



# Standard Test Method for Sampling and Analysis of Liquid Chlorine for Gaseous Impurities<sup>1</sup>

This standard is issued under the fixed designation E 1746; 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.

<sup>ε1</sup> NOTE—Editorial changes were made in August 2001.

## 1. Scope

1.1 This test method covers sampling and analysis of liquid chlorine for the determination of oxygen (200 to 400 ppm), nitrogen (400 to 800 ppm), and carbon dioxide (800 to 1000 ppm) content at levels normally seen in liquid chlorine. Hydrogen and carbon monoxide concentrations in liquid chlorine are typically at or below the detection limit of this test method.

NOTE 1—The minimum detection limit of hydrogen using a 1 cm<sup>3</sup> gas sample and argon carrier gas is 100 to 200 ppm.<sup>2</sup> The detection limit for the other components is significantly lower.

1.2 *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.

1.3 Review the current Material Safety Data Sheets (MSDS) for detailed information concerning toxicity, first aid procedures, and safety precautions.

## 2. Referenced Documents

### 2.1 Code of Federal Regulations:<sup>3</sup>

49 CFR 173, Code of Federal Regulations Title 49, Transportation: Shippers' General Requirements for Shipments and Packaging, including the following 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

<sup>1</sup> 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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<sup>2</sup> Thompson, B., *Fundamentals of Gas Chromatography*, Varian Instruments Division, Sunnyvale, CA, p. 73.

<sup>3</sup> Available from Standardization Documents Order Desk, Bldg. 4 Section D, 700 Robbins Ave., Philadelphia, PA 19111-5094, Attn: NPODS.

### 2.2 Other Document:

Chlorine Institute Pamphlet No. 77 Sampling Liquid Chlorine<sup>4</sup>

## 3. Summary of Test Method

3.1 A sample of liquid chlorine is trapped in a sampling tube and vaporized into a steel bomb. The vaporized chlorine in the steel bomb is introduced into a gas chromatograph by a gas sampling loop (1 cm<sup>3</sup>) using a ten-port gas sampling and switching valve. The separations are made on a Porapak<sup>®</sup> Q column and on a 5A molecular sieve column whose lengths are such that the peaks do not overlap.

3.2 Any component that co-elutes with the components of interest may interfere with this analysis.

## 4. Significance and Use

4.1 It is very difficult to exclude sample contamination by ambient air during the process of sampling. The levels of atmospheric contamination caused by poor sampling methods are often equal to or larger than the levels of the gaseous impurities present in the chlorine. This results in markedly elevated levels of detected impurities. As specifications become tighter, it becomes more important to measure the gaseous impurity levels in liquid chlorine correctly.

4.2 Additional problems are experienced in the sampling of liquefied gases for the gaseous impurities. The gaseous impurities reach an equilibrium between the liquid phase and vapor phase in a sample bomb. The quantity of gases measured in any particular sample containing both liquid and vapor will be a function of the amount of vapor space in the sample bomb. This test method avoids the presence of liquid in the sample bomb.

## 5. Apparatus

5.1 *Gas Chromatograph*—Shimadzu GC-8AIT equipped as shown in Fig. 1, or equivalent, equipped with a thermal

<sup>4</sup> Available from The Chlorine Institute, Inc., 2001 L Street NW, Washington, DC 20036-4919.

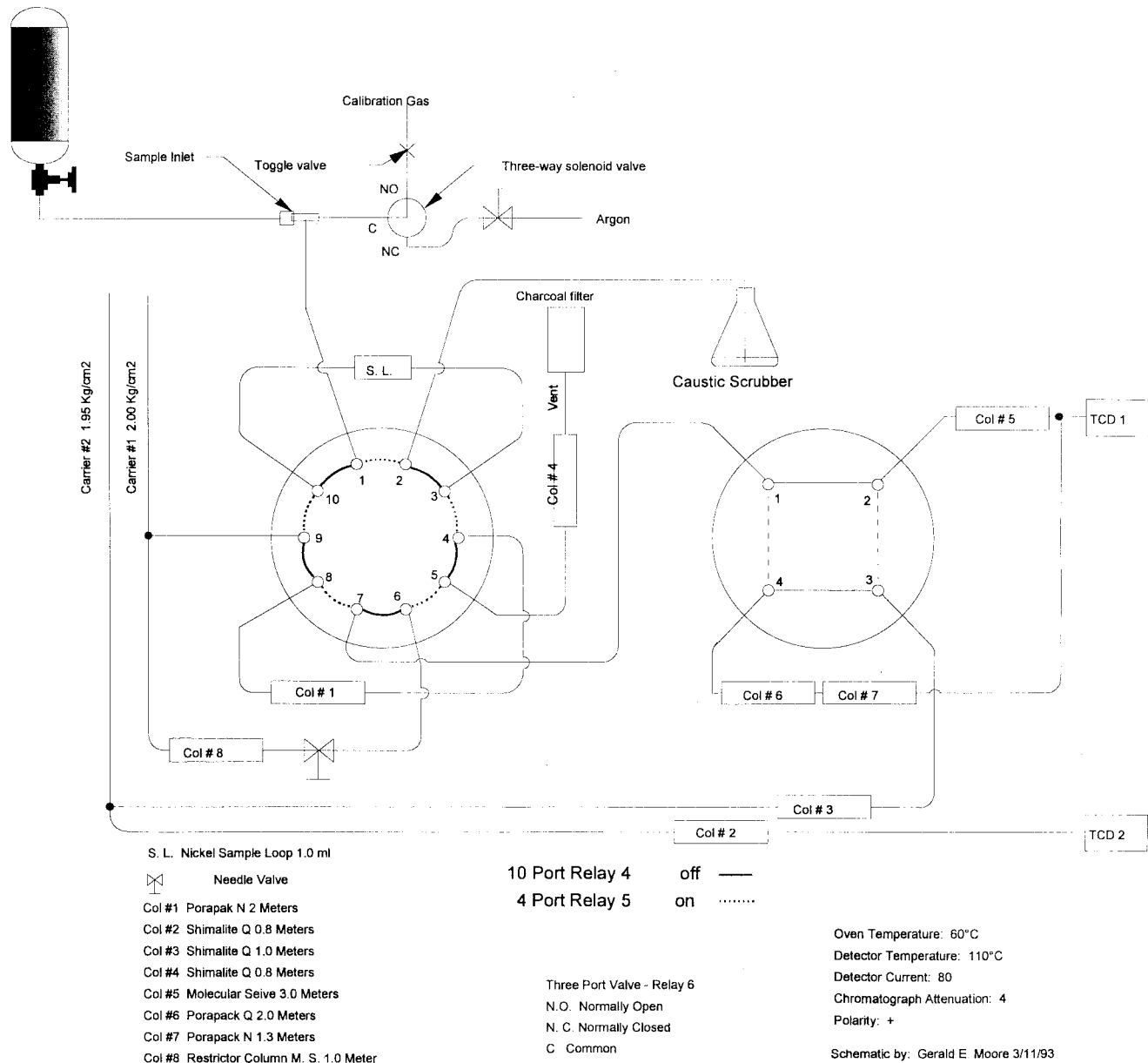


FIG. 1 Chlorine Impurity Analysis System Flow Diagram

conductivity detector.<sup>5</sup>

5.2 Recorder, 1 mV, 0.5 s full-scale response.

5.3 Valve Sequencer and Actuator, for switching valve control.<sup>6</sup>

5.4 Switching Valves.

5.4.1 Ten-Port Switching and Sampling Valve (stainless steel is acceptable).<sup>7</sup>

5.4.2 Four-Port Switching Valve (stainless steel is acceptable).<sup>6</sup>

5.5 Chromatographic Columns, 1/8-in. (3.2-mm) outside diameter, 316 stainless, as follows:

5.5.1 2 m of 80/100 mesh Porapak® N,<sup>8</sup>

5.5.2 0.8 m of 80/100 mesh Shimalite® Q,<sup>9</sup>

5.5.3 1 m of 80/100 mesh Shimalite® Q,<sup>9</sup>

5.5.4 0.8 m of 80/100 mesh Shimalite® Q,<sup>9</sup>

5.5.5 3 m of 45/60 mesh molecular sieve 5A,

5.5.6 2 m of 80/100 mesh Porapak® Q,<sup>8</sup>

5.5.7 2 m of 80/100 mesh Porapak® N,<sup>8</sup> and

5.5.8 1 m of 45/60 mesh molecular sieve 5A.

5.6 Tantalum Tubing, 1/16-in. (1.6-mm) outside diameter, 0.0225-in. (0.57-mm) inside diameter.

NOTE 2—Nickel tubing may be substituted for tantalum.

<sup>5</sup> Shimadzu Scientific Instruments, Inc., Columbia, MD.

<sup>6</sup> Carle Instruments, Inc., Fullerton, CA, or equivalent.

<sup>7</sup> Valco Instruments Co., or equivalent.

<sup>8</sup> Porapak® materials, or their equivalent, have been found satisfactory for this purpose.

<sup>9</sup> Shimalite® materials, or their equivalent, have been found satisfactory for this purpose.

5.7 *Monel® Sampling Tube*, 3/8 by 5.5-in. (9.5 by 140-mm) long (volume 5.4 cm<sup>3</sup>).<sup>10</sup>

5.8 *Electronic Integrator*, or computer integration package.

5.9 *TFE-Fluorocarbon Lined Flex Tubing*, 1/4 in. (6.35 mm).

5.10 *TFE-Fluorocarbon Tubing*, 1/4 in. by 10 ft (6.35 mm by 3.05 m).

5.11 *Cajon® VCR Fitting*.<sup>11</sup>

5.12 *Two-Valves*, 3/8 in. (9.5 mm), Monel®.<sup>10</sup>

5.13 *Four-Valves*, 1/4-in. (6.35-mm) tubing to 1/4-in. pipe, Monel®.<sup>10</sup>

5.14 *Hoke® Sample Cylinder*, 1000 cm<sup>3</sup>, Monel, nickel, tantalum, or stainless steel.<sup>12</sup>

5.15 *Pressure Gage*, 200 lb (91 kg), Monel®.<sup>10</sup>

5.16 *Four-Pipe Tee*, 1/4 in. (6.35 mm), Monel®.<sup>10</sup>

5.17 *Vacuum Source*, suitable for chlorine disposal.

## 6. Reagents

6.1 *Gas Standard*, 500 ppm H<sub>2</sub>, 400 ppm O<sub>2</sub>, 800 ppm N<sub>2</sub>, 50 ppm CO, and 1000 ppm CO<sub>2</sub> in argon.<sup>13,14</sup>

6.2 *Argon Carrier Gas*, chromatographic grade.

## 7. Hazards

### 7.1 Safety Precautions:

7.1.1 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.

7.1.2 The analysis should be attempted only by individuals 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 respirator. Splashes of liquid chlorine destroy clothing and will produce irritations and burns if such clothing is next to the skin.

7.1.3 Do not allow the sample cylinder to become liquid full if liquid samples are to be taken in cylinders. In accordance with 49 CFR 173.304, 173.314, and 173.315, 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.

7.1.4 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.

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

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

7.1.7 It is recommended that means be available for the disposal of excess chlorine in an environmentally safe and

acceptable manner. A chlorine absorption system should be provided if the chlorine cannot be disposed of in a chlorine consuming process. When the analysis and sampling regimen requires an initial purging of chlorine from a container, the purged chlorine should be handled similarly. Purging to the atmosphere should be avoided.

## 8. Sampling

8.1 Assemble the sampling apparatus as shown in Fig. 2, and purge the system with argon before going into the field to sample.

8.2 Attach the sampling apparatus to the source of liquid chlorine to be sampled and the vacuum source.

8.3 Open all valves on the sample apparatus except Valve No. 5 on the sample bomb end opposite the gage. Evacuate the system using the vacuum source.

8.4 Close all of the valves in the system. Leave the apparatus attached to the vacuum system with the vacuum system on.

8.5 Open the valve on the source of liquid chlorine.

8.6 The following describes the cleanout of the sampling tube made from the 3/8-in. (9.5-mm) Monel® tubing:

8.6.1 Open Valve No. 3 from the sample bomb to the vacuum source and leave open.

8.6.2 Open Valve No. 1 on the end of the sampling tube connected to the chlorine source for approximately 15 s.

8.6.3 Close Valve No. 1.

8.6.4 Slowly open Valve No. 2 on the end of the sampling tube that is connected to the sample bomb, and vent the chlorine trapped in the sampling tube into the vacuum system.

8.6.5 Close Valve No. 2.

8.7 Repeat 8.6-8.10 two more times so that the sampling tube has been filled and emptied a total of three times.

8.8 Close Valve No. 3 between the vacuum source and sample bomb, and open Valve No. 4 on the gage end of the sample bomb.

8.9 Open Valve No. 1 on the end of the sampling tube connected to the chlorine source for approximately 15 s.

8.10 Close Valve No. 1 and open Valve No. 2 slowly.

8.11 Slowly open Valve No. 3 between the sample cylinder and the vacuum source.

8.12 Close Valves No. 2 and No. 3.

8.13 Repeat 8.11-8.15 three more times. On the fourth time purging the sample cylinder, do not open Valve No. 3, which connects the sample bomb connections to the vacuum source, but close Valve No. 4 on the gage end of the sample bomb.

8.14 Close the valve on the source of the liquid chlorine.

8.15 Evacuate all lines that might contain liquid chlorine by opening all valves except those on the sample bomb and liquid chlorine source. Check the pressure on the sample bomb to ensure that it is below the vapor pressure of liquid chlorine at room temperature. This ensures that only vapor chlorine is present in the sample bomb.

8.16 Disconnect the sample bomb from the sampling apparatus and the sampling apparatus from the source of the chlorine. The pressure in the sample bomb should be below 120 lb (54 kg) to contain only vapor in the bomb.

8.17 This chlorine sample is now ready for analysis by the following method.

<sup>10</sup> Monel® material, or its equivalent, has been found satisfactory for this purpose.

<sup>11</sup> Cajon® fittings, or their equivalent, have been found satisfactory for this purpose.

<sup>12</sup> Hoke® sample cylinders, or their equivalent, have been found satisfactory for this purpose.

<sup>13</sup> This reagent is used for calibration only.

<sup>14</sup> Standards obtained from Scott Specialty Gases have been found to be suitable for this purpose.

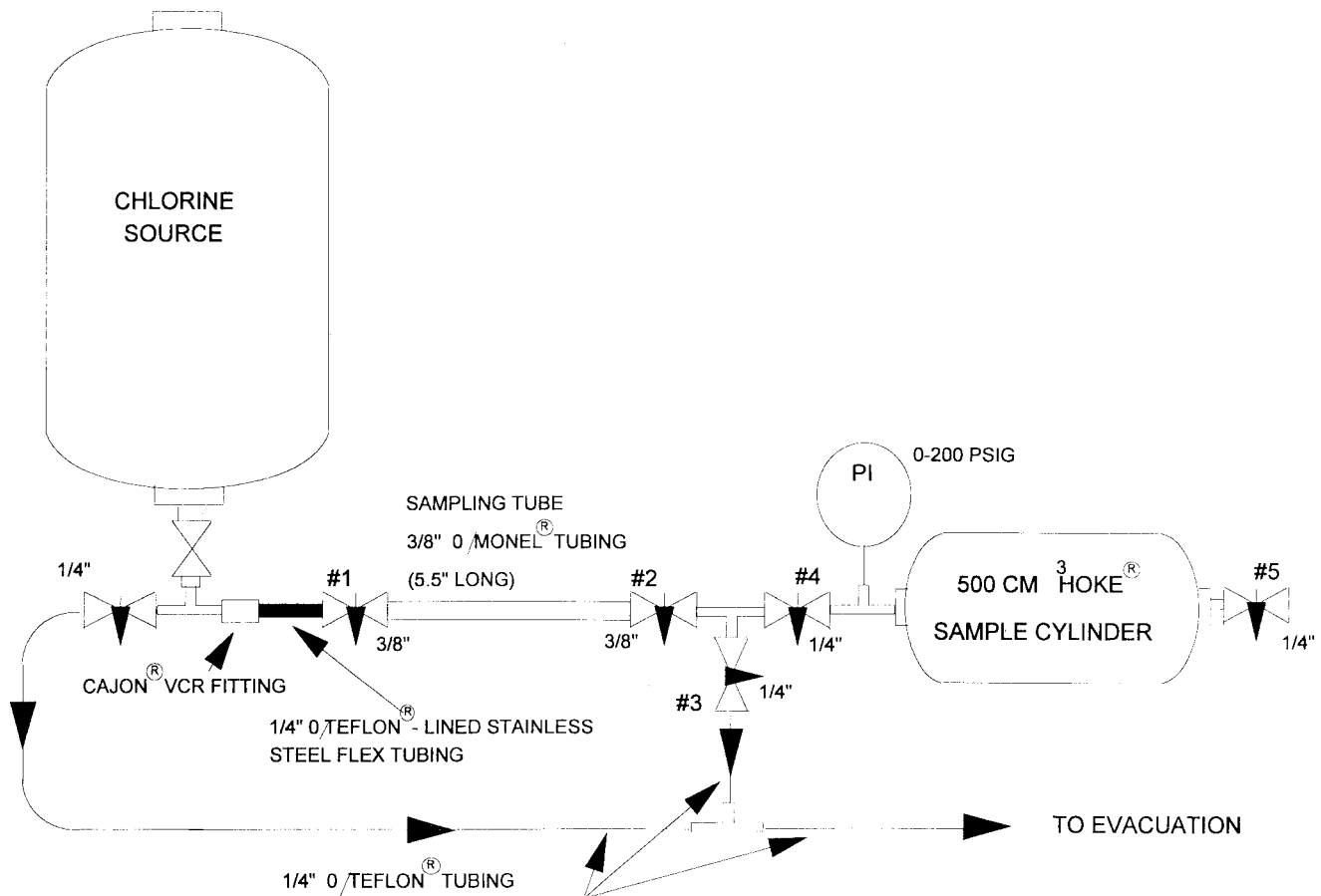


FIG. 2 Chlorine Sampling Apparatus

**9. Preparation of Standards for Calibration**

9.1 Obtain a custom blend of 500 ppm H<sub>2</sub>, 400 ppm O<sub>2</sub>, 800 ppm N<sub>2</sub>, 50 ppm CO, and 1000 ppm CO<sub>2</sub> by volume in argon from a supplier of custom gas standards.<sup>14</sup>

**10. Column Preparation and Instrumental Parameters**

10.1 Remove trace components from the columns by heating them overnight at 175°C with 20 cm<sup>3</sup>/min argon flowing through them. See Fig. 1 for the correct carrier flow path to clean the gas chromatography (GC) columns.  
 10.2 *Temperatures:*

Column:	75°C
Injection port:	110°C
Detector:	110°C

**10.3 Argon Carrier Gas Flows:**

Reference:	20 cm <sup>3</sup> /min
Column:	20 cm <sup>3</sup> /min

10.3.1 Activate the ten-port valve (the dashed line flow path), and check the flow at the thermal conductivity detector (TCD) 1 vent. Adjust the flow to 20 cm<sup>3</sup>/min with the carrier gas No. 1 pressure regulator.  
 10.3.2 Deactivate the ten-port valve (the solid line flow path), and activate the four-port valve (the dashed line flow path). Check the flow at the TCD 1 vent and adjust to 20 cm<sup>3</sup>/min with the carrier gas No. 2 pressure regulator.

10.3.3 Activate the four-port valve (the dashed line flow path), and adjust the flow to 20 cm<sup>3</sup>/min at the TCD 1 vent with the auxiliary pressure regulator.

10.3.4 At this point, check the flow at the end of the needle valve restrictor and before the “T” prior to the TCD 1 detector, and adjust with the restrictor needle valve to 20 cm<sup>3</sup>/min.

10.4 *Detector Current*, 80 ma.

10.5 *Sample Size*, cm<sup>3</sup> gas loop.

10.6 *Valve Switching Time*, see Note 4.

10.7 *Attenuation*, as needed.

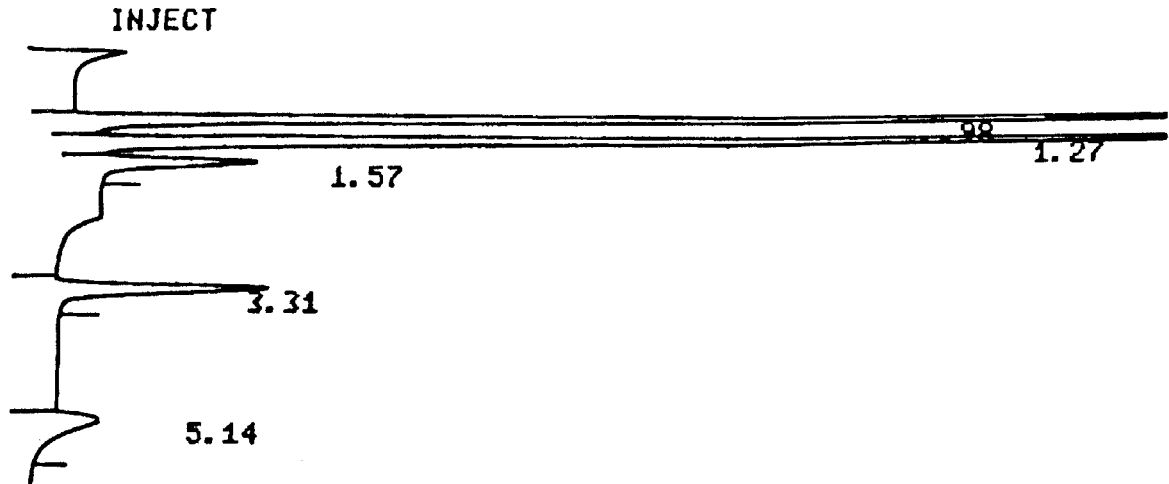
NOTE 3—Conditions are given for a Shimadzu GC-8AIT and are shown in Fig. 1. These conditions may vary for other types of instruments. Since the quality of packing material (especially molecular sieve) varies greatly, the lengths given for each of the columns in Fig. 1 are only approximate. Flow rates and column lengths are varied so as to balance the system to arrive at complete separation of the components and a stable baseline during valve switching.

NOTE 4—The exact timing will depend on the specific resistances of the columns used, flow rates, and column efficiencies. Timing is established by careful study of the system during setup.

NOTE 5—Fig. 3 shows a typical chromatogram that can be obtained with this system. Hydrogen and carbon monoxide concentrations in liquid chlorine are typically at or below the detection limit of this test method. Although carbon monoxide is not shown in this chromatogram, it would have a retention time after nitrogen and before carbon dioxide.

**11. Calibration**

11.1 Determine the response of each component (O<sub>2</sub>, N<sub>2</sub>, CO, CO<sub>2</sub>, and H<sub>2</sub>) by analyzing a 1 cm<sup>3</sup> sample of the custom



CL2

NAME	CONC	RT	AREA BC	RF
H2	0.161	0.98	91364 02	5677.25
O2	1.688	1.27	100801 02	597.297
N2	0.22	1.57	16956 03	769.943
CO2	0.528	3.31	21273 01	402.78
<b>TOTALS</b>	<b>2.537</b>		<b>239781</b>	

FIG. 3 Chromatogram of the Gaseous Impurities in Chlorine

laboratory blend of these gases in argon, as outlined in Section 12.

NOTE 6—A 1 % commercial custom blend of the above components in argon was found to change composition after sitting several months. Although more time consuming, the response factors can be determined by analyzing the individual pure gases. This approach also eliminates the shelf life problem associated with commercially prepared standard blends.

11.2 Determine the area response factors ( $\mu\text{V}\cdot\text{s}/\text{ppm}\cdot\text{cm}^3$ ) for each component as follows:

$$F_i = \frac{A_i}{C_i \times V_i} \quad (1)$$

where:

- $F_i$  = area response factor for component  $i$ ,
- $C_i$  = concentration of component  $i$  in the standard, ppm (volume), and
- $V_i$  = volume of standard injected,  $\text{cm}^3$  (equal to unity when  $1 \text{ cm}^3$  is used).

NOTE 7—Three runs are usually made, and the average of three determinations is used.

## 12. Sample Analysis

12.1 Allow the chromatograph to reach the conditions listed in Section 10.

12.2 Adjust the flow rates to the values indicated in Section 10.

12.3 Turn on the valve sequencer, and set the switching valves to the positions shown in Fig. 1 (dashed line flow path) with the sample system in the inject position.

### 12.4 Sample Injection:

12.4.1 Turn on the argon purge through the sample system.

12.4.2 Connect the sample cylinder to the sample valve as shown in Fig. 1. Argon will be purging from this connection as the bomb is attached. Tighten the nut on the bomb fitting that attaches the bomb to the sample valve.

12.4.3 With the sample system in the inject position and the argon purge still on, break the nut connection and let argon bleed out. Retighten the nut to seal the connection. Repeat this process a second time. This purges inert gases out of the sample transfer line and sample cylinder connections.

12.4.4 Switch the injection valve into the load position (the solid line flow path), and repeat 12.4.3 twice.

12.4.5 Turn the argon purge off and wait 65 s. Activate the integrator and inject the sample. This is a blank injection that will determine whether the lines are free of inert gases before analyzing the chlorine sample. If the argon blank analysis is free of inert gases, continue with 12.4.6. If the argon blank analysis indicates the presence of inert gases, repeat 12.4.1-12.4.5.

12.4.6 Open the valve on the sample cylinder with the sample system in the inject position. Switch the sample valve to the load position immediately, and allow the chlorine to

purge through the sample loop for 35 s.

12.4.7 Shut off the valve on the sample bomb and wait 65 s. This allows the sample to reach atmospheric pressure.

12.5 Start the computer, recorder, and valve sequence in rapid succession (this injects the sample).

12.6 Attenuate, as necessary, if it is desired to keep the peaks on scale.

12.7 Terminate the run after 10 min. The order of elution is H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CO, and CO<sub>2</sub>.

### 13. Calculation

13.1 Calculate the concentration of each component in the sample as follows:

$$C_i = \frac{A_i}{F_i} \quad (2)$$

where:

$C_i$  = concentration, component i, ppm (volume),

$A_i$  = peak area of component i in sample,  $\mu\text{V}\cdot\text{s}$ , and

$F_i$  = area response factor for component i.

### 14. Report

14.1 Report the concentration of each gaseous impurity to the nearest ppm by volume.

### 15. Precision and Bias

15.1 *Precision*—The following criteria should be used for judging the acceptability of the results (see Note 8).

15.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be the value given in Table 1 at the indicated degrees of freedom. The

TABLE 1 Repeatability—Gaseous Impurities in Liquid Chlorine

Gas	Average, ppm by volume	Repeatability, ppm by volume		
		Standard Deviation	Degrees of Freedom	95 % Limit
Oxygen	269	5.2	30	15
Nitrogen	370	8.2	30	23
Carbon dioxide	908	5.6	30	16

95 % limit for the difference between two such runs is the value given in Table 1.

15.1.2 *Within-Days Precision (Process Stream)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst due to the within-days effect, has been estimated to be the value given in Table 2 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is the value given in Table 2.

15.1.3 *Between-Days Precision (Process Stream)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst due to the between-days effect, has been estimated to be the value given in Table 2 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is the value given in Table 2.

NOTE 8—These precision estimates are based on data obtained by one laboratory that analyzed a process stream of liquid chlorine between November 18, 1991, and March 11, 1992. Thirty samples of liquid chlorine were taken, and two analyses for oxygen, nitrogen, and carbon dioxide were made from each cylinder of vaporized sample. These data are the basis for the repeatability values given in Table 1. Because each pair of data is based on one sample, any change in concentration over the period of time has no effect on the precision estimates for repeatability.

The estimates for the within-days and between-days precision (Table 2) are based on a one-way analysis of variance of the averages of duplicate runs on four to seven samples taken on each of four days between November 29, 1991 and March 11, 1992. Because all of the samples were taken from a process line, the standard deviations for within-days and between-days variability include the effect of any variation in the level of oxygen, nitrogen, and carbon dioxide over the time period. These estimates are included as an example of these types of precision on a process line.

15.1.4 *Reproducibility*—Because data from only one laboratory are available, no estimate of reproducibility is possible.

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

### 16. Keywords

16.1 analysis; carbon dioxide; carbon monoxide; gas chromatography; hydrogen; inert gases; liquid chlorine; nitrogen; oxygen

**TABLE 2 Within-Days and Between-Days Precision—Gaseous Impurities in Liquid Chlorine**

Gas	Concentration, ppm by volume			Within-Days Precision, ppm by volume			Between-Days Precision, ppm by volume		
	Low	High	Average	Standard Deviation	Degrees of Freedom	95 % Limit	Standard Deviation	Degrees of Freedom	95 % Limit
Oxygen	245	310	272	16.1	17	45	14.9	3	42
Nitrogen	325	435	364	28.2	17	79	14.0	3	39
Carbon dioxide	640	1005	833	71.0	17	199	92.3	3	258

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