



Designation: E 2036 – 9901

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

This standard is issued under the fixed designation E 2036; 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 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:*

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.

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E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals²
 E 806 Test Method for Carbon Tetrachloride and Chloroform in Liquid Chlorine by Direct Injection (Gas Chromatography Procedure)²

2.2 *Federal Standard*.³

~~49 CFR 173 Code of Federal Regulations~~

~~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; and 173.315; Cars~~

~~173.315 Compressed Gases in Cargo Tanks and Portable Tank Containers~~

2.3 *Other Document*:

Chlorine Institute Pamphlet No. 77 Sampling Liquid Chlorine⁴

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.

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*, $\frac{1}{16}$ -in. outside diameter.

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

6.7 *Graduated Centrifuge Tube*, 15 mL.

6.8 *Reducing Tube Fitting*, $\frac{1}{4}$ to $\frac{1}{16}$ in. tubing.

7. Reagents

7.1 *Purity of Reagents*—Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the

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

³ Available from 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.

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 *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 E 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.

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,
- 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- μ l 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 sodium acetate ($\text{NaOOCCH}_3 \times 3\text{H}_2\text{O}$) and 60 g 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 methanol to 400 mL 0.1 M sodium acetate buffer solution and mix well. Before use purge the solution with helium for 20 min to remove dissolved oxygen.

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.

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 1/16-in. 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 ammonium sulfate in water. Make a series of standards of ammonium sulfate by serial dilution covering the range between 1 and 650 ppm nitrogen trichloride. Calculate the nitrogen trichloride concentration of each standard from the ammonium sulfate concentration by multiplying by the ratio of the molecular weights, as follows:

$$[\text{NCl}_3/(\text{NH}_4)_2\text{SO}_4] = (120.5/152) = 0.79 \quad (1)$$

$$[2\text{NCl}_3/(\text{NH}_4)_2\text{SO}_4] = (2 \times 120.5/132) = 1.826 \quad (1)$$

13.2 Withdraw 0.5 mL of an ammonium sulfate 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. outside diameter fluoropolymer tubing to the valve. Take a second 1-mL plastic syringe and pull the plunger back to the 1-mL mark. Insert the 1/16 in. fluoropolymer tubing into the second syringe and gently purge chlorine through the syringe filling this second syringe with reagent chlorine gas. Remove the fluoropolymer 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 ammonium sulfate standard solution, converting the ammonium ions to nitrogen trichloride. Use of a 1-mL syringe should avoid overchlorination. See Fig. 2.

13.5 Use the entire 0.5 mL standard to flush the sample valve and fill the sample loop. Immediately inject this standard into the HPLC for analysis. The nitrogen trichloride peak will elute between 11 and 12 min in the chromatogram. See Fig. 3.

13.6 Measure and record the peak height of the nitrogen trichloride peak in the analysis of each of the standard solutions. Plot the peak heights of each standard versus the concentrations of the nitrogen trichloride in each standard analyzed. The slope and intercept of this line will be used in the calculation of the sample analysis values. See Figs. 4 and 5.

NOTE 1—Standards over 200 ppm require 2 mL of chlorine gas for complete conversion of the ammonium ions to nitrogen trichloride. If the calibration curve is extended beyond 650 ppm, more than 2 mL of reagent chlorine gas may be needed to obtain complete conversion of the ammonium ions in the standards. Although the amount of chlorine used for the chlorination of 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 ammonium sulfate to serve as a reagent blank.

NOTE 2—Two calibrations, one completed in December 1995 and one completed in February 1996, were not significantly different. This would indicate considerable stability of the UV detector. Considering the ease with which this test method can be calibrated, a one-point check of the calibration curve is recommended on a weekly basis to ensure that the system is working properly.

14. Procedure for Liquid Chlorine

14.1 Tare a metal sample cylinder equipped with a needle valve and cool the cylinder in dry ice making sure that the needle valve is closed. Sample the liquid chlorine source using metal tubing pipe connections. Do not use fluoropolymer or other type of plastic tubing that could transmit UV light. Nitrogen trichloride is very rapidly decomposed in the presence of UV light. Consult the Chlorine Institute Pamphlet No. 77 for specific details involved in the sampling of liquid chlorine.

14.2 Re-weigh 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 some of 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 3—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. Clamp the cylinder in a ring stand with the needle valve and fluoropolymer tubing pointed down.

14.4 Cool a 15-mL centrifuge tube in crushed dry ice for several minutes.

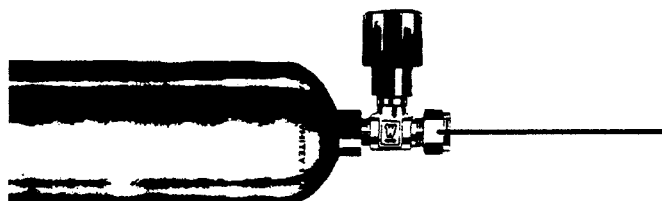


FIG. 1 Sample Cylinder

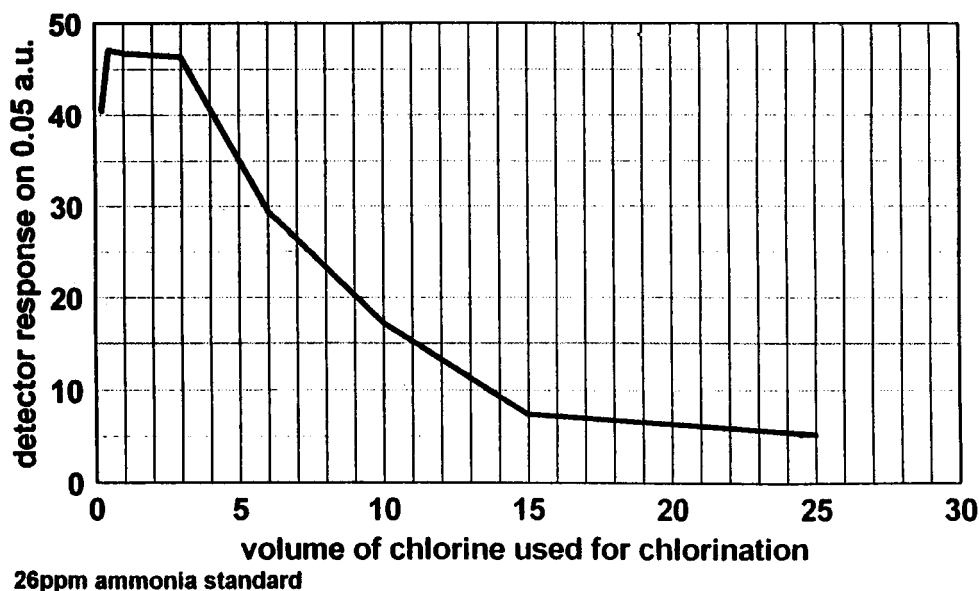


FIG. 2 Standard Preparation By the Chlorination of Ammonia

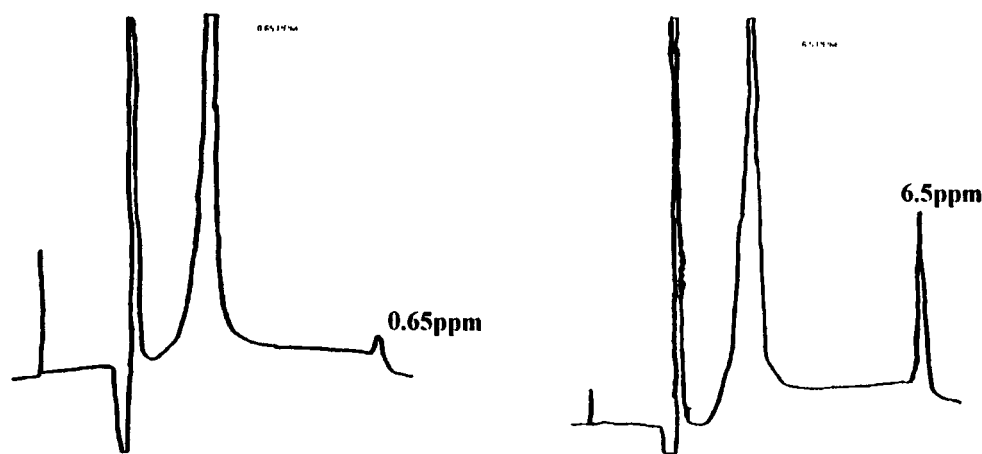


FIG. 3 Typical Chromatograms

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 Remove the tube from the dry ice and hold it on the 1/16 in. fluoropolymer tubing with the tubing extending into the centrifuge tube. Slowly open the needle valve on the cylinder and deliver approximately 5 mL of liquid chlorine into the centrifuge tube. Re-weigh the sample cylinder, record the sample weight to the nearest 0.1g.

14.7 Place the centrifuge tube with chlorine in a small beaker and slowly add the 1 mL of cooled eluent to the chlorine 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's face.

14.8 Add about 0.25 in. of water at room temperature into the beaker holding the centrifuge tube. 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 all of the chlorine to evaporate and the tube to warm slightly to decrease the amount of chlorine dissolved in the eluent. Using the 1-mL eluent syringe, draw up the eluent in the bottom of the centrifuge tube and wash down the sides of the tube with eluent to dissolve any nitrogen trichloride which may be on the walls of the tube. The nitrogen trichloride dissolved in the eluent is not stable at room temperature and should be cooled in dry ice if not analyzed immediately.

14.10 Using the 1-mL eluent syringe, withdraw 0.5 mL of the eluent from the centrifuge tube and use it to flush the injection valve and fill the injection valve sample loop. Inject the eluent onto the HPLC for analysis.

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

14.12 The nitrogen trichloride peak elutes between 11 and 12 min on the chromatogram. Measure and record the peak height of the nitrogen trichloride peak. See Fig. 3.

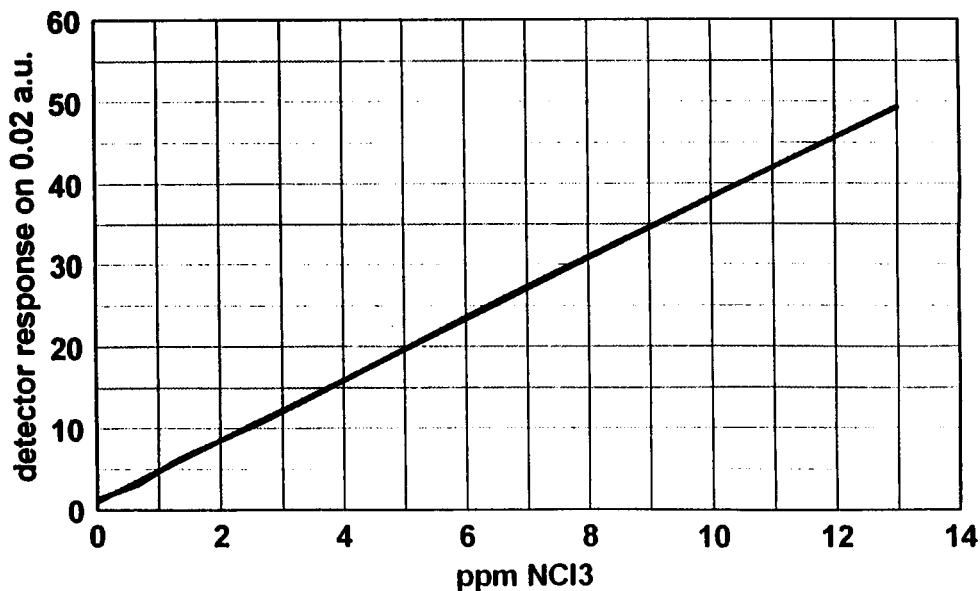


FIG. 4 Low Level Calibration Curve

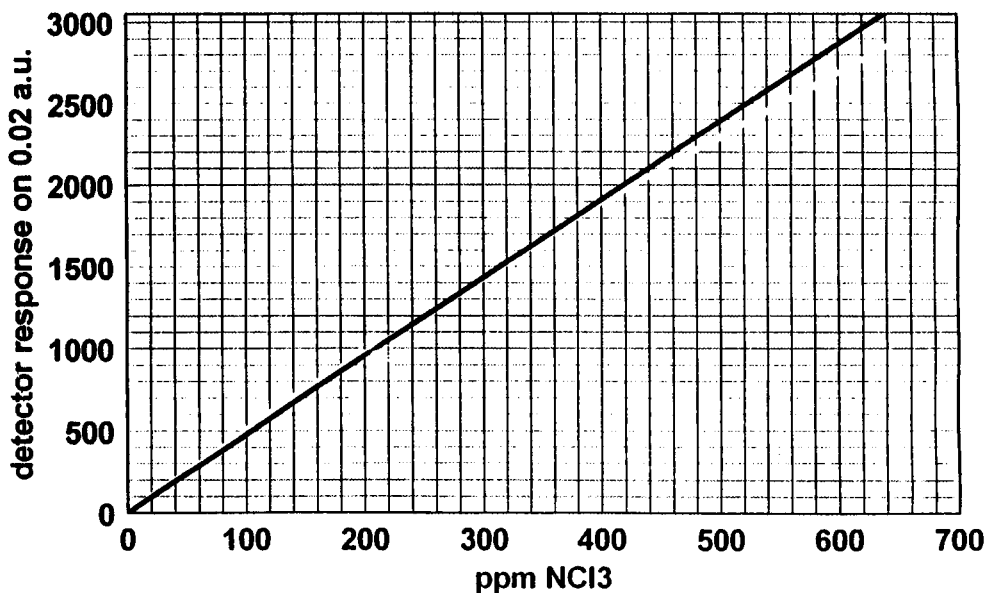


FIG. 5 High Level Calibration Curve

15. Analysis of a Chlorine Production Facility In-process Sample

NOTE 4—Most chlorine production facilities have locations in their processes where nitrogen trichloride tends to buildup or collect. Many of these facilities add carbon tetrachloride or chloroform to these locations as a means of preventing the concentration of the nitrogen trichloride from building up to dangerous levels. To remove the nitrogen trichloride from their systems these solvents are periodically drained and replaced with fresh solvent. These samples are typically very high in nitrogen trichloride concentration.

15.1 Assuming a concentration of 5000 ppm nitrogen trichloride in the solvent, the sample will need to be diluted 1/100. Weigh 1.00 g of the sample into a 100-mL volumetric flask and dilute to volume with methanol.

15.2 Withdraw 0.5 mL of the diluted sample from the volumetric flask using the 1-mL eluent syringe and use the entire quantity to flush the injection valve and fill the injection valve sample loop. Inject the diluted sample into the HPLC for analysis. The nitrogen trichloride peak will elute between 11 and 12 min in the chromatogram. Measure and record the peak height of the nitrogen trichloride peak.

16. Calculation

16.1 Calculate the nitrogen trichloride content, ppm, for liquid chlorine samples as follows:

$$NCl_3 = \frac{(R - B) \times E \times 0.908}{A \times G} \quad (2)$$

where:

- R = Recorder response for 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.

16.2 Calculate the nitrogen trichloride content, ppm, for in-process samples as follows:

$$\text{NCl}_3 = \frac{(R - B) \times 100}{A \times G} \quad (3)$$

where:

- 100 = dilution factor,
- A = slope of the calibration curve, peak height/ppm, and
- G = weight of solvent sample.

17. Report

17.1 Report the concentration of nitrogen trichloride to the nearest 0.1 ppm for product chlorine samples and to the nearest 1.0 ppm for in-process samples. ppm.

18. Precision and Bias

18.1 The following criteria should be used in judging the acceptability of results (see Note 5):

18.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be ~~0.17~~ 0.33 ppm absolute at 17 DF. The 95 % limit for the difference between two such runs is ~~0.5~~ 0.9 ppm absolute.

18.1.2 *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 ~~0.12~~ 0.33 ppm absolute at ~~17~~ 6 DF. The 95 % limit for the difference between two such averages is ~~0.3~~ 0.9 ppm absolute.

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

NOTE 5—The precision statements in Section 18 are based on a study performed in 1998 by one laboratory on a one-ton cylinder of liquid chlorine containing approximately 0.2 ppm nitrogen trichloride. 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. Because data from only one laboratory is available, no estimate of reproducibility is possible.

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

19. Keywords

19.1 chlorine; high performance liquid chromatography; HPLC; nitrogen trichloride; reversed phase

⁶ Details of the interlaboratory study are available as Research Report E15–1058 from ASTM Headquarters.

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