Designation: D2022 − 89 (Reapproved 2016)

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

This standard is issued under the fixed designation D2022; 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 U.S. Department of Defense.

1. Scope

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

	Sections
Sodium Hypochlorite (Soda Bleach) Solutions:	
Sampling	5
Available Chlorine	6 – 9
Sodium Chlorate	10 – 14
Total Chlorine	15 – 18
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:	
Sampling	42
Available Chlorine (Iodometric—Thiosulfate Method)	43 – 46
Available Chlorine (Arsenite—Iodometric Method)	47 – 50
Moisture	51 – 54

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:*[2]

D1193 Specification for Reagent Water

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 D1193.

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.

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[1] These test methods are under the jurisdiction of ASTM Committee D12 on Soaps and Other Detergents and are the direct responsibility of Subcommittee D12.12 on Analysis and Specifications of Soaps, Synthetics, Detergents and their Components.

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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] *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.

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:

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

where:

A = $Na_2S_2O_3$ solution required for titration of the KIO_3 solution, 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:

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

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

9.2 Calculate the sodium hypochlorite content as follows:

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

$$\text{Sodium hypochlorite (NaOCl), weight \%}$$

$$= [(AN \times 0.03722)/VS] \times 100$$

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, 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 %.

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[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.

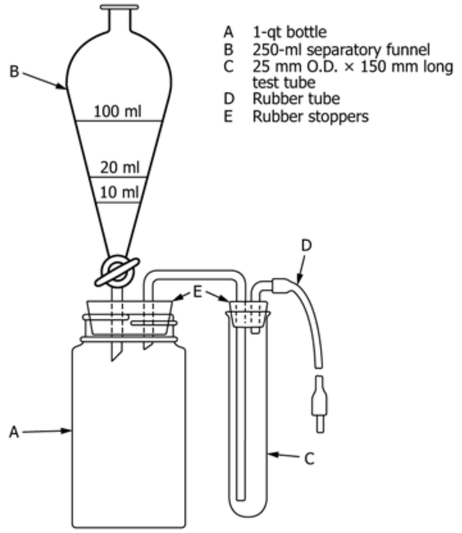

FIG. 1 Apparatus for Determination of Sodium Chlorate in Sodium Hypochlorite (Soda Bleach) Solutions

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* $Na_2S_2\ O_3$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:

$$\text{Sodium chlorate } (\text{NaClO}_3),\ \text{g/L} = [(B - A)N \times 17.74]/V \qquad (4)$$

$$\text{Sodium chlorate } (\text{NaClO}_3),\ \text{weight \%}\ \frac{(B - A)N \times 0.01774}{VS} \times 100$$

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 $H_2 O_2$ 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 10 mL of the liquid bleach, shake or stir vigorously for 1 min, and titrate the NaOH solution with 0.1 *N* HCl until the pink color disappears.

28. Calculation

28.1 Calculate the free alkali as NaOH as follows:

$$\text{Free alkali as NaOH, g/L} = (LN_3 \times 40)/V \tag{8}$$

$$\text{Free alkali as NaOH, weight \%} = [(LN_3 \times 0.040)/VS] \times 100$$

where:

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

CALCIUM HYPOCHLORITE

29. Scope

29.1 These methods, as written, cover the usual products with 70 to 75 % available chlorine and water content between 0.1 and 5.0 %. Water content as high as 10 % may be determined by adjusting the sample size.

30. Sampling

30.1 Samples shall be taken from a well-mixed sample representing various parts of the container. If not powdered or granular, the sample shall be ground to break up lumps with a minimum exposure to the atmosphere.

AVAILABLE CHLORINE

31. Summary of Test Method

31.1 Available chlorine is determined iodometrically by titration, with standard thiosulfate solution, of the iodine released by treatment with potassium iodide and acetic acid.

32. Reagents

32.1 *Acetic Acid,* glacial.

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

32.3 *Sodium Thiosulfate Solution Standard,* (0.1 *N*)—Prepare a 0.1 *N* solution of sodium thiosulfate ($Na_2S_2O_3$) (see 7.3) and standardize against primary standard potassium dichromate ($K_2Cr_2O_7$) or resublimed iodine by standard procedures.

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

33. Procedure

33.1 From a well-mixed sample, transfer 3.6 to 4.0 g to a tared, glass-stoppered, weighing bottle and weigh to the nearest 0.1 mg. Place a dry powder funnel in the neck of a 500-mL volumetric flask containing about 100 mL of water. Carefully transfer the sample through the funnel into the flask and rinse weighing bottle and funnel with a fine stream of water from a wash bottle. Stopper the flask and swirl the solution until most of the sample has dissolved. Make up to volume with water, stopper, and mix thoroughly. While shaking or swirling to keep any solids in suspension and ensure representative sampling, pipet a 25-mL aliquot into a 500-mL Erlenmeyer flask containing 125 to 150 mL of water. Add 2 g of KI crystals, mix, and add 8 mL of glacial acetic acid. Mix and titrate at once with 0.1 *N* $Na_2S_2O_3$ solution. When most of the iodine color has disappeared, add 2 mL of starch indicator solution and continue to the usual starch end point.

34. Calculation

34.1 Calculate the weight percent of available chlorine or of calcium hypochlorite as follows:

$$\text{Available chlorine as Cl, weight \%} = [(VNA \times 0.03546)/W] \times 100 \tag{9}$$

$$\text{Calcium hypochlorite } (\text{Ca(OCl)}_2)\text{, weight \%} = [(VNA \times 0.03575)/W] \times 100$$

where:

V = $Na_2S_2O_3$ solution required for titration of the sample, mL,
N = normality of the $Na_2S_2O_3$solution,
A = aliquot factor (500/25 = 20), and
W = sample taken, g.

WATER

35. Summary of Test Method

35.1 A weighed sample is added to a quantity of *o*-dichlorobenzene (boiling point 180°C). The water is distilled off and collected under petroleum ether in a calibrated receiver.

36. Apparatus (Fig. 2)

36.1 *Heat Source, A,* 500-W Boekeltype electric heater.

36.2 *Boiling Flask, B,* 500-mL borosilicate, round-bottom, with 35/25 socket joint, and 1½-in. minimum length neck to accommodate a clamp to serve as handle.[6]

36.3 *Distillation Column, C,* Vigreaux-type, 12-in. effective length, with 35/25 socket joint at the bottom.[7] The bottom ball-and-socket joint is used to avoid a tendency of taper joints to freeze in this analysis. Insulate by wrapping with wetted asbestos paper, *D.*

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[6] Corning No. 4325 flask modified as to neck length has been found satisfactory for this purpose.

[7] Corning No. 3525 column modified as to bottom joint has been found satisfactory for this purpose.

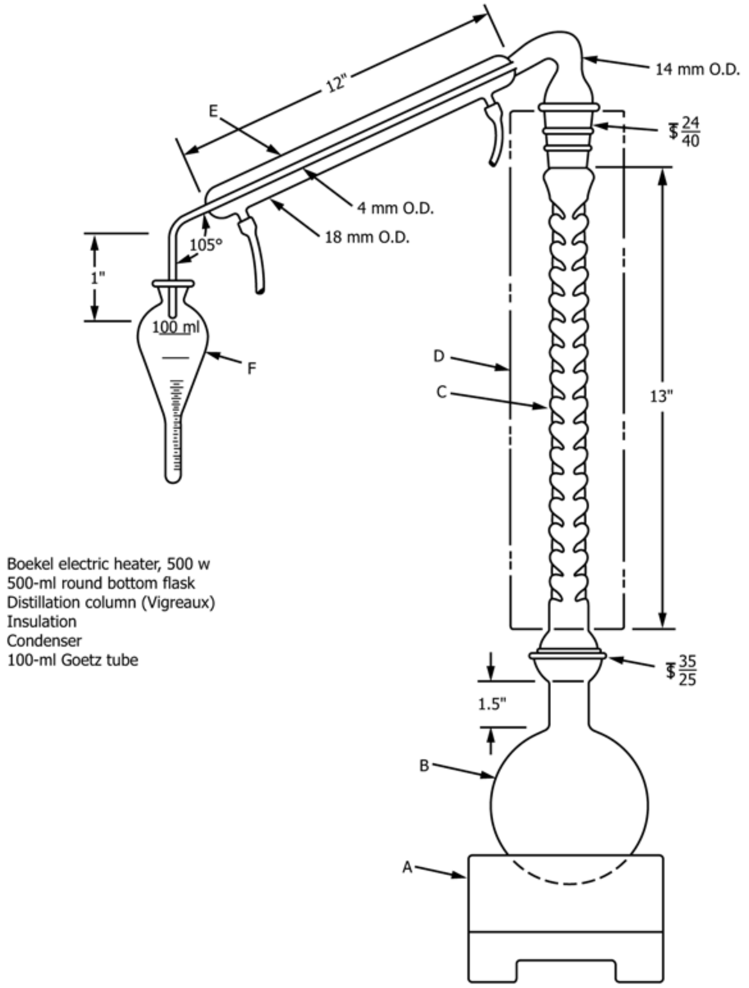

FIG. 2 Apparatus for Determination of Water in Calcium Hypochlorite

36.4 *Condenser, E,* water-cooled, special design with standard-taper 24/40 joint.

36.5 *Receiver, F,* Goetz tube, 100-mL capacity, stem calibrated 0 to 1 mL in 0.02-mL divisions.[8]

37. Reagents

37.1 *o-Dichlorobenzene,* technical, 85 to 87 %.

37.2 *Petroleum Ether (Ligroin),* boiling point 30 to 60°C.

38. Safety Precautions

38.1 *Use adequate protection at all times and follow directions implicitly.* Explosions are possible if the sample is allowed to become dry by boiling off all the *o*-dichlorobenzene or if the petroleum ether is allowed to "suck back" into the hot sample.

39. Procedure

39.1 Mount the column and condenser of the apparatus shown in Fig. 2 with suitable supports and clamps. Attach a simple extension clamp to the neck of the boiling flask to serve as a handle. *Provide a suitable safety glass screen between the operator and apparatus, and goggles and rubber gloves for the operator.*

NOTE 2—Always use the safety screen, goggles, and gloves when performing this analysis.

39.2 Measure 100 mL of *o*-dichlorobenzene in a graduated cylinder and transfer it to the boiling flask. Attach the flask to the condenser with a socket-joint spring clamp. With no water in the condenser and with condenser outlet vented to the atmosphere, apply heat to the flask with the electric heater and boil the *o*-dichlorobenzene until vapors are emitted from the condenser, thus heating the apparatus and driving out any water present. While the apparatus is heating, weigh out 20± 0.1 g of the well-mixed sample. For samples containing 5 to 10 % water, the sample size should be reduced to 10 ± 0.1 g. Protect the sample from the atmosphere until ready to use.

39.3 When the apparatus has been dried out, lower the heater, remove the flask and discard its hot contents into a clean, *dry beaker*. With a graduated cylinder, measure another 100 mL of *o*-dichlorobenzene into the flask (Note 3). Add the sample to the flask through a powder funnel. Swirl the contents of the flask to assure that no sample sticks to the flask. Attach the flask to the column. Add 50 mL of petroleum ether to the

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[8] Emil Greiner No. G-4950 Goetz tube has been found satisfactory for this purpose.

Goetz tube and mount the tube so the end of the condenser extends about 1 in. into the neck of the Goetz tube (Notes 4 and 5). Start a small flow of cooling water through the condenser. Apply heat and boil the sample until all water has been distilled over, followed by sufficient *o*-dichlorobenzene to ensure removal of the last traces of water from the condenser.

NOTE 3—Never pour the sample into a hot flask; add the *o*-dichlorobenzene first, then the sample.

NOTE 4—Never allow the sample in the flask to boil to dryness; it may explode.

NOTE 5—Never allow the level of the petroleum ether to reach the tip of the condenser. If any ether sucks back into the flask, an explosion will result.

39.4 Shut off the heater, lower the Goetz tube, swirl the contents to settle all the water into the stem and read the volume of water collected (Note 6). Disconnect and remove the flask, pour out the contents into a dry beaker and rinse the flask with a little *o*-dichlorobenzene. Another sample can then be run at once.

NOTE 6—For best precision, account must be taken of the fact that water under petroleum ether forms an inverted meniscus. The Goetz tube may be calibrated by adding known amounts of water in the presence of ether. Several drops of colored water, such as methyl orange indicator solution, may be added at the start of a test and readings made before and after water from a sample is collected.

40. Calculation

40.1 Calculate the weight percent of water as follows:

$$\text{Water}\ (H_2O),\ \text{weight}\ \% = (V/W) \times 100 \tag{10}$$

where:

V = water found, mL, and
W = sample taken, g.

CHLOROISOCYANURIC ACIDS AND THEIR DERIVED SALTS

41. Scope

41.1 This method covers procedures for the analysis by determination of available chlorine content, of the chloroisocyanuric acids, their derived salts, and formulations containing these materials. The preferred method is an iodometric titration to a starch end point with standard sodium thiosulfate solution. For formulations containing substances that interfere with the thiosulfate end point, such as nonionic surfactants or finely divided adsorptive materials, an aresenite titration method is included.

42. Sampling

42.1 The chloroisocyanuric acids and salts of these acids with their high available chlorine content are strong oxidizing agents. They are relatively stable, with melting and decomposition points above 200°C, but should not be exposed unduly to sunlight or moist atmosphere. Explosions are possible with ammonia, hydrogen sulfide, ethylene oxide condensates, or other easily oxidized organics. Precautions must be taken therefore to prevent contact with such materials. Laboratory samples preferably are stored in brown glass containers with suitable caps. Because of their low solubilities in water, the sodium salt excepted, the usual practice of weighing and dissolving a large sample and titrating an aliquot thereof cannot be followed, and small samples must be titrated directly. The usual standard sampling procedures should be followed to ensure a representative sample for analysis.

AVAILABLE CHLORINE (IODOMETRIC THIOSULFATE METHOD)

43. Summary of Test Method

43.1 The sample is stirred with water, potassium iodide, and sulfuric acid until completely dissolved and then titrated with standard sodium thiosulfate solution to the usual starch end point.

44. Reagents

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

44.2 *Sodium Thiosulfate Solution Standard,* (0.1 *N*)—Prepare a 0.1 *N* solution of sodium thiosulfate ($Na_2S_2O_3$) (see 7.3) and standardize against primary standard potassium dichromate ($K_2Cr_2O_7$) or resublimed iodine by standard procedures.

44.3 *Starch Indicator Solution (0.5 %)*—See 7.4. Discard when the solution becomes cloudy or gives a reddish color with iodine.

44.4 *Sulfuric Acid (1 + 5)*—Mix slowly 1 volume of concentrated sulfuric acid (H_2SO_4, sp gr 1.82) into 5 volumes of water, while stirring.

45. Procedure

45.1 Provide a clean, dry, 250-mL, glass-stoppered, Erlenmeyer flask containing a TFE-fluorocarbon resin-covered magnetic stirrer bar. Put a quantity of sample into a weighing bottle or vial and weigh the sample and bottle on an analytical balance to the nearest 0.1 mg. Pour out a sample of suitable size (Note 7) into the Erlenmeyer flask, replace the cap and reweigh the bottle. Add approximately 100 mL of water to the sample in the flask and about 3 g of KI crystals. Mix and then add 20 mL of H_2SO_4 (1 + 5) (Note 8). Stopper the flask, place on a magnetic stirrer and stir until all the sample has dissolved and reacted (about 5 min). Remove the cap and rinse down cap and flask wall with about 5 mL of water. Titrate with 0.1 *N* $Na_2S_2O_3$ solution until most of the iodine color has been discharged. Add 2 mL of starch indicator solution and continue the titration slowly until the blue starch-iodine color just disappears. Record the volume of 0.1 *N* $Na_2S_2\ O_3$ solution required. Two or three replicate samples should always be run.

NOTE 7—The following sample sizes will require approximately 40-mL titrations:

	Sample Size, g
Trichloroisocyanuric acid	0.16
Dichloroisocyanuric acid	0.20
Sodium dichloroisocyanurate	0.23
Potassium dichloroisocyanurate	0.24

NOTE 8—Formulations low in available chlorine and high in carbonate or other alkali may require additional acid to maintain a sufficiently low pH for the thiosulfate titration. Precautions may also be necessary to prevent loss of iodine vapors with the released carbon dioxide. Such sample might preferably be run by the arsenite method.

46. Calculation

46.1 Calculate the weight percent of available chlorine as follows:

$$\text{Available chlorine as Cl, weight \%} = \left[\left(AN \times 0.03546 \right) / W \right] \times 100 \tag{11}$$

where:

A = $Na_2S_2O_3$ solution required for titration of the sample, mL,
N = normality of the $Na_2S_2O_3$ solution, and
W = sample taken, g.

AVAILABLE CHLORINE (ARSENITE—IODOMETRIC METHOD)

47. Summary of Test Method

47.1 An excess of standard arsenite solution is added to the sample in the presence of an excess of sodium bicarbonate. The excess of arsenite is then titrated to a starch end point with standard iodine solution.

48. Reagents

48.1 *Iodine Solution Standard,* (0.1 *N*)—Prepare a 0.1 *N* solution of iodine and standardize against 0.1 *N* $NaAsO_2$ solution.

48.2 *Sodium Arsenite Solution Standard,* (0.1 *N*)—Prepare a 0.1 *N* solution of sodium arsenite ($NaAsO_2$) and standardize against resublimed iodine in the presence of excess $NaHCO_3$.

48.3 *Sodium Bicarbonate* ($NaHCO_3$), powder.

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

49. Procedure

49.1 Weigh out a sample of suitable size (Note 9) as in Section 45, using a 500-mL glass-stoppered, Erlenmeyer flask when larger samples are required. Add 50 mL of water, 2 to 3 g of $NaHCO_3$, and 50 mL of 0.1 *N* $NaAsO_2$ solution. Stir on a magnetic stirrer until the sample has dissolved or completely reacted, or both. Then rinse down the flask wall with a few millilitres of water, add 2 mL of starch indicator solution, and titrate the excess of 0.1 *N* $NaAsO_2$ solution with 0.1 *N* iodine solution until the first permanent purple color appears. Record the volumes of 0.1 *N* $NaAsO_2$ and iodine solutions used. Run two or three replicate samples.

NOTE 9—Following are the sample sizes of formulations with the indicated available chlorine content required to give approximately 40-mL titrations:

Available Chlorine, %	Sample Size, g
0.5	28
1.0	14
5.0	2.8
10.0	1.4
15.0	0.95
20.0	0.70

50. Calculation

50.1 Calculate the weight percent of available chlorine as follows:

$$\text{Available chlorine as Cl, weight \%} = \frac{(AN_1) - (BN_2) \times 0.03546}{W} \times 100 \tag{12}$$

where:

A = $NaAsO_2$ solution required for titration of the sample, mL,
B = iodine solution required for back titration, mL,
N_1 = normality of the $NaAsO_2$ solution,
N_2 = normality of the iodine solution, and
W = sample taken, g.

MOISTURE

51. Summary of Test Method

51.1 Moisture in chloroisocyanuric acids and salts is determined gravimetrically after heating for 2 h at 103 to 105°C.

52. Apparatus

52.1 *Weighing Bottles,* 50-mm inside diameter by 30-mm height.

52.2 *Drying Oven,* electric, with accurate thermostatic control to maintain temperature at 104 ± 1.0°C.

53. Procedure

53.1 Weigh 2.000 ± 0.001 g of the well-mixed sample into a clean and dry, tared weighing bottle. Place the bottle, with cap removed, in the oven at 103 to 105°C (Note 10) for 2 h (Note 11). Then remove from the oven, replace cap, cool in a desiccator, and weigh.

NOTE 10—The temperature of the oven *must not exceed* 105°C. Sublimation of the chloroisocyanuric acids may occur at temperatures above this limit.

NOTE 11—Some of the salts may not be thoroughly dried in less than 2 h.

54. Calculation

54.1 Calculate the percentage moisture as follows:

$$\text{Moisture, \%} = (A/W) \times 100 \tag{13}$$

where:

A = loss in weight, g, and
W = sample taken, g.

55. Keywords

55.1 bleaches; chlorine; hypochlorite; iodometric titrations

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