, pour 20 mL of NaBr solution into the funnel, open the stopcock, and with gentle suction on the mouthpiece, draw the NaBr solution into the sample. Close the stopcock and pour 100 mL of HCl into the funnel. Open the stopcock and allow the acid to drain into the sample. Draw in the last drops with suction, close the stopcock, swirl the vessel to mix the acid, and let stand exactly 5 min (use time clock). There will be a tendency for a vacuum to form and draw KI solution from the trap back into the sample. This must be avoided by filling the funnel with water and relieving the vacuum by opening the stopcock and adding a small amount of water.

13.2 After 5 min, open the stopcock and allow the water to drain into the sample, swirling to dilute the acid. Add water through the funnel sufficient to dilute the sample to about 700 mL. Close the stopcock, and add 10 mL of KI solution to the funnel. Apply pressure at the mouthpiece to blow the contents of the trap back into the vessel, opening the stopcock to allow the necessary amount of gas to escape through the funnel. Rinse the trap twice with water, each time blowing the contents into the vessel as above. Finally, allow the contents of the funnel to drain into the vessel, rinse down the funnel and stopper, and thoroughly mix the contents of the vessel. Titrate at once with 0.1 *N* $Na_2S_2O_3$solution. When the iodine color is nearly gone, add 5 mL of starch indicator solution and complete the titration to the disappearance of the blue color. Record the titration as *B*.

14. Calculation

14.1 Calculate the sodium chlorate content as follows:

$$\text{Sodium chlorate } (NaClO_3),\ g/L = [(B - A)N \times 17.74]/V \quad (4)$$

$$\text{Sodium chlorate } (NaClO_3),\ \text{weight \%} \frac{(B - A)N \times 0.01774}{VS} \times 100$$

where:

A = $Na_2S_2O_3$ solution required for titration for available chlorine (Section 8), mL
B = $Na_2S_2O_3$ solution required for titration for sodium chlorate (Section 13), mL
N = normality of the $Na_2S_2O_3$solution,
V = original sample in aliquot used, mL, and
S = specific gravity of the sample.

TOTAL CHLORINE

15. Summary of Test Method

15.1 All hypochlorite and chlorate present is reduced to chloride by sodium metabisulfite in the presence of nitric acid. The total chloride is then determined by a standard Volhard titration.

16. Reagents

16.1 *Iron Indicator Solution*—Dissolve 6.25 g of ferric ammonium sulfate $(Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24\ H_2O)$ in 50 mL of water and add 45 mL of HNO_3.

16.2 *Nitric Acid*, (sp gr 1.42)—Concentrated nitric acid (HNO_3).

16.3 *Potassium Thiocyanate Solution Standard*, (0.05 *N*)—Prepare a 0.05 *N* solution of potassium thiocyanate (KCNS) and standardize against 0.05 *N* $AgNO_3$ solution.

16.4 *Silver Nitrate Solution Standard* (0.05 *N*)—Prepare a 0.05 *N* solution of silver nitrate ($AgNO_3$) and standardize against sodium chloride (NaCl) by Mohr's Method (K_2CrO_4 indicator). 2.923 g of NaCl dissolved and diluted to exactly 1000 mL yields a solution exactly 0.0500 *N*.

16.5 *Sodium Metabisulfite*—($Na_2S_2O_5$), powder.

17. Procedure

17.1 To a 250-mL beaker add 50 mL of water and about 0.5 g of $Na_2S_2O_5$ powder. Then pipet into the mixture a sample aliquot of the same size as used for available chlorine and chlorate. Add about 10 drops of HNO_3 to acidify the solution and boil until all the SO_2 has been expelled. Cool to room temperature and add 5 mL of iron indicator solution. From a

buret add 0.5 mL of 0.05 *N* KCNS solution (Note 1). Then titrate to complete decolorization with 0.05 *N* $AgNO_3$ solution. Filter off the precipitate by suction and wash three times with water. Finally, back-titrate the filtrate and washings with 0.05 *N* KCNS solution until a faint reddish color persists. For less accurate work the filtration may be avoided by adding 1 mL of nitrobenzene to coagulate the suspension before back-titrating the excess $AgNO_3$.

NOTE 1—This small amount of KCNS solution serves as an indicator to show when an excess of $AgNO_3$ solution has been added. The back titration is continued from the same buret and the total volume of KCNS solution used is noted and used in the calculation.

18. Calculation

18.1 Calculate the total chlorine content as follows:

$$\text{Total Chlorine as Cl, g/L} = [(CN_1) - (DN_2) \times 35.46]/V \quad (5)$$

$$\text{Total chlorine as Cl, weight \%} = \frac{[(CN_1) - (DN_2) \times 0.03546]}{VS} \times 100$$

where:

C = $AgNO_3$ solution required for titration of the sample, mL,
D = KCNS solution required for back-titration, total mL
N_1 = normality of the $AgNO_3$ solution,
N_2 = normality of the KCNS solution,
V = original sample in aliquot used, mL, and
S = specific gravity of the sample.

SODIUM CHLORIDE

19. Summary of Test Method

19.1 Any chlorine present as a sodium chloride is determined by calculation as the difference between the total chlorine and the sum of the chlorine present as hypochlorite and as chlorate.

20. Calculation

20.1 Calculate the sodium chloride content as follows:

$$\text{Sodium chloride (NaCl), g/L} = [E - (F/2) - (G/3)] \times 1.649 \quad (6)$$

$$\text{Sodium chloride (NaCl), weight \%} = [J - (K/2) - (L/3)] \times 1.649$$

where:

E = total chlorine, g/L (Section 18),
F = available chlorine, g/L (Section 9),
G = sodium chlorate, g/L (Section 14),
J = total chlorine, in weight percent (Section 18),
K = available chlorine, in weight percent (Section 9), and
L = sodium chlorate, in weight percent (Section 14).

TOTAL ALKALINITY AS SODIUM OXIDE (Na_2O)

21. Summary of Test Method

21.1 A sample is added to neutralized, dilute hydrogen peroxide solution which reduces the hypochlorite to chloride. The alkalinity is then titrated with standard hydrochloric acid using methyl red mixed indicator.

22. Reagents

22.1 *Hydrochloric Acid, Standard* (0.1 *N*)—Prepare a 0.1 *N* solution of hydrochloric acid (HCl) and standardize against primary standard sodium carbonate and methyl red mixed indicator.

22.2 *Hydrogen Peroxide Solution* (3 %)—Prepare a 3 % solution of hydrogen peroxide (H_2O_2).

22.3 *Methyl Red Mixed Indicator Solution*—Dissolve 0.2 g of methyl red in 100 mL of Formula 30 alcohol and 0.3 g bromcresol green in 300 mL of Formula 30 alcohol. Grinding of the methyl red may be necessary to ensure complete solution. When reagents are completely dissolved, mix the two solutions thoroughly.

22.4 *Sodium Hydroxide Solution* (4 g/L)—Dissolve 4 g of sodium hydroxide (NaOH) in water and dilute to 1 L.

23. Procedure

23.1 Neutralize 30 mL of H_2O_2 solution (or three times the volume of sample used) in a 250-mL Erlenmeyer flask with NaOH solution, using methyl red mixed indicator solution. Pipet 10 mL of the sample of liquid bleach (or more, so that the total volume of 0.1 *N* HCl required will be at least 10 mL into the neutralized H_2O_2 solution, shake vigorously for 1 min, and titrate with 0.1 *N* HCl, using methyl red mixed indicator solution.

24. Calculation

24.1 Calculate the total alkalinity as Na_2O as follows:

$$\text{Total alkalinity as } Na_2O, \text{ g/L} = (KN_3 \times 31)/V \quad (7)$$

$$\text{Total alkalinity as } Na_2O, \text{ weight \%} = [(KN_3 \times 0.031)/VS] \times 100$$

where:

K = mL of HCl required for titration of the sample,
N_3 = normality of the HCl,
V = mL of original sample used, and
S = specific gravity of the sample.

FREE ALKALI AS SODIUM HYDROXIDE (NaOH)

25. Summary of Test Method

25.1 A sample is added to a neutralized, mixed solution of barium chloride and hydrogen peroxide, which precipitates any carbonate and reduces the hypochlorite to chloride. The free alkali is then titrated with standard hydrochloric acid using phenolphthalein indicator.

26. Reagents

26.1 *Barium Chloride Solution* (100 g/L)—Dissolve 100 g of barium chloride ($BaCl_2 \cdot 2H_2O$) in water and dilute to 1 L. Filter if turbid.

26.2 *Hydrochloric Acid, Standard* (0.1 *N*)—See 22.1.

26.3 *Hydrogen Peroxide Solution* (3 %)—See 22.2.

26.4 *Phenolphthalein Indicator Solution* (0.5 g/100 mL)—Dissolve 0.5 g of phenolphthalein in 60 mL of 95 % ethyl alcohol and dilute to 100 mL with water.

26.5 *Sodium Hydroxide Solution* (4 g/L)—See 22.4.

27. Procedure

27.1 Place 50 mL of $BaCl_2$ solution and 30 mL of H_2O_2 solution in a 250-mL Erlenmeyer flask (or 6-in. porcelain dish), add 10 drops of phenolphthalein indicator solution, and neutralize with NaOH solution. Introduce into this neutral mixture