



Standard Test Method for Bromine in Chlorine¹

This standard is issued under the fixed designation E 649; 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.

^{ε1} NOTE—Editorial changes were made in June 2005.

1. Scope

1.1 This test method covers the determination of bromine in liquid chlorine and in gaseous chlorine with a lower limit of detection of 4 $\mu\text{g}/\text{kg}$ by weight.

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.* Specific hazard statements are given in Section 7.

1.3 Review the current Materials Safety Data Sheets (MSDS) for detailed information concerning toxicity, first-aid procedures, handling, and safety precautions.

2. Referenced Documents

2.1 *ASTM Standards:*²

D 1193 Specification for Reagent Water

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals

E 200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis

3. Summary of Test Method

3.1 Chlorine gas is sampled by absorption in aqueous sodium hydroxide (NaOH). Liquid chlorine is first vaporized, and the vapor is absorbed in aqueous sodium hydroxide. An aliquot of the sample solution is reduced with an excess of sulfite ion, acidified, and excess sulfur dioxide (SO_2) boiled out. In a carefully buffered solution, bromide is oxidized to bromate by hypochlorite. Excess hypochlorite is reduced to chloride by formate. In the presence of molybdate catalyst,

bromate is reduced to bromide by iodide, and the liberated iodine is titrated with standard sodium thiosulfate solution.

4. Significance and Use

4.1 Low levels of bromine contaminant in chlorine cause problems in some industrial uses. This test method may be used to determine bromine in liquid or gaseous chlorine at levels as low as 4 $\mu\text{g}/\text{kg}$.

5. Apparatus

5.1 The construction of the chlorine gas sampling apparatus and of the assembled sampling equipment is shown in **Figs. 1 and 2**. Modification of the equipment to deal with special sampling circumstances may be necessary. In **Fig. 2**, the control valve is shown with an adaptor for connection to a chlorine cylinder valve. Other adaptors will be required when sampling liquid chlorine in liquefaction plant streams or from large shipping or storage containers.

5.2 A 10-mL buret calibrated in 0.05-mL divisions is used when titrating with 0.01 *N* standard sodium thiosulfate solution.

6. Reagents

6.1 *Purity of Reagents*—Unless otherwise indicated, it is intended that all reagents should 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.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type II or Type III reagent water conforming to Specification **D 1193**.

6.3 *Chloride Solution*—Dissolve 200 g of sodium chloride (NaCl) in 940 mL of water.

¹ This test method is under the jurisdiction of ASTM Committee E15 on Industrial Chemicals and is the direct responsibility of Subcommittee E15.02 on Product Standards.

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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.

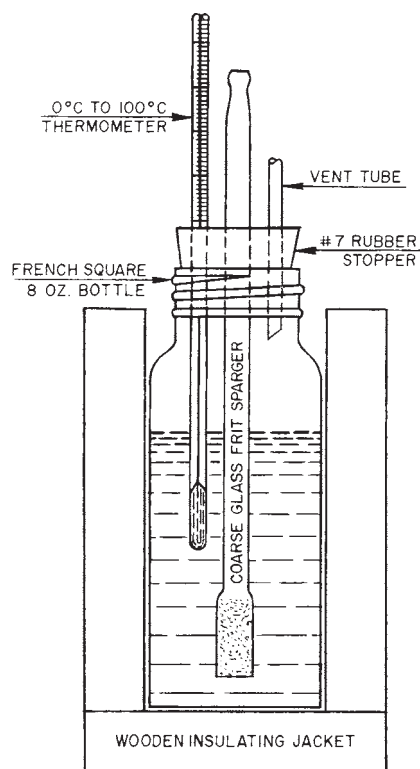


FIG. 1 Chlorine Gas Sampling Apparatus

6.4 *Formate Solution*—Dissolve 50 g of sodium formate in 175 mL of water.

6.5 *Hypochlorite Solution*—Dissolve 6.2 g of NaOH in 190 mL of water and chlorinate slowly, with stirring, to give a gain in weight of 5.0 g.

NOTE 1—If desired, a commercial hypochlorite bleach solution may be used as the hypochlorite solution. Although such commercial bleach solutions are not made from reagent grade chemicals, the reagent blank determination (see 9.4) corrects for the bromine and any chlorate content in such solutions. A proprietary 5.25 % sodium hypochlorite bleach solution is satisfactory for this use. Because the sodium chloride and hypochlorite solutions contribute most to the reagent blanks, dispense these solutions by pipet to ensure uniformity of blanks and determinations (see 9.1 and 9.2).

6.6 *Molybdate Solution (44 g/L)*—Dissolve 4.4 g of ammonium molybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$) in 10 mL of 6 N ammonium hydroxide (NH_4OH) and dilute with 90 mL of water.

6.7 *Phenolphthalein Indicator Solution (1 g/L)*—Dissolve 0.1 g of phenolphthalein and 0.1 g sodium carbonate (Na_2CO_3) in 5 mL of water and dilute to 100 mL.

6.8 *Phosphate Solution (100 g/L)*—Dissolve 50 g of monobasic sodium phosphate ($\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}$) in 500 mL of water.

6.9 *Sodium Hydroxide Solution (10 %)*—Dissolve 1 part by weight of sodium hydroxide (NaOH) in 9 parts of water.

6.10 *Sodium Thiosulfate, Standard Solution (0.01 N)*—Prepare 0.01 N sodium thiosulfate solution fresh daily by accurate dilution of standard 0.1 N sodium thiosulfate solution. Prepare, standardize, and restandardize 0.1 N sodium thiosulfate solution in accordance with Practice E 200.

6.11 *Starch Solution (10 g/L)*—Dissolve 1 g of soluble starch in 100 mL of boiling water. Make up fresh daily.

6.12 *Sulfuric Acid (6 N)*—Add slowly and cautiously with constant stirring, 1 volume of concentrated sulfuric acid (sp gr 1.84, H_2SO_4) to 5.5 volumes of water. **Caution:** Use goggles when preparing this solution. Cool to room temperature before use.

6.13 *Sulfuric Acid (1 + 1)*—Add slowly with stirring 1 volume of concentrated sulfuric acid (H_2SO_4 , sp gr 1.84) to 1 volume of water. **Caution:** Use goggles when preparing this solution.

7. Hazards

7.1 Concentrated sulfuric acid, sodium hydroxide, and sodium hypochlorite solutions are rapidly corrosive to skin and eyes. In case of accidental contact with skin, immediately flush affected part with large volumes of water. For eyes, immediately flush with water for at least 15 min; then get prompt medical attention. Goggles should be worn when handling these chemicals.

7.2 Chlorine sampling should be performed only by persons thoroughly familiar with handling this material and with operation of the sampling system. Personnel should be equipped with a respirator, goggles, faceshield, and gloves. If possible, perform sampling in a hood or other well-ventilated area. In sampling liquid chlorine, do not leave the space between two closed valves filled with liquid chlorine (see 8.6).

7.3 When sampling and working with chlorine out of doors, people downwind from such operation should be warned of the possible release of chlorine vapors.