



Designation: **E806 – 08 E806 – 17**

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

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 ( $\epsilon$ ) 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 ( $\text{CCl}_4$ ) and chloroform ( $\text{CHCl}_3$ ) 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) 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 hazards statements are given in Section 7 and in 9.2.3.

### 2. Referenced Documents

2.1 *ASTM Standards:*<sup>2</sup>

**E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals** (Withdrawn 2009)<sup>3</sup>

2.2 *Federal Standard:*<sup>4</sup>

**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/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. 77-Sampling Liquid Chlorine Chlorine Basics**<sup>5</sup>

### 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  $\text{CCl}_4$  and  $\text{CHCl}_3$  from  $\text{Cl}_2$  and other impurities, using a suitable syringe. The amounts of  $\text{CCl}_4$  and  $\text{CHCl}_3$  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  $\text{CCl}_4$  and  $\text{CHCl}_3$  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  $\text{CCl}_4$  and  $\text{CHCl}_3$  in the liquid chlorine are known, the maximum amounts contributed to the water by the chlorine can be estimated.

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D16 on Aromatic Hydrocarbons and Related Chemicals and is the direct responsibility of Subcommittee D16.16 on Industrial and Specialty Product Standards.

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<sup>2</sup> 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.

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

<sup>4</sup> Available from the U.S. Government Printing Office, Superintendent of Documents, 732 N. Capitol St., NW, Washington, DC 20402; 20401-0001, <http://www.access.gpo.gov>.

<sup>5</sup> Available from The Chlorine Institute Inc., 70 W. 40th St., New York, NY 10018; 1300 Wilson Blvd., Suite 525, Arlington, VA 22209, <https://www.chlorineinstitute.org>.

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

## 5. Apparatus

5.1 *Gas Chromatograph*, equipped with:

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

5.1.2 *Septa*, from Viton.<sup>7</sup> 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<sub>2</sub>, CCl<sub>4</sub>, and CHCl<sub>3</sub>. 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 C<sup>8</sup> (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-F<sup>9</sup> No. 10 oil on 60/80 mesh Chromosorb<sup>10</sup> W AW.

5.1.3.3 *Glass Tubing*, 3.05 m by 2 mm inside diameter, packed with 20 % Halocarbon<sup>11</sup> 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  $\pm 1$  g.<sup>12</sup>

## 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.<sup>13</sup> 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  $\mu\text{g/g}$  each of CCl<sub>4</sub> and CHCl<sub>3</sub>. This may be prepared by condensing the gaseous phase above regular production chlorine.<sup>14</sup>

6.3 *Carbon Tetrachloride*, reagent grade.<sup>14</sup>

6.4 *Chloroform*, reagent grade.<sup>14</sup>

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

6.5.1 *Sample Cylinders*<sup>15</sup>; 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.<sup>16</sup>

6.5.3 *Holder for a Septum*, that can be easily assembled.<sup>17</sup>

NOTE 1—Carbon or stainless steel cylinders and fittings are not suitable as CHCl<sub>3</sub> is unstable in the presence of FeCl<sub>3</sub> and Cl<sub>2</sub>.

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- $\mu\text{L}$ , 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.

<sup>6</sup> Available from the International Nickel Company, Park 80 West, Plaza 2, Saddlebrook, NJ 07662. Monel is a registered trademark of Special Metals Corporation.

<sup>7</sup> 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. Viton is a registered trademark of The Chemours Company.

<sup>8</sup> Porasil is a trademark of Waters Associates, Inc.

<sup>9</sup> Kel-F is a registered trademark of 3M Company.

<sup>10</sup> Chromosorb is a registered trademark of Imerys Minerals California, Inc.

<sup>11</sup> Halocarbon is a registered trademark of Halocarbon Products Corporation.

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

<sup>13</sup> *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.

<sup>14</sup> This reagent is used for calibration purposes only.

<sup>15</sup> 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.

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

<sup>17</sup> Swagelok® Swagelok, registered trademark of Swagelok Company, or equivalent fittings have been found suitable for this purpose.

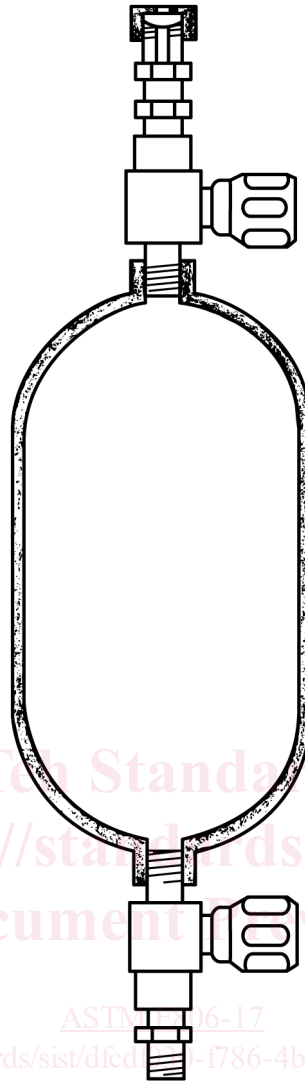


FIG. 1 Sample Cylinder Assembly

## 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.

## 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 See Chlorine Institute Pamphlet No. 77:1.~~

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~~, 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<sub>4</sub> and CHCl<sub>3</sub> 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<sub>4</sub> and CHCl<sub>3</sub>, 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<sub>4</sub> and CHCl<sub>3</sub> 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<sub>4</sub>/CHCl<sub>3</sub> 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<sub>4</sub> and CHCl<sub>3</sub> added.

9.2.7 Shake cylinder No. 2 to assure complete solution of the CCl<sub>4</sub> and CHCl<sub>3</sub> in the chlorine.

9.2.8 Calculate the added concentration of CCl<sub>4</sub> and CHCl<sub>3</sub> in the spiked standard as indicated in 9.4.

9.2.9 Prepare at least three standards containing three different levels of CCl<sub>4</sub> and CHCl<sub>3</sub>, bracketing the expected level. Also, transfer some of the original chlorine into a sample cylinder without adding CCl<sub>4</sub> or CHCl<sub>3</sub>.

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

9.3 Example of amounts of CCl<sub>4</sub> and CHCl<sub>3</sub> to be added to liquid chlorine to produce desired standard:

9.3.1 Proposed mixture of CCl<sub>4</sub> and CHCl<sub>3</sub> (average density about 1.5 g/mL, or 1.5 mg/μL)

CCl <sub>4</sub>		47.55 g
CHCl <sub>3</sub>		44.40 g
Total		91.95 g

9.3.2 To prepare 500 g of chlorine with spiked levels of 20 ppm each of CCl<sub>4</sub> and CHCl<sub>3</sub> (total of 40 μg/g), the necessary grams (W) of the CCl<sub>4</sub>/CHCl<sub>3</sub> 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<sub>4</sub> and CHCl<sub>3</sub> 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 <sub>4</sub> /CHCl <sub>3</sub> added		0.0186g

9.4.2 The weight of cylinder No. 2:

Weight with chlorine  
Weight empty  
Weight of chlorine

3575g  
3088g  

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487g

9.4.3 Weight of CCl<sub>4</sub> added:

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

9.4.4 Concentration of CCl<sub>4</sub> in the spiked chlorine:

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

9.4.5 Weight of CHCl<sub>3</sub> added:

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

9.4.6 Concentration of CHCl<sub>3</sub> in the spiked chlorine:

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

## 10. Chromatographic Conditions

10.1 *Column—NaCl on ~~Porasil~~: 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~~: 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~~: 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- $\mu$ L 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<sub>4</sub> and CHCl<sub>3</sub>, and since the effect varies with detectors, better results may be obtained with some gas chromatographs using a sample size other than 10  $\mu$ L. 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<sub>4</sub> (retention time about 5 min with Porasil C/NaCl) and for the CHCl<sub>3</sub> (retention time about 6 min with Porasil C/NaCl).

11.2.4 Inject at least three samples of the same material for replicates and average those which agree within the values as given in **Table 1**.

NOTE 6—Several injections may be required initially to condition the column and detector before reproducible results can be obtained.

11.2.5 Repeat the injections and measurements for all the spiked samples (at least three) and for the original, unspiked chlorine.

11.3 *Plotting Calibration Curve:*

11.3.1 Plot the µg/g of CCl<sub>4</sub> injected (based on calculations of 9.4) for each spiked sample versus the net peak area for that sample (area of the peak of the spiked sample minus the area of the peak of the original, unspiked chlorine).

11.3.2 Repeat for all spiked samples of CCl<sub>4</sub> and draw in the best curve, for the points entered—curve should go through the origin.

11.3.3 Do the same for all spiked samples of CHCl<sub>3</sub> and draw the curve.

**12. Procedure**

12.1 Transfer a sample of the chlorine to be analyzed into a sample cylinder containing a septum on one of the valves, using the technique described above for transferring the chlorine for calibration (9.2.3).

12.2 Take a sample from the sample cylinder containing the chlorine that is to be analyzed by means of a high-pressure syringe, as described above under preparation of calibration curve (11.1). This sample volume must be *exactly the same* as that used for preparing the calibration curves.

12.3 Inject the sample into the conditioned gas chromatograph, as described above under preparation of calibration curve (11.2.2). Measure the areas of the peaks for the CCl<sub>4</sub> and CHCl<sub>3</sub>. Repeat with at least three replicates until the replicates are as given in **Table 1**. Average the areas obtained for each.

12.4 From the calibration curves, determine the µg/g of CCl<sub>4</sub> and CHCl<sub>3</sub> present in the sample.

**13. Report**

13.1 Report the average CCl<sub>4</sub> and CHCl<sub>3</sub> contents to the nearest whole µg/g.

**14. Precision and Bias**

14.1 The following criteria should be used in judging the acceptability of results (Note 7):

14.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be the values in **Table 1**. The 95 % limit for the difference between two such averages is given in **Table 1**.

14.1.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability)*—The standard deviation of results (each the average of triplicates), obtained by the same analyst on different days, has been estimated to be the value shown in **Table 1**. The 95 % limit for the difference between two such averages is also given in **Table 1**.

14.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of triplicates), obtained by analysts in different laboratories, has been estimated at the values in **Table 1**. The 95 % limit for the difference between two such averages is given in **Table 1**.

NOTE 7—These precision statements are based on an interlaboratory study performed in 1979–1980 on three samples of liquid chlorine, containing approximately 9, 62, and 149 µg/g of CCl<sub>4</sub> and 10, 48, and 122 µg/g of CHCl<sub>3</sub>. One analyst in each of 13 laboratories performed three replicate determinations and repeated on a second day, for a total of 468 determinations.<sup>18</sup> Practice E180 was used in developing these precision estimates.

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

<sup>18</sup> Supporting data are available from ASTM Headquarters. Request have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E15-1030. Contact ASTM Customer Service at service@astm.org.

**TABLE 1 Precision Values**

Level, mg/kg	Repeatability			Laboratory Precision			Reproducibility		
	Standard Deviation, mg/kg	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 <sub>4</sub> )									
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 <sub>3</sub> )									
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