



Standard Test Method for Nitrogen Trichloride in Liquid Chlorine by High Performance Liquid Chromatography (HPLC)¹

This standard is issued under the fixed designation E2036; 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 nitrogen trichloride levels in liquid chlorine at the 0.1 to 600 $\mu\text{g/g}$ (ppm) range. Solvent samples from chlorine production facilities containing very high concentrations of nitrogen trichloride may be analyzed by dilution with methanol.

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 *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:²

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Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)³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

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 June 1, 2015. Published June 2015. Originally approved in 1999. Last previous edition approved in 2007 as E2036-07. DOI: 10.1520/E2036-15.

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.

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. 152 Safe Handling of Chlorine Containing Nitrogen Trichloride

3. Summary of Test Method

3.1 Weighed samples of chlorine are 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 nitrogen trichloride concentration.

3.2 In-process solvent samples from chlorine production facility may be analyzed by dilution in methanol followed by direct HPLC analysis of the diluted solution.

4. Significance and Use

4.1 This test method was developed for the determination of nitrogen trichloride in samples of carbon tetrachloride liquid taken from the compressor suction chiller bottoms of chlorine production plants and other places in the plants that may collect and concentrate nitrogen trichloride to levels that could explode. The test method was then modified to measure the lower levels of nitrogen trichloride observed in product liquid chlorine. This test method is sensitive enough to measure the levels of nitrogen trichloride observed in the normal production of liquid chlorine.

4.2 This test method for nitrogen trichloride will require the dilution (100:1) of highly concentrated in-process samples to bring them within the working range of the analysis.

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 (CI), 1300 Wilson Blvd., Ste. 525, Arlington, VA 22209, <http://www.chlorineinstitute.org>.

5. Interferences

5.1 This test method is selective for nitrogen trichloride. At this time there is 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.

5.3 Nitrogen trichloride is decomposed by UV light, heat or strong acid. The presence of metal ions will increase the rate of decomposition. Special care should be taken to avoid exposure of the samples to direct sunlight. Samples and standards should be analyzed immediately upon preparation. Samples not immediately analyzed must be stored in dry ice until just before analysis.

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 light path,

6.1.3 *HPLC Injection Valve*, 20 μ L sample 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, 10, 20, and 60 mL.

6.3 *Nonmetallic Syringe Needles*.

6.4 *Top Loader Balance*, capable of 0.01 g resolution and 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.

6.8 *Reducing Tube Fitting*, 6.35 mm to 1.59 mm tubing.

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.

7.4 *Sodium Acetate*, reagent grade.

7.5 *Glacial Acetic Acid*, reagent grade.

7.6 *Dry Ice*.

7.7 *Ammonium Sulfate*, reagent grade.

7.8 *Chlorine*, reagent grade.

7.9 *Helium*.

8. Hazards

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

8.2 Concentrations of nitrogen chloride over 2 % pose the risk of explosion and should be considered dangerous. Never allow any solutions containing nitrogen chloride to evaporate, concentrating the nitrogen chloride in the remaining residue. The concentrations of nitrogen trichloride synthesized in this test method are small and should not pose any significant risk of explosion. All of the solutions prepared in this test method can be disposed of by flushing them down any laboratory sink using a reasonable amount of water.

8.3 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.

8.4 This analysis should only be performed 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, will produce irritations and burns.

8.5 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.

8.6 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.

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

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

8.9 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.

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 μ m,

⁶ *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.