Designation: E 2037 – 01

Standard Test Method for Bromine Chloride in Liquid Chlorine by High Performance Liquid Chromatography (HPLC)[1]

This standard is issued under the fixed designation E 2037; 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 uses high performance liquid chromatography (HPLC) to determine bromine chloride levels in liquid chlorine at the 10 to 1400 µg/g (ppm) range.

1.2 Review the current material safety data sheet (MSDS) for detailed information concerning toxicity, first aid procedures, 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 8.

2. Referenced Documents

2.1 *ASTM Standards:*

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals[2]

E 806 Test Method for Carbon Tetrachloride and Chloroform in Liquid Chlorine by Direct Injection (Gas Chromatography Procedure)[2]

2.2 *Federal Standards*[3]

49 CFR 173 Code of Federal Regulations Title 49 Transportation: Shipper's General Requirements for Shipments and Packaging, including Sections 173.304, Charging of Cylinders with Liquefied Compressed Gas; 173.314, Requirements for Compressed Gases in Tank Cars; and, 173.315 Compressed Gases in Cargo Tanks and Portable Tank Containers.

2.3 *Other Document*

Chlorine Institute Pamphlet No. 77 Sampling Liquid Chlorine[4]

3. Summary of Test Method

3.1 Weighed samples of chlorine delivered into a cooled graduated centrifuge tube. One mL of cooled HPLC eluent is added before the chlorine is allowed to evaporate. After the chlorine has evaporated the remaining eluent is analyzed directly on the HPLC for bromine chloride concentration.

4. Significance and Use

4.1 This test method was developed for the determination of bromine chloride in liquid chlorine. Bromide is a common contaminant in all salt sources that are used in the production of chlorine. This bromide content of the salt is converted into bromine chloride in the liquid chlorine product. This test method is sensitive enough to measure the levels of bromine chloride observed in normal production chlorine.

5. Interferences

5.1 This test method is selective for bromine chloride. At this time there are no known interference in the materials used in this test method.

5.2 Contact with any metal surfaces should be avoided due to the corrosive nature of the sample.

6. Apparatus

6.1 A high performance liquid chromatograph (HPLC) composed of the following:

6.1.1 *HPLC Pump*, capable of 1 mL/min flow,

6.1.2 *HPLC UV Detector*, capable of operating at 221 nm with a 1-cm cell,

6.1.3 *HPLC Injection Valve*, 20 µl loop, all nonmetal, and

6.1.4 *HPLC Column*, C18 reverse phase, 25 cm by 4.6 mm.

6.2 *Plastic Syringes*, 1, 2.5, 5, 10, 20, and 60 mL.

6.3 *Nonmetallic Syringe Needles*.

6.4 *Top Loader Balance*, capable of 0.01 g resolution with a 1-kg capacity.

6.5 *TFE-Fluorocarbon Tubing*, 1⁄16 in. outside diameter.

6.6 *Stainless Steel Sample Cylinder*, with a needle valve on one end.

6.7 *Graduated Centrifuge Tube*, 15 mL.

7. Reagents

7.1 *Purity of Reagents*—Unless otherwise indicated, it is

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

Current edition approved Oct. 10, 2001. Published December 2001. Originally published as E 2037–99. Last previous edition E 2037–99.

[2] *Annual Book of ASTM Standards*, Vol 15.05.

[3] Available from the U.S. Government Printing Office, Superintendent of Documents, Washington, DC 20402.

[4] Available from The Chlorine Institute Inc., 70 W. 40th St., New York, NY 10018.

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.[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 *Water*, HPLC grade.

7.3 *Methanol*, HPLC grade.

7.4 *Sodium Acetate*, reagent grade.

7.5 *Glacial Acetic Acid*, reagent grade.

7.6 *Dry Ice*.

7.7 *Potassium Bromide*, reagent grade.

7.8 *Chlorine*, reagent grade.

8. Hazards

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

8.2 The analysis should be attempted only by persons who are thoroughly familiar with the handling of chlorine, and even an experienced person should not work alone. The operator must be provided with adequate eye protection and a respirator. Splashes of liquid chlorine destroy clothing and if such clothing is next to the skin, it will produce irritations and burns.

8.3 If liquid samples are to be taken in cylinders, do not allow the sample cylinder to become liquid full. Test Method 806, 49 CFR 173.314, 173.315, and 173.304 advise that the weight of the chlorine in the cylinder should not be more than 125 % of the weight of the water that the cylinder could contain. See the Chlorine Institute Pamphlet No. 77 for specific instructions on the sampling of liquid chlorine.

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

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

8.6 Store pressurized samples where involuntary release would not cause excessive risk to people or property.

8.7 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.

8.8 *Safety and Health Precautions*—Exposure to all solvents used in this test method should be avoided.

9. Typical Instrument Parameters

9.1 Adjust the chromatograph in accordance with the following parameters and allow the instrument to equilibrate until a steady baseline is obtained:

9.1.1 *Column*—C18 reverse phase ODS (C18) 25 cm by 4.6 mm, 10 µm,

9.1.2 *Eluent*—60 % by volume methanol, 40 % by volume 0.1 M acetate buffer, pH 4.5, helium sparged,

9.1.3 *Flow Rate*—1 mL/min,

9.1.4 *Injection Volume*—20-µl sample loop, and

9.1.5 *Detector Wavelength*—UV at 221 nm.

10. Preparation of Buffer Solution

10.1 *Sodium Acetate Buffer Stock Solution (1 M)*—Dissolve 136 g of sodium acetate ($NaOOCCH_3 \cdot 3H_2O$) and 60 g of glacial acetic acid ($HOOCCH_3$) in water and dilute to 1 L.

10.2 *Sodium Acetate Buffer (0.1 M)*—Transfer 100 mL of the stock buffer solution into a 1-L volumetric flask and dilute to volume with water.

11. Preparation of Eluent

11.1 Add 600 mL of methanol to 400 mL of 0.1 M sodium acetate buffer solution and mix well. Before use, purge the solution with helium for 20 min to remove dissolved oxygen.

12. Preparation of the Sample Cylinder

12.1 Clamp the sample cylinder in a vertical position with the needle valve in the downward position. Insert the 0.25-in. end of the reducing tube fitting into the needle valve and set the 0.25-in. nut and ferrule of the fitting. Insert the 1⁄16in. fluoropolymer tubing in the reducing tube fitting and tighten the 1⁄16-in. nut and ferrule. See Fig. 1. It may be helpful to cut a 0.25-in. circle of fluoropolymer frit material and place it into the reducing fitting prior to assembly to prevent plugging of the 1⁄16 in. tubing. Cut the length of the 1⁄16 in. tubing so that only 1.5 in. protrudes out of the fitting.

13. Standardization of the HPLC

13.1 Prepare a 1000 ppm stock solution of potassium bromide in water. Make a series of standards of potassium bromide by serial dilution covering the range between 1 and 650 ppm potassium bromide. Calculate the bromine chloride concentration of each standard from the potassium bromide concentration by multiplying by the ratio of the molecular weights:

$$(BrCl/KBr) = (115.4/119) = 0.97 \quad (1)$$

13.2 Withdraw 0.5 mL of a potassium bromide standard into a 1-mL plastic syringe and then pull the plunger back to the 1 mL mark to fill the remainder of the syringe with air.

13.3 Clamp a sample cylinder containing reagent chlorine vertically in a ring stand and attach a 6-in. piece of 1⁄16 in.

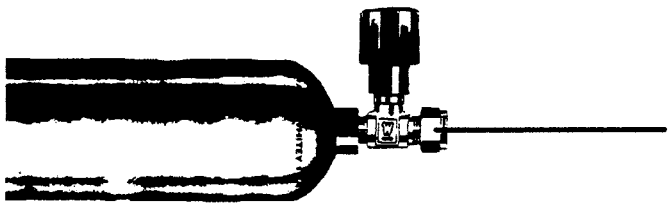

FIG. 1 Sample Cylinder

[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.

outside diameter TFE-fluorocarbon tubing to the top valve. Take a second 1-mL plastic syringe and pull the plunger back to the 1 mL mark. Insert the 1⁄16 in. TFE-fluorocarbon tubing into the syringe and gently purge chlorine through the syringe filling this second syringe with reagent chlorine gas. Remove the TFE-fluorocarbon tubing from the syringe and attach a nonmetal needle to the luer tip.

13.4 Holding the first syringe pointed upward, use the second syringe equipped with the nonmetal needle to bubble the reagent chlorine gas through the potassium bromide standard solution, converting the bromide ions to bromine chloride. One mL of reagent chlorine gas is required for the conversion of each 500 ppm of bromide ion in the standard. Although the amount of chlorine used to chlorinate the standards is extremely small when compared to that of the sample, it is always a good idea to prepare the first standard in any calibration curve without the addition of the potassium bromide to serve as a reagent blank.

13.5 Using the entire 0.5 mL of standard flush the injection valve and fill the sample loop in the injection valve. Immediately inject this standard into the HPLC for analysis. The bromine chloride peak will elute between 4 and 4.25 min in the chromatogram. The bromide chloride peak elutes between the water dip and the peak caused by the excess chlorine. See Fig. 2.

13.6 Measure and record the peak height of the bromine chloride peak in the analysis of each of the standard solutions. Plot the peak heights of each standard versus the concentrations of the bromine chloride in each standard analyzed. The slope and intercept of this line are used in the calculation of the sample analysis values. See Fig. 3.

NOTE 1—Bromine chloride is formed by simply mixing bromine and chlorine. This is a reversible equilibrium reaction that can rapidly exchange back to bromine and chlorine depending on the amounts of bromine and chlorine present. The response to a particular bromine chloride standard can be influenced by the amount of bromide already present in the HPLC column from previous injections. In Fig. 4, the lower line on the calibration graph is the response to bromine chloride standards with one or more blank runs between the analysis of each standard to ensure that the column was background-free. The upper response line in the calibration curve was obtained by injecting a 94 ppm standard between the analysis of each standard. These two curves very rapidly merge above 200 ppm in the injected solution. Keep in mind that the concentrations listed on the calibration curve are the concentrations of the injected solution and must be divided by the number of grams of chlorine that was evaporated (typically > 10 g), to obtain the concentration in the original chlorine. The bromine chloride concentration in most chlorine samples is high enough that the lower level calibration will never be used.

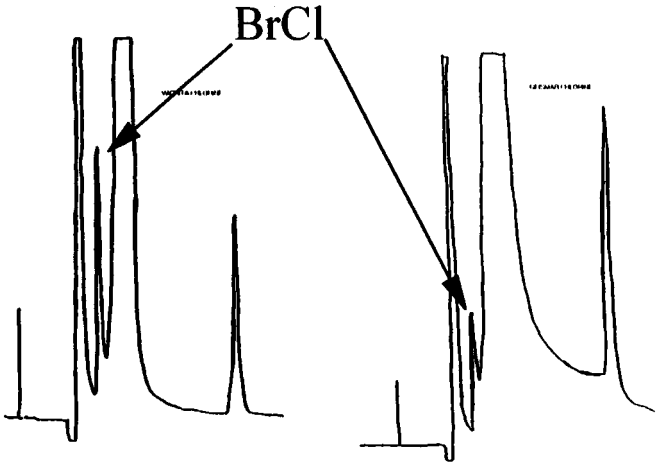

FIG. 2 Typical Chromatograms

14. Procedure

14.1 Tare a metal sample cylinder equipped with a closed needle valve on one end and cool the cylinder in dry ice. Sample the liquid chlorine source using metal tubing or pipe connections.

14.2 Reweigh the sample cylinder to determine the weight of chlorine collected in the cylinder before the cylinder is allowed to warm. If the cylinder is more than 60 % full, drain the liquid chlorine out of the bottom of the cylinder and reweigh until the weight of the chlorine is within acceptable limits for that cylinder.

NOTE 2—For example, a 150-mL cylinder should not contain more than 90 mL of chlorine at a density of 1.467 g/mL (that is, 132 g of chlorine).

14.3 Attach a 1.5-in. piece of 1⁄16 in. TFE-fluorocarbon tubing and reducing fitting to the needle valve on the chlorine cylinder, weigh, and record the sample cylinder weight to the nearest 0.1 g.

14.4 Clamp the cylinder in a ring stand with the needle valve and fluoropolymer tubing pointed down.

14.5 Fill a 1-mL plastic syringe with 1 mL of HPLC eluent and cool by placing it in crushed dry ice.

14.6 Cool a 15-mL centrifuge tube in crushed dry ice for several minutes. Remove the tube from the dry ice and hold it on the 1⁄16 in. TFE-fluorocarbon tubing with the tubing extending down to the bottom of the centrifuge tube. Slowly open the needle valve on the cylinder and deliver 5 mL of liquid chlorine into the centrifuge tube. Reweigh the sample cylinder, record the sample weight to the nearest 0.1 g.

14.7 Before the chlorine starts to evaporate slowly add the 1 mL of cooled eluent and mix. Some spattering can be expected when the eluent first contacts the chlorine. Be sure that the tube is pointed away from the analyst.

14.8 Place the centrifuge tube with chlorine in a small beaker containing about 0.25 in. of water at room temperature. This will start the evaporation of the chlorine at a moderate rate. The total amount of chlorine will evaporate in about 3 to 5 min.

14.9 Allow the chlorine to evaporate and the tube to warm slightly to decrease the amount of chlorine dissolved in the eluent. This sample must not be allowed to warm to room temperature and must be analyzed as soon as it can be drawn into the syringe.

14.10 Withdraw 0.5 mL of the eluent from the centrifuge tube and use the entire quantity to flush the injection valve and fill the injection valve sample loop. Inject the sample into the HPLC for analysis. This may require working the plunger several times in the eluent to help remove some of the dissolved chlorine before it is possible to get enough of the eluent into the syringe to inject.

14.11 The other 0.5 mL can be placed in crushed dry ice and saved for a second analysis, if needed. This sample will not be stable for the time period of the analysis unless it is frozen.

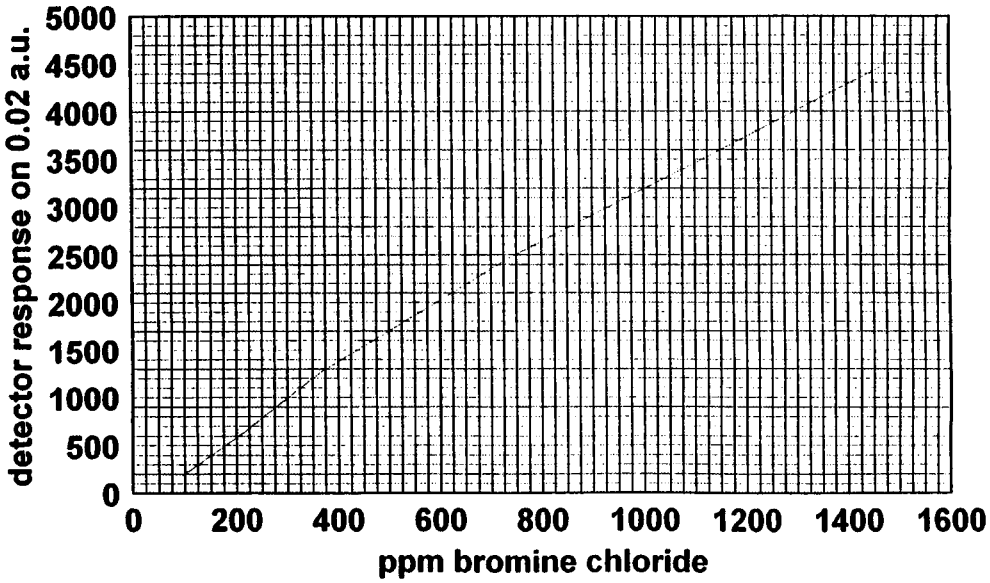

FIG. 3 High Level Calibration

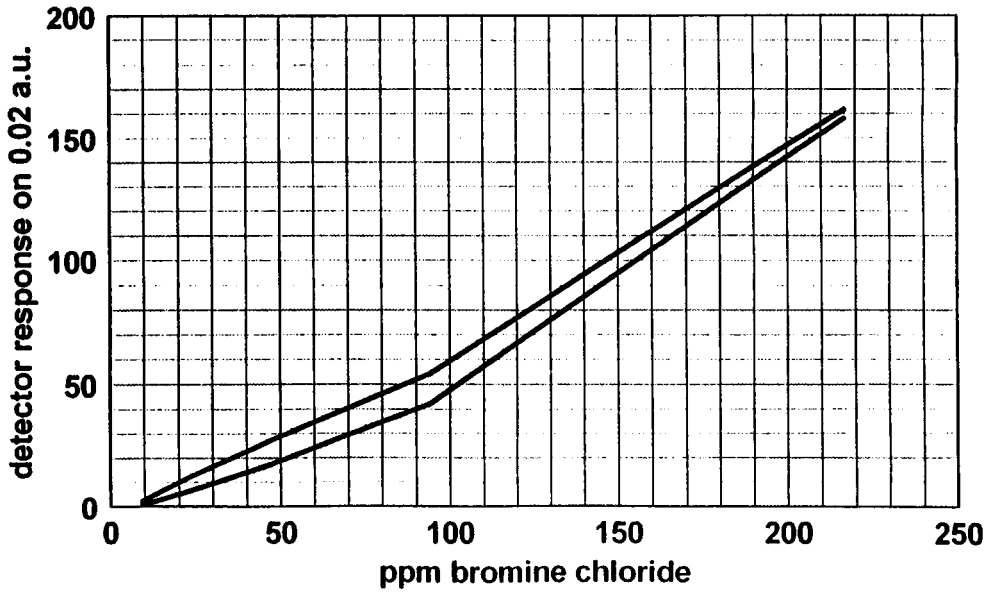

FIG. 4 Low Level Calibration

14.12 The bromine chloride peak elutes between 4 and 4.25 min on the chromatogram. Measure and record the peak height of the bromine chloride peak.

15. Calculation

15.1 Calculate the bromine chloride content, ppm, to the sample as follows:

$$\mathrm{BrCl} = \frac{(R - B) \times E \times 0.908}{A \times G} \quad (2)$$

where:

R = recorder response of the bromine chloride in the sample,
B = recorder response at standard curve intercept,
A = slope of the calibration curve, recorder response/ppm,
G = weight of sample, g,
0.908 = density of the eluent, g/mL, and
E = volume of eluent used, mL.

16. Report

16.1 Report the concentration of bromine chloride to the nearest 1.0 ppm.

17. Precision and Bias

17.1 The following criteria should be used in judging the acceptability of results (see Note 3):

17.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 14 ppm absolute at 17 DF. The 95 % limit for the difference between two such runs is 39 ppm absolute.

17.1.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability, Formerly Called Repeatability*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 10 ppm absolute at 17 DF. The 95 % limit for the difference between two such averages is 27 ppm absolute.

17.1.3 *Reproducibility (Multilaboratory)*—The reproducibility of this test method has not been determined.

NOTE 3—The precision statements in Section 17 are based on a study performed in 1998 by one laboratory on a one-ton cylinder of liquid chlorine containing approximately 129 ppm bromine chloride. One analyst in the laboratory performed two to six determinations on each of seven days, for a total of 24 determinations.[6] An analysis of variance using a one-way classification with unequal observations was used in developing these precision estimates. The definitions for repeatability, laboratory precision, and repeatability are given in Practice E 180. No estimate of reproducibility is possible because data from only one laboratory is available.

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

18. Keywords

18.1 bromine chloride; chlorine; high performance liquid chromatography; HPLC; reversed phase

[6] Details of the interlaboratory study are available as Research Report E15-1057 from ASTM Headquarters.