



Designation: E806 – 21

Standard Test Method for Carbon Tetrachloride and Chloroform in Liquid Chlorine by Direct Injection (Gas Chromatographic Procedure)¹

This standard is issued under the fixed designation E806; 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 is designed for the determination of carbon tetrachloride (CCl_4) and chloroform (CHCl_3) in liquid chlorine. The lower limit of detection is dependent on the sample size and the instrument used; five ppm (w/w) is achievable.

1.2 In determining the conformance of the test results using this method to applicable specifications, results shall be rounded off in accordance with the rounding-off method of Practice E29.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific hazards statements are given in Section 7 and in 9.2.3.

1.5 *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

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

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.

Current edition approved Nov. 1, 2021. Published December 2021. Originally approved in 1981. Last previous edition approved in 2017 as E806 – 17a. DOI: 10.1520/E0806-21.

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.

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

2.2 Federal Standard:⁴

OSHA Regulations, 29 CFR paragraphs 19100.1000 and 1910.1200 Air contaminants – Table of exposure limits and Hazard Communication

49 CFR 173 Code of Federal Regulations Title 49 Transportation; Shippers' General Requirements for Shipments and Packagings, 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:

Chlorine Institute Pamphlet No. 1 Chlorine Basics⁵

3. Summary of Test Method

3.1 A sample of liquid chlorine is injected into a gas chromatograph (GC), equipped with a column capable of separating CCl_4 and CHCl_3 from Cl_2 and other impurities, using a suitable syringe. The amounts of CCl_4 and CHCl_3 in the sample are determined by comparison of the areas of the peaks, obtained with the samples, to areas of peaks obtained with suitable calibration standards, under the same conditions.

4. Significance and Use

4.1 CCl_4 and CHCl_3 may be present in trace amounts in liquid chlorine. The use of chlorine to purify water would then transfer these compounds to the water. Therefore, when the concentrations of the CCl_4 and CHCl_3 in the liquid chlorine are

³ The last approved version of this historical standard is referenced on www.astm.org.

⁴ Available from U.S. Government Printing Office, Superintendent of Documents, 732 N. Capitol St., NW, Washington, DC 20401-0001, <http://www.access.gpo.gov>.

⁵ Available from The Chlorine Institute Inc., 1300 Wilson Blvd., Suite 525, Arlington, VA 22209, <https://www.chlorineinstitute.org>.

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

known, the maximum amounts contributed to the water by the chlorine can be estimated.

5. Apparatus

5.1 *Gas Chromatograph*, equipped with:

5.1.1 *Injection Port*, must be lined with glass, Monel,⁶ or nickel; or column must be installed for on-column injection.

5.1.2 *Septa*, from Viton.⁷ Silicone septa may produce artifacts that may interfere with the analysis.

5.1.3 *Column, Column Materials, and Packing*, must be compatible with chlorine. Silanized supports and silanized glass wool must be avoided. Column must be able to separate Cl₂, CCl₄, and CHCl₃. Columns that have been found to be suitable are:

5.1.3.1 *Nickel Tubing*, 3.05 m by 3.175 mm outside diameter, packed with 10 % sodium chloride solution on Porasil C⁸ (see [Appendix X1](#) for packing preparation). This is the preferred packing.

5.1.3.2 *Polytetrafluoroethylene Tubing*, 3.05 m by 2 mm inside diameter, packed with 20 % Kel-F⁹ No. 10 oil on 60/80 mesh Chromosorb¹⁰ W AW.

5.1.3.3 *Glass Tubing*, 3.05 m by 2 mm inside diameter, packed with 20 % Halocarbon¹¹ 1025 on 60/80 mesh Chromosorb W AW.

5.1.4 *Flame Ionization Detector*.

5.1.5 *Recorder*, compatible with the GC detector output.

5.1.6 *Electronic Integrator* (optional), compatible with the GC detector output.

5.2 *Balance*, capacity 5000 g, reading to ± 1 g.¹²

5.3 Autoinjectors are required for all gas chromatograph standards using an external standard to calculate results.

6. Reagents and Materials

6.1 *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.¹³ 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.

6.2 *Chlorine*, liquid, with less than 10 µg/g each of CCl₄ and CHCl₃. This may be prepared by condensing the gaseous phase above regular production chlorine.¹⁴

6.3 *Carbon Tetrachloride*, reagent grade.¹⁴

6.4 *Chloroform*, reagent grade.¹⁴

6.5 *Sample Cylinder Assembly* ([Fig. 1](#)), consisting of:

6.5.1 *Sample Cylinders*;¹⁵ nickel, Monel, or tantalum ([Note 1](#)), 400-mL capacity, double-ended, specially cleaned ([Note 2](#)).

6.5.2 *Valves*, having a packing resistant to liquid chlorine.¹⁶

6.5.3 *Holder for a Septum*, that can be easily assembled.¹⁷

NOTE 1—Carbon or stainless steel cylinders and fittings are not suitable as CHCl₃ is unstable in the presence of FeCl₃ and Cl₂.

NOTE 2—A procedure for cleaning cylinders and valves, for use with liquid chlorine, is given in [Appendix X2](#).

6.6 *Fittings*, for transferring chlorine from one cylinder to another.

¹⁵ If samples are to be shipped outside any plant, cylinders approved by the U.S. Department of Transportation must be used.

¹⁶ Packing made from Teflon, registered trademark of The Chemours Company, Viton, Kel-F, or equivalent have been found suitable for this purpose.

¹⁷ Swagelok, registered trademark of Swagelok Company, or equivalent fittings have been found suitable for this purpose.



FIG. 1 Sample Cylinder Assembly

⁶ Monel is a registered trademark of Special Metals Corporation.

⁷ Viton is a registered trademark of The Chemours Company.

⁸ Porasil is a trademark of Waters Associates, Inc.

⁹ Kel-F is a registered trademark of 3M Company.

¹⁰ Chromosorb is a registered trademark of Imerys Minerals California, Inc.

¹¹ Halocarbon is a registered trademark of Halocarbon Products Corporation.

¹² A 400-mL nickel cylinder filled with liquid chlorine weighs about 4000 g.

¹³ *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.

¹⁴ This reagent is used for calibration purposes only.

6.7 *Syringe*, 10 to 100- μ L, capable of holding liquid chlorine under pressure, with 26-gage disposable needle.

NOTE 3—Disposable needles are recommended because corrosion with permanent needles may cause problems.

7. Hazards

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

7.2 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, will produce irritations and burns.

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

8. Sampling

8.1 Sampling from tank cars, barges, storage tanks, and large cylinders presents unique problems. Each facility, however, must be capable of delivering a liquid sample (not gas) for test. See Chlorine Institute Pamphlet No. 1.

8.2 Since the location of these larger facilities may not be at the immediate site of analysis, sample collection in a suitable secondary container is recommended to facilitate its safe transport to the laboratory for tests (DOT regulations may be applicable).

8.3 It is recommended that samples be collected from these facilities in small-size cylinders, with cylinders and valves fabricated of tantalum, Monel, or nickel (carbon or stainless steel are unsuitable), and capable of being negotiated in the laboratory fume hood. Proper and safe sampling techniques must be followed. Do not allow the sample cylinder to become liquid full. A good rule is 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. This rule is stated in accordance with 49 CFR 173.

9. Preparation of Standards for Calibration

9.1 Prepare standards in liquid chlorine, so that matrix effects of the chlorine on the gas chromatographic column and detector are compensated.

9.2 *Method of Additions*—Add CCl_4 and CHCl_3 to cylinder containing liquid chlorine as follows:

9.2.1 Obtain a supply cylinder of liquid chlorine that has less than 10 ppm each of CCl_4 and CHCl_3 , and that contains at least 5000 g of chlorine. Label this cylinder No. 1.

9.2.2 Obtain a clean, evacuated, sample cylinder equipped with a septum on one of the valves. Label this cylinder No. 2 and weigh it to ± 1 g.

9.2.3 Connect cylinder No. 1 to cylinder No. 2 by means of fittings (6.6) such that the liquid phase of chlorine can flow from 1 to 2. Open the valves between the cylinders and cool cylinder No. 2 with ice. Liquid chlorine will be transferred from cylinder No. 1 to cylinder No. 2. Close the valves when sufficient chlorine has been transferred. Disconnect the cylinders and weigh cylinder No. 2 to ± 1 g to determine the weight of chlorine transferred. (**Warning**—Do not allow cylinder No. 2 to become liquid full. A good rule is that the weight of chlorine in the cylinder should not be more than 125 % of the weight of water that the cylinder could contain.)

9.2.4 Retain cylinder No. 1 to prepare further standards.

9.2.5 Prepare an approximately 50/50 mix of CCl_4 and CHCl_3 and record amounts of each added. Calculate the volume of this mixture needed to prepare one level of standard for calibration, using a calculation similar to that given in 9.3.

9.2.6 Fill the high-pressure syringe (6.7) with approximately the volume of the $\text{CCl}_4/\text{CHCl}_3$ mixture as calculated in 9.3.3. Weigh the syringe plus liquid to ± 0.1 mg. Transfer the liquid mixture through the septum into the vapor space of cylinder No. 2. Keep a finger tightly over the plunger to prevent blow out. Immediately remove and reweigh the syringe to ± 0.1 mg. The difference between the two weights is the total weight of CCl_4 and CHCl_3 added.

9.2.7 Shake cylinder No. 2 to assure complete solution of the CCl_4 and CHCl_3 in the chlorine.

9.2.8 Calculate the added concentration of CCl_4 and CHCl_3 in the spiked standard as indicated in 9.4.

9.2.9 Prepare at least three standards containing three different levels of CCl_4 and CHCl_3 , bracketing the expected level. Also, transfer some of the original chlorine into a sample cylinder without adding CCl_4 or CHCl_3 .

9.2.10 The long term stability of the calibration standards has not been evaluated.

9.3 Example of amounts of CCl_4 and CHCl_3 to be added to liquid chlorine to produce desired standard:

9.3.1 Proposed mixture of CCl_4 and CHCl_3 (average density about 1.5 g/mL, or 1.5 mg/ μ L):

CCl_4	47.55 g
CHCl_3	44.40 g
Total	<hr/> 91.95 g

9.3.2 To prepare 500 g of chlorine with spiked levels of 20 ppm each of CCl_4 and CHCl_3 (total of 40 μ g/g), the necessary grams (*W*) of the $\text{CCl}_4/\text{CHCl}_3$ mixture is as follows:

$$\frac{W}{500} = \frac{40}{10^6} \quad (1)$$

or

$$W = 0.020 \text{ g} = 20 \text{ mg} \quad (2)$$

9.3.3 The necessary volume in μL (V) is then:

$$V = \frac{W}{\text{density}} = \frac{20}{1.5} = 13 \mu\text{L} \quad (3)$$

9.4 Example of calculation of spiked amounts of CCl_4 and CHCl_3 added:

9.4.1 The weight of mixture added is:

Initial syringe weight with 13 μL	17.6715g
Weight of syringe after transfer	17.6529g
$\text{CCl}_4/\text{CHCl}_3$ added	0.0186g

9.4.2 The weight of cylinder No. 2:

Weight with chlorine	3575g
Weight empty	3088g
Weight of chlorine	487g

9.4.3 Weight of CCl_4 added:

$$(0.0186) \frac{47.55}{91.95} = 0.0096 \text{ g} \quad (4)$$

9.4.4 Concentration of CCl_4 in the spiked chlorine:

$$\frac{0.0096}{487} (10^6) = 19.7 \mu\text{g/g (w/w)} \quad (5)$$

9.4.5 Weight of CHCl_3 added:

$$(0.0186) \frac{44.40}{91.95} = 0.0090 \text{ g} \quad (6)$$

9.4.6 Concentration of CHCl_3 in the spiked chlorine:

$$\frac{0.0090}{487} (10^6) = 18.5 \mu\text{g/g (w/w)} \quad (7)$$

10. Chromatographic Conditions

10.1 *Column—NaCl on Porasil or equivalent:*

10.1.1 *Detector—Flame ionization.*

10.1.2 *Detector Temperature—150°C.*

10.1.3 *Carrier Gas—Nitrogen at 30 mL/min.*

10.1.4 *Column Temperature—Programmed, 60 to 200°C at 15°C/min.*

10.1.5 *Injector Temperature—90°C.*

10.2 *Column—Kel F on Chromosorb or equivalent:*

10.2.1 *Detector—Flame ionization.*

10.2.2 *Detector Temperature—150°C.*

10.2.3 *Carrier Gas—Nitrogen at 30 mL/min.*

10.2.4 *Column Temperature—60°C.*

10.2.5 *Injector Temperature—75°C.*

10.3 *Column—Halocarbon on Chromosorb or equivalent:*

10.3.1 *Detector—Flame ionization.*

10.3.2 *Detector Temperature—150°C.*

10.3.3 *Carrier Gas—Nitrogen at 30 mL/min.*

10.3.4 *Column Temperature—55°C.*

10.3.5 *Injector Temperature—90°C.*

NOTE 4—The conditions listed have produced acceptable results. These parameters serve only as a guide in optimizing conditions for the column used.

11. Preparation of Calibration Curve

11.1 *Obtaining Sample from Cylinders Containing Calibration Standards:*

11.1.1 Invert the cylinder and open the sampling valve so that there will be liquid chlorine at the septum.

11.1.2 With the plunger in place, close the syringe valve and insert the needle of the syringe through the septum into the sample cylinder.

11.1.3 Open the syringe valve and withdraw a 10- μL sample of liquid chlorine (Note 5). It may be necessary to pump the plunger several times to eliminate bubbles from the sample. Keep a finger tightly over the plunger to prevent blowout. Close the syringe valve and withdraw the syringe from the septum. For best results, the sample cylinder and syringe should be at the same temperature.

NOTE 5—Since chlorine reduces the response of flame ionization detectors to CCl_4 and CHCl_3 , and since the effect varies with detectors, better results may be obtained with some gas chromatographs using a sample size other than 10 μL . A smaller sample size may, in fact, result in greater sensitivity. However, precision may suffer from variations in sample size injections with smaller samples.

11.2 *Procedure:*

11.2.1 Adjust the gas chromatograph to the optimum conditions for the system.

11.2.2 Insert the needle of the syringe containing the sample through the septum on the gas chromatograph. Open the syringe valve and depress the plunger to transfer all the chlorine in the syringe into the gas chromatograph. Close the syringe valve and withdraw the needle from the system.

11.2.3 Measure the areas of the peaks for the CCl_4 (retention time about 5 min with Porasil C/NaCl) and for the CHCl_3 (retention time about 6 min with Porasil C/NaCl).

TABLE 1 Precision Values

Level, mg/kg	Standard Deviation, mg/kg	Repeatability		Laboratory Precision			Reproducibility		
		Degrees of Freedom	95 % Limit, mg/kg	Standard Deviation, mg/kg	Degrees of Freedom	95 % Limit, mg/kg	Standard Deviation, mg/kg	Degrees of Freedom	95 % Limit, mg/kg
Carbon Tetrachloride (CCl_4)									
9	0.8	44	2	1.9	11	5	5.3	10	15
62	3.9	40	11	4.6	10	13	10.4	9	29
149	6.8	44	19	7.7	11	21	21.4	10	60
Chloroform (CHCl_3)									
10	1.1	44	3	0.94	11	3	2.7	10	8
48	2.4	44	7	1.5	11	4	8.1	10	23
122	7.1	48	20	4.5	12	13	13.3	11	37