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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 E 806; 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 Review the current material safety data sheet (MSDS) for detailed information concerning toxicity, first aid procedures, and safety precautions.

~~1.3~~

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 hazards statements are given in Section 7 and in 9.2.3.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals

2.2 *Federal Standard:*[3]

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 Liquified 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. 77 Sampling Liquid Chlorine[4]

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

5. Apparatus

5.1 *Gas Chromatograph*, equipped with:

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[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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[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] 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.

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

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5.1.1 *Injection Port*, must be lined with glass, Monel,®[5] or nickel; or column must be installed for on-column injection.

5.1.2 *Septa*, from Viton.®[6] 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 Cl_2, CCl_4, and $CHCl_3$. Columns that have been found to be suitable are:

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

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

5.1.3.3 *Glass Tubing*, ~~10 ft~~3.05 m by 2 mm inside diameter, packed with 20 % Halocarbon® 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.[7]

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.[8] 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 ~~ppm~~µg/g each of CCl_4 and $CHCl_3$. This may be prepared by condensing the gaseous phase above regular production chlorine.[9]

6.3 *Carbon Tetrachloride*, reagent grade.[9]

6.4 *Chloroform*, reagent grade.[9]

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

6.5.1 *Sample Cylinders* [10]; 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.[11]

6.5.3 *Holder for a Septum*, that can be easily assembled.[12]

NOTE 1—Carbon or stainless steel cylinders and fittings are not suitable as $CHCl_3$ is unstable in the presence of $FeCl_3$ and Cl_2.

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.

6.7 *Syringe*, 10 to 100-µL, capable of holding liquid chlorine under pressure, with 26-gage disposable needle.[13]

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.

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[5] Available from the International Nickel Company, Park 80 West, Plaza 2, Saddlebrook, NJ 07662.

[6] Viton® septa can be prepared from Pierce No. 13235 Viton® hypo vial seals, available from the Pierce Chemical Co., Rockford, IL 61105. The septum is prepared by using a sharp blade to cut off the tip of the seal and then punching out a septum from the remaining flat disc. A cork borer or leather punch can be used to punch out the septum. Viton® septa are also available from Canton Bio-Medical Products, P.O. Box 2017, Boulder, CO 80302, Catalog No. V-101.

[7] A 400-mL nickel cylinder filled with liquid chlorine weighs about 4000 g.

[8] *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.

[9] This reagent is used for calibration purposes only.

[10] If samples are to be shipped outside any plant, cylinders approved by the U.S. Department of Transportation must be used. DoT-approved (1979) nickel cylinders are available from Crown Controls, Inc., 388 Getty Ave., Clifton, NJ 07011, Hoke quotation SP78-12-26.

[11] 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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[12] Swagelok® fittings have been found suitable for this purpose.

[13] Two sources have been found to be suitable: Glenco Scientific Inc., 2802 Oak Drive, Houston, TX 77007, model 925-MV-2 micro valve and model KFLL Luer lock adapter; and Precision Sampling Co., P.O. Box 15119, Baton Rouge, LA 70815, Pressure-Lok, series A.

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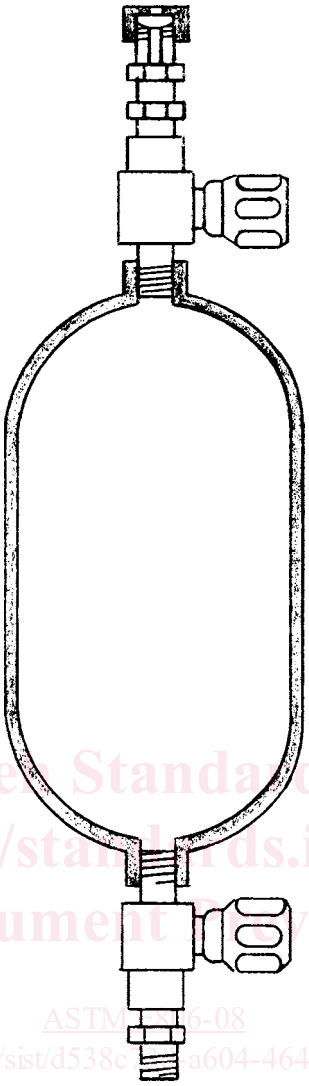

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FIG. 1 Sample Cylinder Assembly

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.

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. Acceptable samples can be obtained by sampling in accordance with the Chlorine Institute Pamphlet No. 77.

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 $CCl_4/CHCl_3$ 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/µL)

CCl_4	47.55 g
$CHCl_3$	44.40 g
Total	91.95 g

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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 ~~ppm~~ µg/g), the necessary grams (W) of the $CCl_4/CHCl_3$ mixture is as follows:

$$\frac{W}{500} = \frac{40}{10^6} \tag{1}$$

or

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$$W = 0.020 \text{ g} = 20 \text{ mg} \tag{2}$$

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

$$V = \frac{W}{density} = \frac{20}{1.5} = 13\ \mu L \tag{3}$$

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
$CCl_4/CHCl_3$ 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:

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

9.4.4 Concentration of CCl_4 in the spiked chlorine:

$$\frac{0.0096}{487}(10^6) = 19.7 \text{ ~~ppm(w/w)~~ µg/g (w/w)} \tag{5}$$

9.4.5 Weight of $CHCl_3$ added: