Designation: E2037 – 24

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

This standard is issued under the fixed designation E2037; 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 µg⁄g (ppm) to 1400 µg/g (ppm) range.

1.2 Review the current safety data sheet (SDS) for detailed information concerning toxicity, first aid procedures, and safety precautions.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 The following applies for the purposes of determining the conformance of the test results using this test method to applicable specifications, results shall be rounded off in accordance with the rounding-off method of Practice E29.

1.5 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific hazard statements are given in Section 8.

1.6 *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]

D180 Methods of Testing Tolerances for Cotton Yarns; Replaced by D 2645 (Withdrawn 1967)[3]

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

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

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Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]

E806 Test Method for Carbon Tetrachloride and Chloroform in Liquid Chlorine by Direct Injection (Gas Chromatographic Procedure)

2.2 *Federal Standards:*[4]

CFR 173 Title 49 Transportation; Shippers' 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

173.315 Compressed Gases in Cargo Tanks and Portable Tank Containers

2.3 *Other Document:*[5]

Chlorine Institute Pamphlet No. 1 Chlorine Basics

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

[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 D16.13 on Chlorine.

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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] Available from U.S. Government Publishing Office, 732 N. Capitol St., NW, Washington, DC 20401-0001, http://www.gpo.gov.

[5] Available from The Chlorine Institute, 1300 Wilson Blvd., Ste. 525, Arlington, VA 22209, http://www.chlorineinstitute.org.

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

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 mL, 2.5 mL, 5 mL, 10 mL, 20 mL, 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,* 1.59 mm 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 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.[6] 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. CAS# 67-56-1.

7.4 *Sodium Acetate,* reagent grade. CAS# 127-09-3.

7.5 *Glacial Acetic Acid,* reagent grade. CAS# 64-19-7.

7.6 *Dry Ice.* CAS# 124-38-9, CO_2.

7.7 *Potassium Bromide,* reagent grade. CAS# 7758-02-3.

7.8 *Chlorine,* reagent grade. CAS# 7782-50-5, Cl_2.

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.

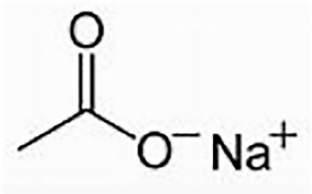

FIG. 1 Sodium Acetate, reagent grade. CAS# 127-09-3.

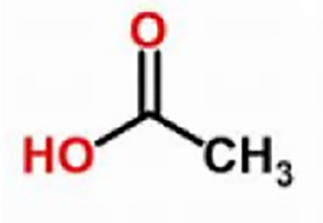

FIG. 2 Glacial Acetic Acid, reagent grade. CAS# 64-19-7.

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 E806, 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. 1 for additional technical information regarding 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.

8.9 Consult current OSHA regulations, suppliers' Safety Data Sheets, and local regulations for all materials used in this test method.

[6] *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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.

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 mol/L (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 mol/L (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 mol/L (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 mol/L (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 6.35 mm end of the reducing tube fitting into the needle valve and set the 6.35 mm nut and ferrule of the fitting. Insert the 1.59 mm fluoropolymer tubing in the reducing tube fitting and tighten the 1.59 mm nut and ferrule. See Fig. 3. It may be helpful to cut a 6.35 mm circle of fluoropolymer frit material and place it into the reducing fitting prior to assembly to prevent plugging of the 1.59 mm tubing. Cut the length of the 1.59 mm tubing so that only 38.10 mm protrudes out of the fitting.

13. Standardization of the HPLC

13.1 Prepare a 1000 µg/g (ppm) stock solution of potassium bromide in water. Make a series of standards of potassium bromide by serial dilution covering the range between 1 µg/g (ppm) and 650 µg/g (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:

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

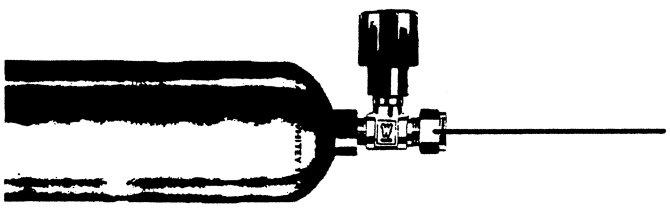

FIG. 3 Sample Cylinder

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 152.40 mm piece of 1.59 mm 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 1.59 mm 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 µg/g (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 min 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. 4.

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. 5.

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

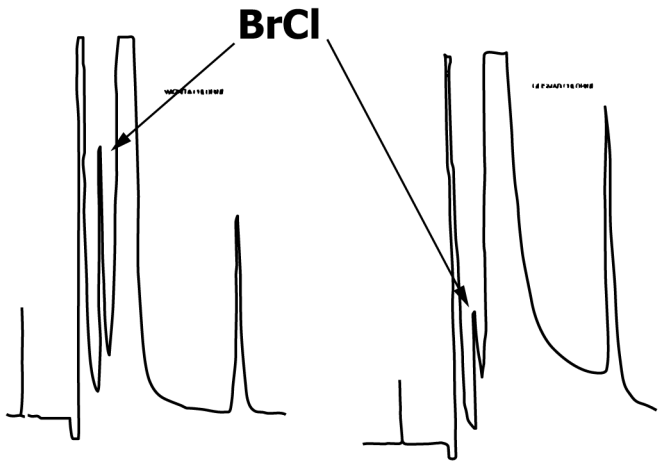

FIG. 4 Typical Chromatograms