Designation: E649 – 17a

Standard Test Method for Bromine in Chlorine[1]

This standard is issued under the fixed designation E649; 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.

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 ug/kg by weight.

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

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.* Specific hazard statements are given in Section 7.

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

D6809 Guide for Quality Control and Quality Assurance Procedures for Aromatic Hydrocarbons and Related Materials

E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]

E200 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 ug/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.[4] Other grades may be used, provided it is first ascertained that

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[1] This test method is under the jurisdiction of ASTM Committee D16 on Aromatic, Industrial, Specialty and Related Chemicals and is the direct responsibility of Subcommittee D16.16 on Industrial and Specialty 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] The last approved version of this historical standard is referenced on www.astm.org.

[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.

***A Summary of Changes section appears at the end of this standard**

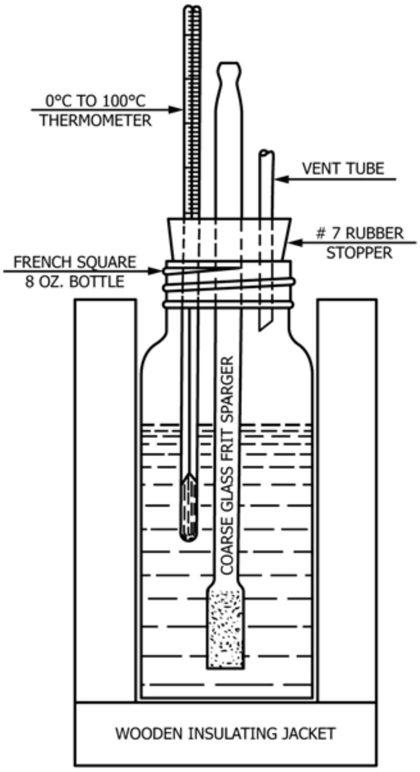
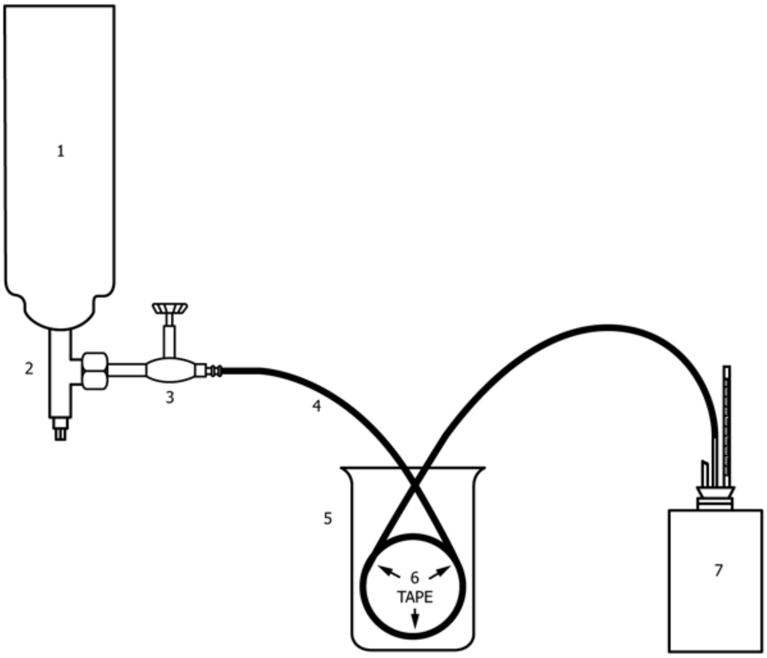


FIG. 1 Chlorine Gas Sampling Apparatus



1. Inverted liquid chlorine cylinder
2. Chlorine cylinder valve
3. Control valve (¼-in. 316 stainless steel needle valve)
4. ¼-in. PTFE instrument air tubing
5. Small pail or 2-L beaker filled with water
6. Evaporating coil (two loops held with tape at indicated points)
7. Gas sampling apparatus of Fig. 1

FIG. 2 Liquid Chlorine Sampling Equipment 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 D1193.

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

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 $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ 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 ($NaH_2PO_4\cdot H_2O$) 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 E200.

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. **Warning:** 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. **Warning:** 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.

7.4 It is recommended that means be available for disposal of excess chlorine in an environmentally safe and acceptable manner. If chlorine cannot be disposed of in a chlorine-consuming process, a chlorine absorption system should be provided. When the analysis and sampling regimen requires an initial purging of chlorine from a container, the purged chlorine should be similarly handled. Purging to the atmosphere should be avoided.

7.5 In the event chlorine is inhaled, first aid should be summoned immediately and oxygen administered without delay.

7.6 Chlorine is a corrosive and toxic material. A well-ventilated fume hood should be used to house all test equipment when this product is analyzed in the laboratory.

8. Sampling

8.1 Record to the nearest 0.1 g the tare of the clean and dry chlorine gas sampling apparatus of Fig. 1, except for the insulating jacket. Add 150 mL of 10 % NaOH solution and seal the stopper firmly in place. Record the tare of this assembly to the nearest 0.1 g. Place the apparatus in the insulating jacket and allow to stand to reach temperature equilibrium.

8.2 Saturated chlorine vapor will contain only about 0.3 as much bromine as the liquid chlorine with which it is in equilibrium. Hence, when sampling containers of liquid chlorine, it is necessary to make sure that only the liquid phase is sampled. Gaseous chlorine sources may be sampled directly, using a small valve to control the chlorine flow. Feed the liquid chlorine through vaporizing equipment before passing the resulting vapor into the chlorine gas sampling apparatus. There is no need for a vaporizer when sampling a source of gaseous chlorine.

8.3 A satisfactory vaporizer for sampling liquid chlorine is readily prepared from a 1.5 to 2-m length of ¼-in. (6.35-mm) outside diameter polytrafluoroethylene (PTFE) instrument air tubing. This had adequate flexibility, and is easily coiled to form a 120-mm diameter evaporating coil. When sampling a liquid chlorine cylinder, invert the cylinder and connect the apparatus as shown in Fig. 2. Do not wire the tubing connections. This will allow the tube to blow off in case of excessive pressure. With the small control valve closed, open the liquid chlorine supply valve about a half turn to bring the liquid chlorine to the control valve.

8.4 Swirl the NaOH solution in the chlorine sampling apparatus thoroughly and note the initial temperature; then very carefully open the control valve to allow a small stream of chlorine gas to purge the air from the line leading to the sampling apparatus. Lift the sampling apparatus partially out of its insulating jacket to observe the bubbles rising from the fritted gas sparger. As the air is purged from the system, increase the chlorine flow, so that the chlorine bubbles entering the solution from the sparger shrink to minimum size about 20 mm below the surface of the liquid. Lower the sampling bottle into the insulating jacket and observe the temperature of the solution.

8.5 The temperature should rise at 2 to 5°C/min. If the rate of temperature rise is higher or lower than this, adjust the chlorine flow accordingly. Swirl the sampling apparatus frequently to mix thoroughly and achieve temperature uniformity. When the temperature reaches 20°C above the initial temperature, remove the sampling apparatus from the insulating jacket, turn off the control valve, and immediately disconnect the PTFE tubing from the control valve. With an aspirator bulb, blow air through the tubing to force all chlorine in the PTFE tubing into the sample solution.

8.6 Close the chlorine supply valve and immediately open slightly the control valve to vent liquid chlorine trapped between the valves. Direct the vented chlorine into a hood or a chlorine disposal system. **Warning:** Do not overlook this venting procedure. If the space between the closed supply and control valves is left completely filled with liquid chlorine, dangerous pressures rapidly build up when the temperature is allowed to rise.

8.7 Thoroughly blend the sample solution while using the aspirator bulb to push the sample solution back and forth through the sparger frit. Carefully clean and dry the outside of the sampling assembly and weigh to the nearest 0.1 g. The gain in weight of the apparatus is the weight of chlorine absorbed. The final weight less the tare of the empty apparatus is the weight of the sample solution.

9. Procedure

9.1 Take about one third of the sample solution (±1 g), weigh to the nearest 0.1 g, and transfer into a 500-mL Erlenmeyer flask with a volume calibration mark at 100 mL. Add by pipet, 25 mL of chloride solution, add 9 g of sodium sulfite (Na_2SO_3), and 25 mL of water, swirl, and warm, to dissolve; then add slowly, while swirling, 9 mL of H_2SO_4 (1 + 1). Add three boiling beads, heat to boiling, and immediately test the vapor with moist starch iodide paper that has been treated with a trace of chlorine vapor to give a light blue color. The starch iodide paper should be bleached colorless, indicating an excess of sulfite over the chlorine in the sample. Continue to boil for 10 min, adding water if necessary to bring any deposited salts into solution. At this point, the solution volume should be less than 100 mL.

9.2 Cool the sample to below 50°C, add 1 drop of phenolphthalein indicator solution, and neutralize to within 1 drop excess of 10 % NaOH solution. Add 20 mL of phosphate solution, and add by pipet, 10 mL of hypochlorite solution. Heat the solution nearly to boiling for 5 min, then boil the solution for 2 min. At the end of this boiling period, the steam from the sample solution should rapidly turn moist starch iodide paper blue. This indicates an adequate excess of hypochlorite in the sample.

9.3 Slowly add 10 mL of the formate solution while swirling. Wash down the flask and again bring the solution to boiling. Cool to room temperature, add 1 g of potassium iodide (KI), 25 mL of 6 *N* H_2SO_4, and 2 drops of molybdate solution. Immediately titrate the liberated iodine with standard 0.01 *N* sodium thiosulfate solution until the sample solution is pale yellow. Add 2 mL of starch solution and titrate until the blue color disappears. Record the volume of thiosulfate consumed (*A* mL).

NOTE 2—Titrate samples that turn very dark from liberation of large amounts of iodine with 0.1 *N* thiosulfate solution.

9.4 Run a blank determination substituting 50 mL of 10 % NaOH solution for the weighed aliquot of sample solution. Use 17 mL of H_2SO_4 (1 + 1) rather than the 9 mL used with the sample. Record the volume of 0.01 *N* thiosulfate solution consumed (*B* mL).

NOTE 3—The blank determination is necessary so that correction can be made for the traces of bromine normally present in reagent grade sodium chloride and in hypochlorite solutions. The blank determination also makes correction for small concentrations of chlorate that hypochlorite solutions may also contain.

10. Calculation

10.1 To determine the mass of chlorine in the aliquot, use the following equation:

$$\frac{\text{grams } Cl_2 \text{ absorbed} \times \text{grams sample aliquot}}{\text{grams total sample solution}} = \text{grams chlorine in aliquot} \tag{1}$$

10.2 To determine bromine by weight, ug/kg, use the following equation:

$$\frac{(A - B) \times \text{normality} \times 13\,318}{\text{grams chlorine in aliquot}} = \text{ppm bromine by weight} \tag{2}$$

where:

A = volume of 0.01 *N* thiosulfate solution consumed in the determination, mL, and

B = volume of 0.01 *N* thiosulfate solution consumed in the blank determination, mL.

11. Report

11.1 Report the bromine content to the nearest whole ug/kg.

12. Precision and Bias

12.1 The following criteria should be used for judging the acceptability of results (Note 4):

12.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be the value shown in Table 1 at the indicated degrees of freedom. The 95 % limit for the difference between two such runs is the value shown in Table 1.

12.1.2 *Within-Laboratory, Between-Days Variability*—The standard deviation of results (each the average of duplicates),

TABLE 1 Precision of Bromine Method

Bromine Level, ug/kg	Repeatability			Within-Laboratory, Between Days Variability			Reproducibility		
	Standard Deviation, ug/kg	Degrees of Freedom	95 % Limit, ug/kg	Standard Deviation, ug/kg	Degrees of Freedom	95 % Limit, ug/kg	Standard Deviation, ug/kg	Degrees of Freedom	95 % Limit, ug/kg
8	1.3	14	4	1.5	7	4	2	6	6
23	1.7	16	5	2.0	8	6	3	7	8
280	5.3	14	15	11	7	31	14	6	39

obtained by the same analyst of different days, has been estimated to be the value shown in Table 1 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is the value shown in Table 1.

12.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each average of duplicates), obtained by analysts in different laboratories, has been estimated to be the value shown in Table 1 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is the value shown in Table 1.

NOTE 4—The preceding precision estimates are based on an interlaboratory study performed in 1978 on three samples of liquid chlorine. One analyst in each of eight laboratories performed duplicate determinations and repeated one day later. Practice E180 was used in developing these precision estimates.

12.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

13. Quality Guidelines

13.1 Laboratories shall have a quality control system in place.

13.1.1 Confirm the performance of the test instrument or test method by analyzing a quality control sample following the guidelines of standard statistical quality control practices.

13.1.2 A quality control sample is a stable material isolated from the production process and representative of the sample being analyzed

13.1.3 When QA/QC protocols are already established in the testing facility, these protocols are acceptable when they confirm the validity of test results.

13.1.4 When there are no QA/QC protocols established in the testing facility, use the guidelines described in Guide D6809 or similar statistical quality control practices.

14. Keywords

14.1 analysis; bromine; chlorine; sampling

SUMMARY OF CHANGES

Subcommittee D16.16 has identified the location of selected changes to this standard since the last issue (E649–17) that may impact the use of this standard. (Approved July 1, 2017.)

(1) Section 13 Quality Guidelines was added.

Subcommittee D16.16 has identified the location of selected changes to this standard since the last issue (E649-00(2011)) that may impact the use of this standard. (Approved March 1, 2017.)

(1) Added Summary of Changes section.
(2) Removed "Material" from (MSDS) statement in Scope section 1.3.