

### 8.2.6.3

$$\frac{F}{E} \times 100 = \%air$$

Report to the nearest 0.01%.

**8.3 Sulfur Dioxide** — This procedure describes the determination of sulfur dioxide in boron trifluoride gas. A sample of the solution prepared in Section 8.1.4 is titrated with standard iodine solution to a starch endpoint (blue). The sulfur dioxide is determined from the equivalents of iodine used in the titration.

**8.3.1 Method Capabilities:** The range of this method is 5 ppm to 1500 ppm.

#### 8.3.2 Apparatus

8.3.2.1 Burette, 10 mL, graduated in units of 0.05 mL.

8.3.2.2 Beaker, 250-mL.

**8.3.3 Reagents** — All reagents used are reagent grade unless otherwise specified.

**8.3.3.1 Water** — All water used in the preparation of reagents and in the procedure is either distilled or deionized.

**8.3.3.2 Iodine solution, 0.01 N** — Prepare fresh daily and standardize.

**8.3.3.3 Starch indicator solution, 10 g/L** — Prepare a thin paste of 1 g of soluble starch with water. Pour the paste with constant stirring, into 100 mL of boiling water. Boil for one minute. Allow the solution to cool and add 2.5 g of potassium iodide. Keep the solution in a glass-stoppered bottle. Prepare fresh when the color obtained for end points is violet or red instead of blue. Alternatively, Thyodene dry indicator powder may be used.

#### 8.3.4 Operating Procedure

**8.3.4.1** Calculate the amount of sample (prepared in Section 8.1.4 that contains about 20 grams of BF<sub>3</sub> gas, rounding off to the nearest milliliter. Calculate the grams of BF<sub>3</sub> gas in this volume to the nearest 0.01 g, using the "F" factor in Section 8.1.4.8. Transfer this amount to a 250-mL beaker and add 5 drops of starch indicator.

**8.3.4.2** Using a 10-mL burette graduated in 0.05 mL, titrate with iodine to a starch end-point (blue). Stir constantly with a Teflon stir-bar or equivalent. Record the volume of the iodine solution to the nearest 0.01 mL.

#### 8.3.5 Calculations

$$\frac{\text{mL I}_2 \times \text{Normality of I}_2 \times 0.032 \times 1 \times 10^6}{\text{Grams of Water-Soluble Material}} = \text{ppm SO}_2$$

where : 0.032 the milliequivalent weight of SO<sub>2</sub>;  
 $1 \times 10^6$  is factor for conversion to ppm.

**8.4 Silicon Tetrafluoride** — This procedure describes the determination of silicon tetrafluoride in boron trifluoride gas. This method is based on the reaction of soluble silica with molybdate ion to form a greenish-yellow complex, B-silicomolybdic acid. This complex is then reduced to a blue complex by 1-amino-2-naphthol-4-sulfonic acid. The absorbance is measured at 650 nm and the amount of silicon tetrafluoride present is obtained from a calibration curve.

**8.4.1 Method Capabilities** — The range of this method is 45–450 ppm.

#### 8.4.2 Apparatus

**8.4.2.1 Photometer:** One of the following is required, with preference in the order given.

- Spectrophotometer, suitable for measurements at 650 nm.
- Filter photometer, for measurements from 640–700 nm, if less sensitivity is preferred.
- Fisher Electrophotometer, with a red filter and 23-mm cells.

NOTE 2: If the photometer being used measures in units other than absorbance, the appropriate conversion to absorbance must be made before calculating any results.

**8.4.2.2 Absorption cells, 1.0-cm light path** (for use with a or b above).

**8.4.2.3 Plastic beakers, 150-mL capacity.**

**8.4.2.4 Polyethylene weighing bottle with cap, 250-mL.**

**8.4.2.5 Plastic volumetric flasks, 100-mL.**

**8.4.2.6 Plastic pipets, 0, 1.0, 2.0, 3.0, 4.0, 6.0, 8.0 and 10.0-mL sizes.**

**8.4.3 Reagents** — All reagents are reagent grade unless otherwise specified.

**8.4.3.1 Water** — All water used in this method is either distilled or deionized and must be silica-free.

**8.4.3.2 Boric acid solution, saturated** — Dissolve 70 g of boric acid, H<sub>3</sub>BO<sub>3</sub>, in 800 mL of hot water. Dilute to 1000 mL and mix. Store in a plastic bottle.

**8.4.3.3 Ammonium molybdate solution, 10%** — Dissolve 50 g of ammonium molybdate,

$(\text{NH}_4)_6\text{MO}_7\text{O}_{24}\text{H}_2\text{O}$ , in water and dilute to 500 mL. Store in a plastic bottle. Prepare fresh weekly.

8.4.3.4 *Sulfuric acid, 5N,  $\text{H}_2\text{SO}_4$*  — Carefully pour 35 mL of concentrated sulfuric acid into about 150 mL of water in an ice bath. Cool to room temperature, dilute to 250 mL and mix. Store in a plastic bottle.

8.4.3.5 *Tartaric acid solution, 40%* — Dissolve 80 g of tartaric acid in 140 mL of water. Dilute to 200 mL and mix. Store in a plastic bottle. Prepare fresh weekly.

8.4.3.6 *l-Amino-2-naphthol-4 sulfonic acid solution, 2.5 g/L* — Dissolve 30 g of sodium bisulfite in 100 mL of water in a 250-mL beaker. In a 100-mL beaker, dissolve 1 g of sodium sulfite in 25 mL of water and add 0.5 g of l-amino-2-naphthol-4-sulfonic acid. Mix the two solutions and dilute to 200 mL. Store in a plastic bottle and filter before using. Prepare fresh weekly.

8.4.3.7 *Sodium silicate standard solution, 1 mL = 10 micrograms Si* — Dissolve 1.012 g sodium silicate (meta),  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ , in water in a 100-mL plastic volumetric flask and dilute to volume. Pipet 10.00 mL of this solution, using a polyethylene pipet, into a 1-liter plastic volumetric flask and dilute to volume. One mL of this dilution contains the equivalent of 10 micrograms Si.

#### 8.4.4 Calibration

8.4.4.1 To a series of nine 150-mL plastic beakers, pipet 0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 8.0, and 10.0 mL of sodium silicate standard solution. These additions correspond to 0, 10, 20, 30, 40, 50, 60, 80, and 100 micrograms of Si.

8.4.4.2 Into each beaker, pipet 25.0 mL of boric acid solution. Dilute to about 60 mL with water and mix.

8.4.4.3 Continue with Procedure Sections 8.4.5.3–8.4.5.9. Measure the absorption of each standard and then return to Calibration, Section 8.4.4.4.

8.4.4.4 Subtract the absorbance of the 0 microgram standard from each of the other standard absorbances and plot the net absorbance versus the corresponding micrograms of Si. Draw the best smooth line fitting the points and passing through the origin.

#### 8.4.5 Procedure (To be run in triplicate)

8.4.5.1 Calculate the amount of sample prepared in Section 8.1.4 that contains about 0.5 g of  $\text{BF}_3$  gas. Transfer this amount to a polyethylene bottle and weigh to the nearest 0.0001 g.

8.4.5.2 Wash this solution into a 150-mL plastic beaker. Add 25 mL of boric acid solution. Dilute to about 60 mL and mix.

8.4.5.3 Add 5 mL of ammonium molybdate solution and mix.

8.4.5.4 Adjust the pH to 1.1–1.5 with 5N sulfuric acid. Allow to stand 10 minutes.

8.4.5.5 Transfer the solution to a 100-mL plastic volumetric flask and add 10 mL of tartaric acid solution. Mix well.

8.4.5.6 Add 1 mL of l-amino-2-naphthol-4-sulfonic acid solution. Dilute to 100 mL and mix. Allow to stand 30 minutes.

8.4.5.7 Prepare a reagent blank by treating a 50-mL aliquot of water as directed in Sections 8.4.5.2–8.4.5.6.

8.4.5.8 Set the wavelength of the spectrophotometer to 650 nm.

a. *Single Beam Spectrophotometer* — Rinse and then fill a 1-cm absorption cell with water. Place the cell into the cell holder and adjust the instrument to zero absorbance.

b. *Double Beam Spectrophotometer* — Rinse and then fill two matched 1-cm absorption cells with water and zero the instrument with water in both beams. Keep water in the reference beam and use the other matched cell for the blank, standards and samples.

8.4.5.9 Rinse a second matched 1-cm absorption cell with the blank solution and measure its absorbance. Then, using the same cell, measure the absorbance of each sample solution. Be sure to rinse the cell completely with the solution to be measured before each measurement. Recheck the instrument zero before each measurement.

8.4.5.10 Subtract the blank absorbance from the absorbance of the sample. Determine the corresponding micrograms of Si from the standard curve.

#### 8.4.6 Calculations

$$\text{ppm SiF}_4 = \frac{\text{Micrograms of Si} \times 3.706 \times 1,000,000}{\text{Weight of sample} \times 1,000,000}$$

where :

3.706 converts Si to  $\text{SiF}_4$   
1,000,000 converts ug to g  
1,000,000 converts to ppm.

8.5 *Sulfate* — This procedure describes the determination of sulfate in boron trifluoride gas. Sulfate ion is converted to a barium sulfate suspension under controlled conditions in such a manner as to form barium sulfate crystals of uniform size. Solutions are added to stabilize the suspension and minimize interferences. The resulting turbidity is determined by a turbidimeter, filter photometer or spectrophotometer

and compared to a curve prepared from standard sulfate solutions.

**8.5.1 Method Capabilities** — The range of the method is 7-70 ppm.

NOTE 3: Color or suspended matter in large amounts may interfere with this procedure.

### 8.5.2 Apparatus

8.5.2.1 Platinum dish, 100-mL capacity.

8.5.2.2 Steam bath (or Argand burner, if available).

8.5.2.3 Photometer: One of the following is required, with preference in the order given:

a. Turbidimeter

b. Spectrophotometer, for use at 420 nm, providing a light path of 4 to 5 centimeters.

c. Filter photometer, equipped with a violet filter having a maximum transmittance near 420 nm and providing a light path of 4 to 5 centimeters.

d. Fisher Electrophotometer, using a #525 Green Filter and 23-mm cells.

### 8.5.2.4 Stopwatch.

8.5.3 Reagents — All reagents used are reagent grade unless otherwise specified.

8.5.3.1 Water — All water used in the preparation of reagents and in the procedure is either distilled or deionized.

8.5.3.2 Sodium carbonate,  $\text{Na}_2\text{CO}_3$ .

8.5.3.3 Hydrochloric acid, concentrated,  $\text{HC}_1$ .

8.5.3.4 Barium chloride,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ .

8.5.3.5 Sodium chloride solution, 10% in water — Dissolve 10 grams sodium chloride in 100 mL water.

8.5.3.6 Gum Arabic Solution — Dissolve 0.5 gram gum arabic (acacia) in 100 mL of water, heat if necessary to dissolve, filter before using. Conditioning Reagent (may be used in place of gum arabic solution): Mix 50 mL glycerol with a solution containing 30 mL concentrated hydrochloric acid, 300 mL water, 100 mL 95% ethyl alcohol or isopropyl alcohol and 75 grams sodium chloride.

8.5.3.7 Standard sulfate solution, 1.00 mL = 0.100 mg  $\text{SO}_4^{2-}$  — Dissolve 0.1479 grams anhydrous sodium sulfate in 4 water and dilute to 1 L.

8.5.3.8 Sodium hydroxide, 1N,  $\text{NaOH}$ ; dissolve 40 g of sodium hydroxide pellets in water and dilute to 1 L.

8.5.3.9 Nitric acid, concentrated,  $\text{HNO}_3$ .

### 8.5.4 Calibration

8.5.4.1 Calibrate the photometer according to the manufacturer's instructions.

8.5.4.2 Pipet 0, 1.0, 3.0, 3.0, 4.0, 5.0, 10.0 and 20.0 mL of the 0.100 mg  $\text{SO}_4^{2-}$  standard into each of eight separate 150-mL beakers. These additions correspond to 0, 0.1, 0.2, 0.3, 0.4, 0.5, 1.0, and 2.0 mg  $\text{SO}_4^{2-}$ .

8.5.4.3 Follow the Procedure described in Sections 8.5.5-8.5.5.7.

8.5.4.4 Plot, on linear graph paper, the sulfate ion in grams against the corresponding photometer reading and draw the best smooth line through the points.

NOTE 4: A specific calibration curve must be prepared for each photometer. A new curve must be prepared if the instruments cell, lamp, or filter are changed, or if any other significant change in instrument or reagents is made.

### 8.5.5 Procedure

8.5.5.1 Weigh a clean platinum dish to 0.0001 g; weight = A.

8.5.5.2 Calculate the amount of sample prepared in Section 8.1.4 that contains about 50 grams of  $\text{BF}_3$  gas; transfer this amount to the platinum dish, then weigh the dish to the nearest 0.0001 g; weight = B.

8.5.5.3 Add about 0.1 gram of sodium carbonate and 10 mL of hydrochloric acid to the dish. Evaporate to dryness over a steam bath or an Argand burner. Repeat the evaporation 4 more times with 10-mL portions of hydrochloric acid.

8.5.5.4 Add 1 mL of hydrochloric acid and 5 mL of water to the dish; warm to dissolve any residue. Filter through Fisher G4 or equivalent filter paper in a 55-mm Buchner funnel, then transfer the filtrate to a 150-mL beaker. Wash the filter with water and transfer washings to the same 150-mL beaker.

8.5.5.5 Dilute to approximately 90 mL. Add 1 mL of 10% sodium chloride solution, 1.5 mL of freshly filtered gum arabic solution and mix. Adjust the pH to 1.75 with 1:10 hydrochloric acid or sodium hydroxide (1N). Dilute to 100 mL.

NOTE 5: The conditioning reagent may be substituted for the gum arabic solution. In this case Procedure, Step 8.5.5 reads: Add 5.0 mL of conditioning reagent, then dilute to 100 mL with water. Proceed to Step 8.5.6.

8.5.5.6 Place the beaker on a magnetic stirrer and while the solution is being stirred add 1 gram of barium chloride ( $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ) crystals. Begin timing immediately and stir for exactly 1 minute at a constant speed.

NOTE 6: It is recommended that a timer be used to permit the magnetic stirrer to operate exactly one minute with a constant

stirring speed. The important point is the speed of stirring and time should be constant for the standards and the samples.

8.5.5.7 Immediately after the stirring is completed, pour some of the solution into the absorption cell of the photometer. Record the measured turbidity after 4 minutes.

NOTE 7: If the reading is off the calibration curve, prepare a new curve with standards in the required range, or take a smaller portion of sample.

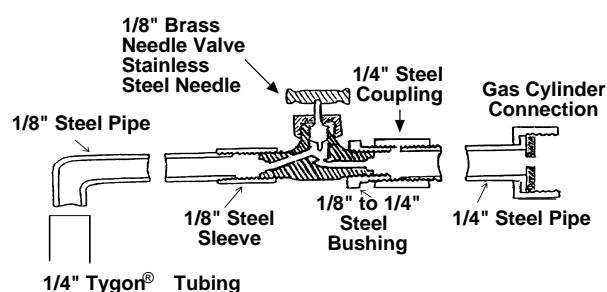
8.5.5.8 Prepare a sample blank using the same quantities of all reagents except the barium chloride, which is withheld. Read the blank and obtain the correction.

8.5.5.9 After proper correction for the blank, determine the mg of sulfate from the calibration curve.

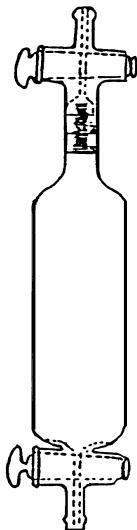
#### 8.5.6 Calculations

$$\frac{\text{mg SO}_4^{-} \times 1 \times 10^6}{1000 (B - A) \times F} = \text{ppm SO}_4^{-2}$$

where : F is from Section 8.1.4.8



**Figure 1**  
**Preparation of Sample Solution in Ice**



**Figure 2**  
**Modified Gas Collecting Tube**

**NOTICE:** SEMI makes no warranties or representations as to the suitability of the standards set forth herein for any particular application. The determination of the suitability of the standard is solely the responsibility of the user. Users are cautioned to refer to manufacturer's instructions, product labels, product data sheets, and other relevant literature respecting any materials mentioned herein. These standards are subject to change without notice.

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# SEMI C3.57-0600

## SPECIFICATION FOR CARBON DIOXIDE, CO<sub>2</sub>, ELECTRONIC GRADE IN CYLINDERS

This specification was technically approved by the Global Gases Committee and is the direct responsibility of the European Gases Committee. Current edition approved by the European Regional Standards Committee on April 4, 2000. Initially available at [www.semi.org](http://www.semi.org) May 2000; to be published June 2000.

### 1 Description

1.1 Carbon dioxide is a non-flammable, colorless, odorless, slightly acidic gas which is stable under normal conditions.

### 2 Specifications

Purity: 99.999%

<i>Impurities</i>	<i>Maximum Acceptable Level</i>
Nitrogen	4 ppm
Oxygen	1 ppm
Methane	0.5 ppm
Moisture	2 ppm

### 3 Referenced Standards

#### 3.1 DIN Standard<sup>1</sup>

DIN 50457-1

NOTE 1: As listed or revised, all documents cited shall be the latest publications of adopted standards.

### 4 Physical Constants (for information only)

Formula	CO <sub>2</sub>
Molecular weight	44
Melting point	-56.6°C
Boiling point	-78.5(s)°C
Critical temperature	30°C
Relative density, gas	1.52 (air=1)
Relative density, liquid	0.82 (water=1)
Vapor pressure 20°C	57.3 bar
Appearance/Color	Colorless gas
Odor	none

### 5 Analytical Procedures

5.1 *Nitrogen, oxygen and methane* — This procedure is for the determination of nitrogen, oxygen and methane using a gas chromatograph with discharge ionization detector and heartcut column switching.

5.1.1 *Detection Limit* — 100 ppb.

1 Deutsches Institut für Normung e.V., BeuthVerlag GmbH, burggrafenstrasse 4-10, D10787 Berlin, Germany, [www.din.de](http://www.din.de)

#### 5.1.2 Instrument Parameters

##### 5.1.2.1 Columns

Column 1: Hayesep Q, 2 meters by 3 mm (Stainless-steel or nickel rich alloy).

Column 2: Molecular sieve 5A, 3 meters by 3 mm (Stainless-steel or nickel rich alloy) 80/100 mesh or equivalent.

5.1.2.2 *Carrier Flow*: 25 mL/minute helium.

5.1.2.3 *Sample Volume*: 2 mL.

5.1.2.4 *Temperatures*:

Detector	110°C
Column Oven	50°C
Injector	Ambient

5.1.3 *Calibration Standard* — 1–10 ppm (mole/mole) nitrogen, oxygen and methane, balance helium.

#### 5.1.4 Operating Procedure

5.1.4.1 Inject the calibration standard into the gas chromatograph via the gas sampling valve. Record the retention times and peak areas for the components within the standard. The order of elution is: oxygen, nitrogen, methane.

5.1.4.2 Inject the sample to be tested in the same manner as the calibration standard. Record the retention times and peak areas. The carbon dioxide matrix gas is vented via the heartcut.

5.1.4.3 Repeat 5.1.4.1.

5.1.4.4 Compare the average peak areas of the calibration standard to that of the unknown carbon dioxide sample being tested. Calculate the concentrations of oxygen, nitrogen and methane using the formula below. The results shall not exceed the values specified in Section 2 of this standard.

$$\frac{\text{Sample Peak Area}}{\text{Standard Peak Area}} \times \frac{\text{Concentration}}{\text{Standard}} = \frac{\text{Concentration}}{\text{Sample}}$$

5.2 *Moisture* — This procedure is for the determination of moisture in carbon dioxide using a direct readout moisture analyzer with a phosphorus pentoxide electrolytic cell.

5.2.1 *Detection Limit* — 100 ppb.

#### 5.2.2 *Instrument Parameters*

5.2.2.1 *Flow requirements* — Zero and span the analyzer in accordance with the instrument manufacturers instructions. Set the sample gas flow to the rate specified by the manufacturer.

5.2.3 *Calibration standard* — The analyzer shall be calibrated at the time of use by reference to a standard gas calibration mixture containing a certified moisture content close to the expected value of the gas under test. If the analyzer indicates the certified moisture content, within the overall measurement uncertainties stated by the instrument and gas manufacturers, it may be used without further adjustment or calibration.

NOTE 2: Further Experimental detail may be found in DIN 50450-1.

#### 5.2.4 *Sample system*

5.2.4.1 Use insulated stainless steel sample lines to prevent frosting during sampling.

5.2.4.2 Keep sample lines to a minimum length.

#### 5.2.5 *Operating Procedure*

5.2.5.1 Follow the procedures specified in the instrument manufacturer's manual.

5.2.5.2 Allow the system to run until a stable reading is obtained for 5 minutes.

5.2.5.3 Read and record the concentration of moisture, in ppm, indicated on the moisture analyzer. The result obtained shall not exceed the value specified in Section 2 of this standard.

NOTE 3: This specification applies to gaseous phase product from a cylinder supply.

NOTE 4: It is recommended that the user discontinue use of the cylinder prior to the complete consumption of the liquid phase contents. The contents of cylinders containing liquefied product should be determined by weight and not pressure.

NOTE 5: Adopt a replicate sampling protocol for both calibration standard and unknown to achieve the required measurement uncertainty.

**NOTICE:** SEMI makes no warranties or representations as to the suitability of the specification set forth herein for any particular application. The determination of the suitability of the specification is solely the responsibility of the user. Users are cautioned to refer to manufacturer's instructions, product labels, product data sheets, and other relevant literature respecting any materials mentioned herein. These specifications are subject to change without notice.

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# SEMI C3.40-1000

## STANDARD FOR CARBON TETRAFLUORIDE (CF<sub>4</sub>), VLSI GRADE

This standard was technically approved by the Global Gases Committee and is the direct responsibility of the North American Gases Committee. Current edition approved by the North American Regional Standards Committee on July 11, 2000. Initially available at www.semi.org September 2000; to be published October 2000. Originally published in 1989; previously published in 1992.

### 1 Description

1.1 Carbon tetrafluoride is an odorless, colorless, nonflammable gas. It is a simple asphyxiant. It is also known as tetrafluoromethane.

### 2 Specifications

QUALITY: 99.997%

<i>Impurities</i>	<i>Maximum Acceptable Level (ppm) *</i>
Carbon Dioxide (CO <sub>2</sub> )	1
Carbon Monoxide (CO)	1
Nitrogen (N <sub>2</sub> )	20
Other Halocarbons (CF <sub>3</sub> Cl, CF <sub>2</sub> Cl <sub>2</sub> , CF <sub>3</sub> H)	1
Oxygen (O <sub>2</sub> )	5
Sulfur Hexafluoride (SF <sub>6</sub> )	1
Water (H <sub>2</sub> O) (v/v)	1
TOTAL IMPURITIES	30

\* An analysis of significant figures has not been considered. The number of significant figures will be based on analytical accuracy and the precision of the provided procedure.

### 3 Chemical Specification

Total Hydrolyzable Fluorides as HF	1 ppm max.
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### 4 Physical Constants (for information only)

	<i>Metric Units</i>	<i>US Units</i>
Molecular weight	88.005	88.005
Boiling point at 1 atm	-128.0°C	-198.4°F
Density of gas at 0°C (32°F) and 1 atm	3.946 kg/m <sup>3</sup>	0.246 lb/ft <sup>3</sup>
Specific gravity of gas at 0°C and 1 atm	3.05	3.05
Density of liquid at -80°C	1317 kg/m <sup>3</sup>	82.22 lb/ft <sup>3</sup>

### 5 Analytical Procedures (See Notes 1 and 2, and Figures 1 and 2.)

5.1 *Carbon Dioxide* — This procedure is for the determination of carbon dioxide in carbon tetrafluoride using a gas chromatograph with an ultrasonic detector.

5.1.1 *Detection Limit* — 0.5 ppm (mole/mole).

5.1.2 *Instrument Parameters*

5.1.2.1 Columns:

Column 1:	Haysep D, 100/120 mesh, 4.6 m (15 ft) by 3.2 mm (1/8 in) OD ss or equivalent.
Column 2:	Porapak QS, 100/120 mesh, 2.1 m (7 ft) by 3.2 mm OD ss or equivalent.

5.1.2.2 *Carrier Flow*: 16 mL/min heliu m.

5.1.2.3 *Temperatures*:

Detector	120°C
Column	50°C
Valve	90°C

5.1.2.4 *Sample Volume*: 1.0 mL

5.1.2.5 *Time Table* — Determine the times for valve switching and signal changes, and enter into the run table.

An example of a run table follows.

Valve	On	Off
1	0.01	*
2	9.20	*
3	0.01	12.00

\* Valve left on until end of run.

5.1.3 *Calibration Standard* — 1–5 ppm carbon dioxide and balance helium.

5.1.4 *Operating Procedure*

5.1.4.1 Inject the calibration standard into the column using a gas sampling valve. Record retention times and peak areas. The retention time for carbon dioxide is approximately 16 minutes.

5.1.4.2 Inject the sample to be tested in the same manner as the calibration standard. Record the retention times and peak areas.

5.1.4.3 Repeat 5.1.4.1.

5.1.4.4 Compare the average peak areas of the calibration standard to those of the carbon tetrafluoride

sample being tested. Calculate the concentration of carbon dioxide in the sample, using the formula below. The result may not exceed the specification in Section 2 of this Standard.

$$\frac{\text{Sample Peak Area}}{\text{Standard Peak Area}} \times \frac{\text{Concentration of Standard}}{\text{Concentration of Sample}} = \text{Concentration}$$

**5.2 Oxygen, Nitrogen and Carbon Monoxide** — This procedure is for the determination of oxygen, nitrogen, and carbon monoxide in carbon tetrafluoride using a gas chromatograph with an ultrasonic detector.

**5.2.1 Detection Limits** — 0.5 ppm (mole/mole) for each impurity.

### 5.2.2 Instrument Parameters

#### 5.2.2.1 Columns:

Column 3:	Porapak QS, 100/120 mesh, 3.6 m (12 ft) by 3.2 mm (1/8 in) OD ss or equivalent.
Column 4:	Haysep D, 100/120 mesh, 4.6 m (15 ft) by 3.2 mm OD ss or equivalent.
Column 5:	Molecular Sieve 13X, 45/60 mesh, 2.1 m (7 ft) by 3.2 mm OD ss or equivalent.

5.2.2.2 Carrier Flow: 16 mL/min helium m.

#### 5.2.2.3 Temperatures:

Detector	120°C
Column	50°C
Valve	90°C

5.2.2.4 Sample Volume: 2.0 mL

**5.2.2.5 Time Table** — Determine the times for valve switching and signal changes, and enter into the run table.

An example of a run table follows.

Valve	On	Off
1	0.01	*
2	9.20	*
3	0.01	12.00

\* Valve left on until end of run.

**5.2.3 Calibration Standard** — 1–5 ppm (mole/mole) each nitrogen, oxygen and carbon monoxide, balance helium.

### 5.2.4 Operating Procedure

**5.2.4.1** Inject the calibration standard into the column using a gas sampling valve. Record retention times and peak areas. The approximate retention times are:

oxygen 11.1 minutes, nitrogen 11.6 minutes, carbon monoxide 14.5 minutes.

**5.2.4.2** Inject the sample to be tested in the same manner as the calibration standard. Record the retention times and peak areas.

**5.2.4.3** Repeat 5.2.4.1.

**5.2.4.4** Compare the average peak areas of the calibration standard to those of the carbon tetrafluoride sample being tested. Calculate the concentrations of oxygen, nitrogen and carbon monoxide in the sample, using the formula below. The results may not exceed the specifications in Section 2 of this Standard.

$$\frac{\text{Sample Peak Area}}{\text{Standard Peak Area}} \times \frac{\text{Concentration of Standard}}{\text{Concentration of Sample}} = \text{Concentration}$$

**5.3 Fluorocarbon and Chlorofluorocarbon Impurities** — This procedure is for the determination of the volatile organic impurities in carbon tetrafluoride using a gas chromatograph with a flame ionization detector.

**5.3.1 Detection Limits** — 0.5 ppm (mole/mole) for each impurity.

### 5.3.2 Instrument Parameters

**5.3.2.1 Column:** 1% SP-1000 on Carbopak B (60/80), 7.3 m (24 ft) by 3.2 mm (1/8 in) OD ss or equivalent.

**5.3.2.2 Carrier Flow:** 40 mL/min helium m.

**5.3.2.3 Support Gases:** Set the flow rates as specified by the instrument manufacturer.

#### 5.3.2.4 Temperatures:

Injection Port	200°C
Detector	250°C
Initial Oven	35°C
Pre-Program Hold	7 min
Temperature Rise	10°C/min
Final Oven	150°C
Final Hold	10 min

**5.3.2.5 Sample Volume:** 2 mL.

**5.3.3 Calibration Standard** — 1–10 ppm (by volume) desired impurities in helium. Practical impurities may be trifluoromethane ( $\text{CHF}_3$ ), hexafluoroethane ( $\text{C}_2\text{F}_6$ ), dichlorodifluoromethane ( $\text{CCl}_2\text{F}_2$ ), and chlorotrifluoromethane ( $\text{CClF}_3$ ).

### 5.3.4 Operating Procedure

**5.3.4.1** Attach a stainless steel diaphragm two-stage regulator to the standard cylinder. Connect the regulator to the 6 port chromatographic sampling valve.

5.3.4.2 Purge the sampling lines with the standard for at least one minute.

5.3.4.3 Pressurize the sampling lines to 5 psig.

5.3.4.4 Inject the standard into the gas chromatograph, and start the scan. Record the retention times and peak areas. Order of elution for the above mentioned standard is carbon tetrafluoride, trifluoromethane, hexafluoroethane, chlorotrifluoromethane, and dichlorodifluoromethane.

5.3.4.5 Inject the sample to be tested in the same manner as the calibration standard.

5.3.4.6 Repeat 5.3.4.1–5.3.4.4.

5.3.4.7 Compare the average peak areas of the calibration standard to those of the carbon tetrafluoride sample being tested. Calculate the concentration of each of the impurities using the formula below. The results may not exceed the specifications in Section 2 of this Standard.

$$\frac{\text{Sample Peak Area}}{\text{Standard Peak Area}} \times \frac{\text{Concentration of Standard}}{\text{Concentration of Sample}} = \text{Concentration of Sample}$$

**5.4 Sulfur Hexafluoride** — This procedure is for the determination of sulfur hexafluoride in carbon tetrafluoride using a gas chromatograph with a thermal conductivity detector. (See Figure 2.)

5.4.1 Detection Limit — 0.5 ppm.

#### 5.4.2 Instrument Parameters

5.4.2.1 Column: Super Q, 80/100 mesh h, 4.9 m (16 ft) by 1.75 mm (1/16 in) ID, 3.2 mm (1/8 in) OD, ss or equivalent.

5.4.2.2 Carrier Flow: 19 mL/min heliu m.

5.4.2.3 Temperatures:

Detector	100°C
Oven	70°C
Gas sampling valve	70°C

5.4.2.4 Sample Volume: 1 mL.

5.4.3 Calibration Standard — 1 ppm sulfur hexafluoride, balance helium.

#### 5.4.4 Operating Procedures

5.4.4.1 Inject the calibration standard into the column using a gas sampling valve. Record retention time and peak area.

5.4.4.2 Inject the sample to be tested in the same manner as the calibration standard. Record the retention times and peak areas.

5.4.4.3 Repeat 5.4.4.1.

5.4.4.4 Compare the average peak areas of the calibration standard to those of the carbon tetrafluoride sample being tested. Calculate the concentration of sulfur hexafluoride using the formula below. The result may not exceed the specification in Section 2 of this Standard.

$$\frac{\text{Sample Peak Area}}{\text{Standard Peak Area}} \times \frac{\text{Concentration of Standard}}{\text{Concentration of Sample}} = \text{Concentration of Sample}$$

**5.5 Water** — This procedure is for the determination of trace moisture (water) in carbon tetrafluoride using a continuous flowing electrolytic hygrometer.

5.5.1 *Detection Limit* — 1.0 ppm (vol/vol) or -76°C (-105°F).

5.5.2 *Flow Requirements* — Set the sample pressure and flow rate in accordance with the instrument manufacturer's instructions.

5.5.3 *Operation Check* — Check the electrolytic hygrometer periodically. A gas, containing a known amount of water, should be passed through the hygrometer. Agreement between the electrolytic hygrometer and the moisture standard should be within their relative accuracies.

#### 5.5.4 Operating Procedure

5.5.4.1 Obtain a continuous flow sample of gas, from the CF<sub>4</sub> source, using a clean, passivated stainless steel line which has been purged dry after exposure to ambient moisture. (See Notes 3 and 4.)

5.5.4.2 After prepurging with a dry gas, allow the sample gas to flow through the sampling system and the electrolytic moisture analyzer until a stable reading is obtained. The result may not exceed the specification in Section 2 of this standard.

**5.6 Hydrolyzable Fluorides as HF** — This procedure is for the determination of hydrolyzable fluorides in carbon tetrafluoride using fluoride ion selective electrode.

5.6.1 *Detection Limit* — Detection limits should be checked for any new implementation of a method. Detection limits below 0.1 ppm have been determined with this method. Detection limits can be improved by increasing the volume of gas sampled.

#### 5.6.2 Equipment

5.6.2.1 mV meter (0.1 mV scale)

5.6.2.2 Reference electrode (single junction type)

- 5.6.2.3 Fluoride ion selective electrode
- 5.6.2.4 Magnetic stir bars (PTFE coated)
- 5.6.2.5 Magnetic stirrer
- 5.6.2.6 Plastic beakers (See note 5)
- 5.6.2.7 PTFE bubblers
- 5.6.2.8 1000 ml and 100 ml plastic volumetric flasks (See note 5)
- 5.6.2.9 0.2 ml and 1 ml plastic volumetric pipettes (See note 5)
- 5.6.2.10 Flow controller or flowmeter (0-1000 sccm CF<sub>4</sub>)
- 5.6.3 Reagents
- 5.6.3.1 Distilled or deionized water
- 5.6.3.2 5 N sodium hydroxide
- 5.6.3.3 0.2 N sodium hydroxide
- 5.6.3.4 Glacial acetic acid
- 5.6.3.5 *Buffer Solution* — To 500 ml distilled or deionized water in a 1000 ml volumetric flask, add 57 ml glacial acetic acid and 58 g of sodium chloride. Adjust the pH to between 5.0–5.5 with 5 M sodium hydroxide. Cool to room temperature. Dilute to one liter with distilled or deionized water.
- 5.6.4 *Calibration Standard* — Sodium fluoride standard (10<sup>-3</sup> M F<sup>-</sup> in water, freshly prepared)
- 5.6.5 *Operating Procedure*
- 5.6.5.1 Prepare working standard by adding 100 ml 10<sup>-3</sup> M F<sup>-</sup> to 100 ml buffer solution.
- 5.6.5.2 Prepare a blank containing 50.0 ml 0.2 N NaOH and 50.0 ml buffer solution in a plastic beaker.
- 5.6.5.3 While stirring blank gently, record mV reading from the blank once reading is stable.
- 5.6.5.4 Successively add increments of working standard to the blank to generate a calibration curve. Record stable mV reading after each addition. Table 1 shows recommended increments and resultant concentrations.

**Table 1 Calibration Concentrations**

Added volume of Working Standard (ml)	Total Volume (ml)	Resulting F-Concentration (M)
0.2	100.2	1.0 x 10 <sup>-6</sup>
0.2	100.4	2.0 x 10 <sup>-6</sup>
0.4	100.8	4.0 x 10 <sup>-6</sup>
0.4	101.2	5.9 x 10 <sup>-6</sup>
0.8	102.0	9.8 x 10 <sup>-6</sup>
1.0	103.0	1.5 x 10 <sup>-5</sup>
2.0	105.0	2.4 x 10 <sup>-5</sup>

5.6.5.5 Put 50 ml 0.2 N NaOH into each of two bubblers connected in series

5.6.5.6 Establish a flow of < 1000 sccm of CF<sub>4</sub> through the bubblers using a suitable flow controller or flowmeter.

5.6.5.7 Sample approximately 15 liters of CF<sub>4</sub>. Record flowrate and time of sampling to determine total volume sampled (flowrate x time). A wet test meter can also be used to measure total volume. The amount of gas sample must be the volume at STP. If the flowmeter or wet test meter is not reference to 0° and 760 torr, use the formula below to correct sample volume.

$$\text{Liters at STP} = \text{Measured Liters} \times \frac{760 \text{ Torr}}{\text{P}} \times \frac{\text{T} + 273}{273 \text{ K}}$$

P: Pressure of sampled gas (mm Hg)

T: Temperature of sampled gas or reference temperature of the flow controller or meter in °C.

5.6.5.8 Transfer contents of each bubbler to individual 100 ml volumetric flasks and add 50 ml Buffer solution to each. Then, if necessary, add deionized or distilled water to bring the volume up to 100 ml.

5.6.5.9 Transfer contents to a plastic beaker

5.6.5.10 While stirring, measure and record mV readings for each sample.

5.6.5.11 Determine F<sup>-</sup> concentration in solution using calibration curve generated in section 5.6.5.4.

5.6.5.12 Calculate gas phase hydrolyzable fluoride concentration using the equation below. Note: the equation assumes the hydrolyzable fluoride is hydrogen fluoride.

$$\text{Gas Phase HF (ppm}_y\text{)} = C \times 0.11 \times \frac{22.4 \text{ l/mole}}{V_s} \times 10^6$$

C: Measured hydrolyzable fluoride concentration (M) determined in section 5.6.5.11

V<sub>s</sub>: Volume of CF<sub>4</sub> sampled (liters at STP)

5.6.5.13 The HF concentration of the second bubbler should be insignificant compared to the first bubbler. If significant HF levels are found in the second bubbler, resample with a lower flowrate.

### 5.7 Notes

Note 1: Introduce the calibration standard as many times as necessary to achieve the desired precision.

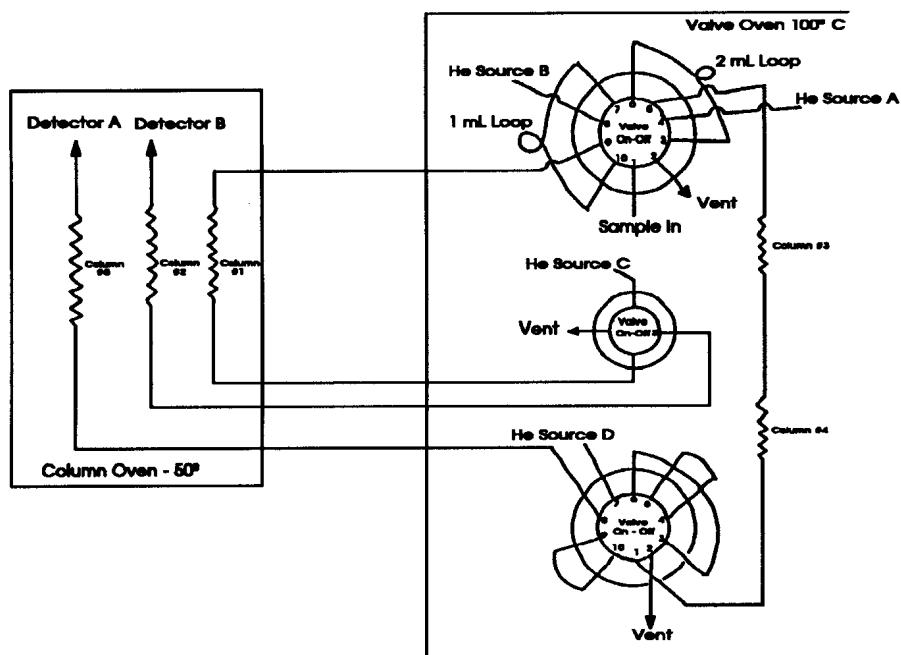
Note 2: All gases used in the analysis of the sample should not contain more than 10% of the specified

value of the component of interest, unless otherwise stated.

Note 3: A passivation procedure is described in the Metals Handbook, 10th ed., Vol. 2, American Society for Metals, Metals Park, OH.

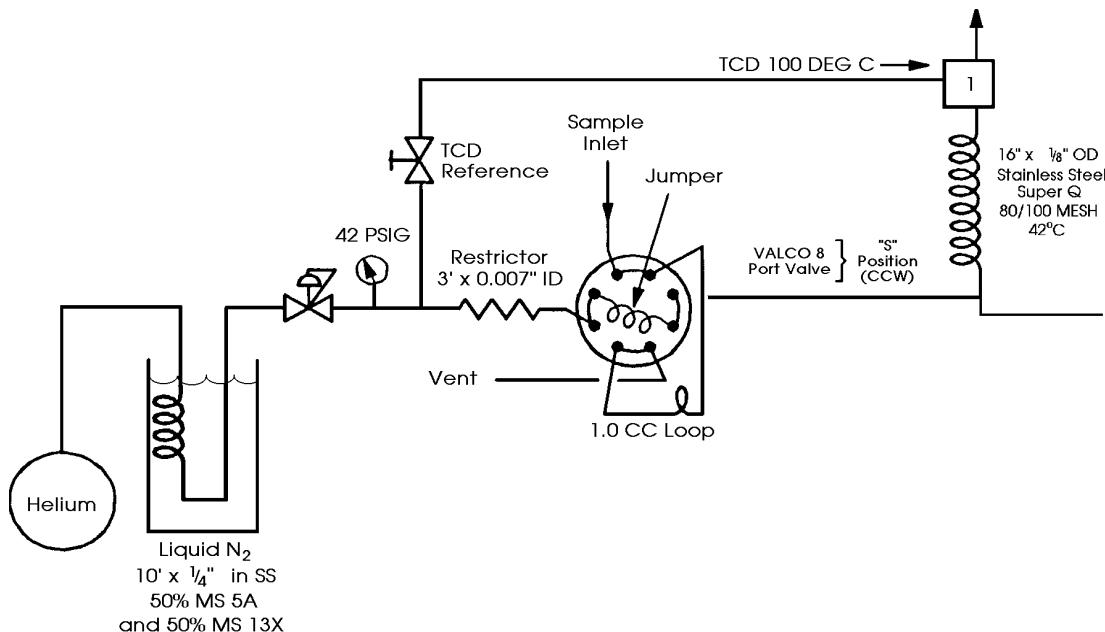
Note 4: The sampling system and hygrometer must be designed to operate at the sample pressure, or the sample pressure must be reduced, by a regulator with a diaphragm of stainless steel or other suitable material, to accommodate the pressure restrictions of the hygrometer.

Note 5: Polytetrafluoroethylene, polymethylpentene and polypropylene are suitable plastic materials.



**Figure 1**

Configuration for the Analysis of CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and CO in CF<sub>4</sub>



**Figure 2**  
**Configuration for the Analysis of SF<sub>6</sub> in CF<sub>4</sub>**

**NOTICE:** These standards do not purport to address safety issues, if any, associated with their use. It is the responsibility of the user of these standards to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. SEMI makes no warranties or representations as to the suitability of the standards set forth herein for any particular application. The determination of the suitability of the standard is solely the responsibility of the user. Users are cautioned to refer to manufacturer's instructions, product labels, product data sheets, and other relevant literature respecting any materials mentioned herein. These standards are subject to change without notice.

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## SEMI C3.32-0301

# SPECIFICATION FOR CHLORINE (Cl<sub>2</sub>), 99.996% QUALITY

This specification was technically approved by the Global Gases Committee and is the direct responsibility of the North American Gases Committee. Current edition approved by the North American Regional Standards Committee on October 17, 2000. Initially available at [www.semi.org](http://www.semi.org) January 2001; to be published March 2001. Originally published in 1987; previously published in 1995.

### 1 Description

1.1 Gaseous chlorine is greenish-yellow and about 2.5 times as heavy as air. Chlorine has a disagreeable and suffocating odor.

Specific gravity	2.473	2.473
Density liquid at -118°C (-180.8°F)	1574.8 kg/m <sup>3</sup>	98.26 lb/ft <sup>3</sup>

### 2 Specifications

QUALITY: 99.996%

Impurities	Maximum Acceptable Level (ppm) (See NOTE 1.)
Carbon dioxide (CO <sub>2</sub> )	10
Carbon monoxide (CO)	1
Hydrocarbons (C <sub>1</sub> – C <sub>2</sub> )	1
Nitrogen (N <sub>2</sub> )	20
Oxygen (O <sub>2</sub> )	4
Water (H <sub>2</sub> O) (v/v)	(See NOTE 2.)
TOTAL LISTED IMPURITIES (excluding chromium, iron, nickel, and sodium)	36

	Maximum Acceptable Level (ppm) (See NOTE 1.)
Chromium (Cr)	0.2 by wt. Liquid Phase
Iron (Fe)	0.2 by wt. Liquid Phase
Nickel	0.2 by wt. Liquid Phase
Sodium	1 by wt. Liquid Phase

NOTE 1: An analysis of significant figures has not been considered. The number of significant figures will be based on analytical accuracy and on the precision of the provided procedure.

NOTE 2: It is not known whether H<sub>2</sub>O remains as H<sub>2</sub>O in Cl<sub>2</sub> or reacts to other species. For this reason, interpretation of H<sub>2</sub>O measurement data is questionable. Test and acceptance criteria shall be determined between user and supplier. Possible methods include: a) determination of HCl by Fourier transform infrared spectrometry (FTIR), mass spectrometry, or gas chromatography; b) measurement of water by electrolysis in a P<sub>2</sub>O<sub>5</sub> cell (reported in terms of H<sub>2</sub>O equivalents); c) determination of water by FTIR.

### 3 Physical Constants (for information only)

	Metric Units	US Units
Molecular weight	70.9	70.9
Boiling point at 1 atm	-34.05°C	-29.3°F
Density gas at 20°C (68°F) and 1 atm	2.980 kg/m <sup>3</sup>	0.1860 lb/ft <sup>3</sup>

### 4 Analytical Procedures

4.1 *Carbon Monoxide, Carbon Dioxide, and Hydrocarbons (CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>)* — This procedure is for the determination of carbon monoxide, carbon dioxide, and C<sub>1</sub>–C<sub>2</sub> hydrocarbons in chlorine. The sample shall be vapor phase and analyzed using a gas chromatograph with a flame ionization detector/methanizer combination. (See Figure 1 and Notes 1, 2, and 3.)

4.1.1 *Detection Limit* — 0.1 ppm (mol/mol).

4.1.2 *Instrument Parameters*

4.1.2.1 *Injection Valve* — 10 port corrosion-resistant.

4.1.2.2 *Sample Volume* — 2 mL.

4.1.2.3 *Columns*:

Column 1:	Porapak P, 3.1 m (10 ft) by 3.2 mm (1/8 in) OD ss or equivalent.
Column 2:	Porapak P, 3.1 m by 3.2 mm OD ss or equivalent.

4.1.2.4 *Carrier Flow* — 20 mL/min nitrogen.

4.1.2.5 *Column Temperature* — 40°C.

4.1.2.6 *Air and Hydrogen Pressure and Flow* — As specified by the instrument manufacturer.

4.1.3 *Calibration Standard* — 1–5 ppm (mol/mol) each component in nitrogen.

4.1.4 *Operating Procedure*

4.1.4.1 Place the 10 port valve in the sample load position.

4.1.4.2 Turn on the methanizer heater and establish hydrogen flow. Allow unit to heat to operating temperature (as specified by the manufacturer).

4.1.4.3 Establish air flow and ignite burner following the instrument manufacturer's instructions. Allow the system to stabilize for 15 minutes.

4.1.4.4 Determine the time at which ethane elutes from the first column and absorbs onto the second column so one can vent the chlorine. Inject the calibration ethane standard and record the retention time of ethane obtained without returning the valve to the load position. Multiply this time by 0.6. The result will be the time during the analysis at which the injection valve should be returned to the load position, backflushing the chlorine to vent.

Repeat the injection of the ethane calibration standard, including the backflush, to ensure that enough time has passed to allow elution of ethane onto the second column.

4.1.4.5 Inject the remaining standards using the backflush technique. Record the retention times and peak areas.

4.1.4.6 Analyze the chlorine sample to be tested in the same manner as in 4.1.4.5. Repeat the sample injection until peak areas of the impurity of interest agree within 5%.

4.1.4.7 Analyze each of the calibration standards again as in 4.1.4.5.

4.1.4.8 Compare the average peak areas of the calibration standards to those of the chlorine sample being tested. Calculate the concentration of each impurity, using the formula below. The results may not exceed the specifications in Section 2 of this standard.

$$\frac{\text{Sample Peak Area}}{\text{Standard Peak Area}} \times \frac{\text{Concentration of Standard}}{\text{Concentration of Sample}} = \frac{\text{Concentration of Sample}}{\text{Concentration of Standard}}$$

**4.2 Oxygen and Nitrogen** — This procedure is for the determination of oxygen and nitrogen in chlorine. The sample shall be vapor phase and analyzed using a gas chromatograph with a thermal conductivity detector. (See Figure 2 and Notes 1 and 2.)

4.2.1 *Detection Limits* — 2 ppm (v/v) oxygen, 5 ppm (v/v) nitrogen.

#### 4.2.2 *Instrument Parameters*

4.2.2.1 *Injection Valve* — 10 port corrosion-resistant.

4.2.2.2 *Sample Volume* — 2 mL.

#### 4.2.2.3 *Columns:*

Column 1:	Porapak Q, 1.8 m (6 ft) by 3.2 mm (1/8 in) OD ss or equivalent.
Column 2:	Molecular sieve 13 $\times$ , 3.1 m (10ft) by 3.2 mm OD ss or equivalent.

4.2.2.4 *Carrier Flow* — 20 mL/min helium.

#### 4.2.2.5 *Temperature:*

Column	30°C
Detector	50°C

4.2.3 *Calibration Standard* — 10–40 ppm (v/v) each component in helium.

#### 4.2.4 *Operating Procedure*

4.2.4.1 Place the 10 port valve in the sample load position.

4.2.4.2 Inject the standard, wait one minute, then return the valve to the sample load position to backflush the principal gas to vent while allowing the oxygen and nitrogen to pass to the analytical column. Record the retention times and peak areas.

4.2.4.3 Inject the standard at least three times. All peak areas for a specific impurity should agree within 5%.

4.2.4.4 Inject the chlorine sample to be tested in the same manner as in 4.2.4.2 and 4.2.4.3. Record the retention times and peak areas.

4.2.4.5 Repeat 4.2.4.2 and 4.2.4.3.

4.2.4.6 Compare the average peak areas of calibration standards with that of the chlorine sample being tested. Calculate the concentrations of oxygen and nitrogen, using the formula below. The results may not exceed the specifications in Section 2 of this standard.

$$\frac{\text{Sample Peak Area}}{\text{Standard Peak Area}} \times \frac{\text{Concentration of Standard}}{\text{Concentration of Sample}} = \frac{\text{Concentration of Sample}}{\text{Concentration of Standard}}$$

**4.3 Trace Elements** — This procedure gives instructions for the determination of trace elements in liquid phase chlorine using inductively coupled plasma mass spectrometry (ICP-MS). (See Note 4.)

4.3.1 *Detection Limit* — (See Note 4.)

4.3.2 *Instrument Parameters* — (See Note 4.)

4.3.3 *Calibration Standards* — (See Note 4.) All instrument calibration standards should be prepared from NIST-traceable reference standards.

4.3.4 *Sample Collection Apparatus* — (See Notes 5 and 6 and Figures 3 and 4.)

4.3.4.1 *Cylinder Connector* — Stainless steel, or other suitable material, dependent on the cylinder valve used.

4.3.4.2 *Fluorocarbon Tubing* — 6.4 mm (1/4") and 3.2 mm (1/8") outer diameters required, lengths dependent on construction of apparatus.

4.3.4.3 *Fluorocarbon Needle Valve* — Two 6.4 mm (1/4") needle valves (designated as V1 and V2). (See Figure 3.)

4.3.4.4 *Fluorocarbon Ball Valve* — One 6.4 mm (1/4") ball valve and one 3.2 mm (1/8") ball valve (designated as V3 and V4, respectively). (See Figure 3.)

4.3.4.5 *Fluorocarbon T-Joint* — One 6.4 mm (1/4") T-joint.

4.3.4.6 *Fluorocarbon Cylinder Union* — One 6.4 mm (1/4") to 15.9 mm (5/8") iron pipe size female pipe thread adapter to attach to the stainless steel cylinder connector.

4.3.4.7 *Fluorocarbon Reducer* — One 6.4 mm (1/4") to 3.2 mm (1/8") reducing union.

4.3.4.8 *Flask Connector* — One Plasmatech #16F424 flask connector, or similar, attached to a cap for the 100 mL sampling flask.

4.3.4.9 *Sampling Flasks* — 100 mL polypropylene volumetric flask.

4.3.4.10 *Nitrogen Source* — A source of high-purity nitrogen to purge the sampling system prior to and after sampling and for evaporation.

4.3.4.11 *Scrubber Source* — A caustic scrubber source to neutralize chlorine from the sampling process. The scrubber is connected to an eductor tube, with the vacuum created by an N<sub>2</sub> source regulated at 20 psi.

#### 4.3.5 *Operating Procedure*

4.3.5.1 Assemble the system according to Figures 3 and 4, ensuring that the connections are leak tight.

4.3.5.2 Wrap Teflon tape around the threads of a 100 mL volumetric flask to ensure a good seal. Connect the 100 mL polypropylene flask to the flask connector as shown in Figure 3. All 100 mL volumetric flasks used for sample collection should be prepared in a similar manner.

4.3.5.3 Clean the exterior of the cylinder CGA by rinsing it with (in succession) 10% HNO<sub>3</sub>/DI H<sub>2</sub>O, isopropanol/DI H<sub>2</sub>O, and DI H<sub>2</sub>O. The CGA must be free of residue. The CGA is then cleaned and dried with a cotton swab. Dry the exterior of the CGA with the high-purity N<sub>2</sub>. Repeat the process for the nut and gland. The cylinder CGA must be completely dry prior to connecting the nut and gland.

4.3.5.4 Invert the cylinder with a cylinder inverter and connect the cylinder CGA to the nut and gland.

4.3.5.5 Purge the system by opening V1 and V2 and allowing high purity N<sub>2</sub> to flow through the system at

5–10 psig for a minimum of three minutes. The ball valves (V3 and V4) remain in the open position.

4.3.5.6 Close V1 and V2. To condition the sampling system, open the cylinder valve, then slowly open V2 to allow Cl<sub>2</sub> to flow into the sample flask. After collecting 70–100 mL of Cl<sub>2</sub>, close the cylinder valve and open V1 to purge the system.

4.3.5.7 Discard the initial Cl<sub>2</sub> sample by passing it through to the scrubber, remove the flask and replace it with a labeled sample flask. Continue to purge the system for at least two minutes. Close V1 and V2. Open the cylinder valve, then slowly open V2.

4.3.5.8 Allow 100 g of sample to be introduced into the sample flask. Once this is completed, close V2, then close the cylinder valve. Open V1 and V2 to allow for purging of the Cl<sub>2</sub> in the sample flask with high purity N<sub>2</sub> flowing through the system at 5 psig. This will purge the Cl<sub>2</sub> at a rate of 7–10 gms per minute.

4.3.5.9 When the sample has been flushed, replace the sample flask with another flask. Loosely cap the sample flask to allow for any residual Cl<sub>2</sub> to evaporate. If additional samples from the same cylinder are desired, repeat Steps 4.3.5.5 through 4.3.4.9.

4.3.5.10 Close V1 and disconnect the cylinder valve connector from the cylinder valve. Return the cylinder to the upright position. Rinse the cylinder CGA and nut, gland with DI H<sub>2</sub>O, and dry with N<sub>2</sub>. Remove the cylinder from the cylinder inverter.

4.3.5.11 Repeat Steps 4.3.5.3 to 4.3.5.10 for additional cylinders.

4.3.5.12 After obtaining all samples of interest, hand dry the connector and place it into an oven to prevent corrosion and build-up of condensation. Clean the tubing and valve system with a 10% HNO<sub>3</sub>/DI H<sub>2</sub>O solution and store in a 25% HNO<sub>3</sub>/DI H<sub>2</sub>O solution.

4.3.5.13 Fill each sample flask with a solution of 5% ultrapure HNO<sub>3</sub>/DI H<sub>2</sub>O spiked with 25 ppb of an internal standard (such as indium) up to the graduation mark. Allow the samples to digest in the solution in the flasks for a minimum of one hour. (See Note 7.)

4.4 *Water* — This procedure is for the determination of moisture in gas phase chlorine using a continuous flow electrolysis of water in a phosphorous pentoxide (P<sub>2</sub>O<sub>5</sub>) cell. (See Notes 2 and 8.)

4.4.1 *Detection Limit* — 1 ppm (vol/vol).

4.4.2 *Flow Rate* — Set the sample flow rate and pressure in accordance with the instrument manufacturer's instructions.

**4.4.3 Calibration Standards** — Construct a calibration curve which contains at least two points covering the range of interest.

#### 4.4.4 Operating Procedure

**4.4.4.1** Leak check the entire system using helium and a helium leak detector prior to use.

**4.4.4.2** Pre-purge through the regulator/cross-purge assembly with a dry gas of known moisture content until the moisture content is measured below 1 ppm (vol/vol).

**4.4.4.3** Direct samples of two standards, independently verified with a dewpoint/frostpoint hygrometer, spanning the range of moisture content of interest to the analyzer. After a stable reading is obtained, record the instrument's response to each standard.

**4.4.4.4** Obtain a representative sample of the gas to be analyzed and direct it to the unit as with the standards. After a stable reading is obtained, record the instrument's response.

**4.4.4.5** Construct a calibration curve from the standard data and determine the moisture content in the sample gas. The result may not exceed the specification in Section 2 of this standard.

#### 4.5 Notes

NOTE 1: Sample system should be constructed entirely of stainless steel or other suitable material due to the corrosive nature of the product.

NOTE 2: Sample must be appropriately vented for health and safety of operating personnel.

NOTE 3: Individual standards are required for accuracy and identification by retention time.

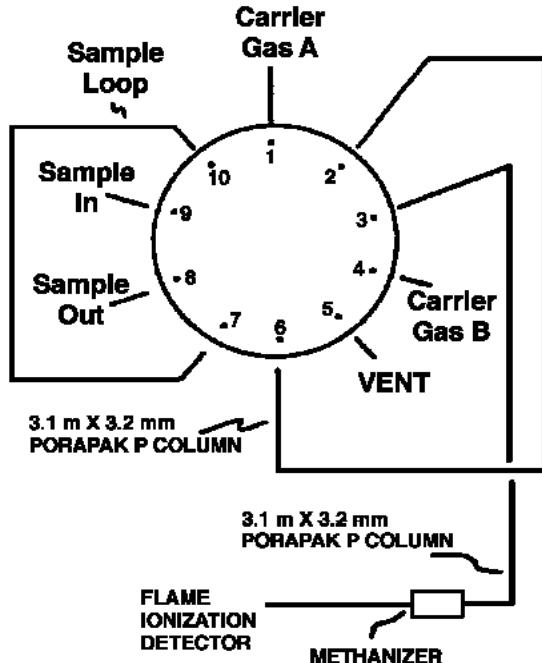
NOTE 4: Other accepted instrumental techniques are also appropriate for this analysis. In addition, operating procedures for ICP-MS instruments vary, depending on the manufacturer. In all cases, refer to individual instrument vendor instructions.

NOTE 5: All sampling flasks are leached with a 25% HNO<sub>3</sub>/H<sub>2</sub>O solution for at least 24 hours, rinsed thoroughly with DI H<sub>2</sub>O, and filled with DI H<sub>2</sub>O for at least 24 hours prior to use. On the day of sampling, flasks are rinsed thoroughly with DI H<sub>2</sub>O and dried with N<sub>2</sub> prior to system setup.

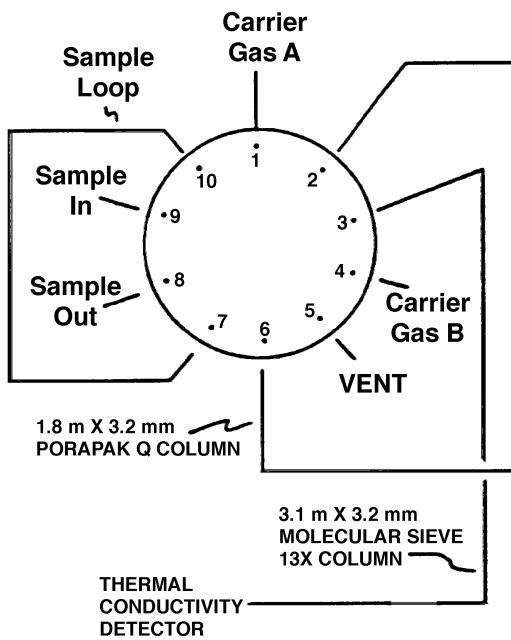
NOTE 6: The tubing and Fluorocarbon valves are soaked in a 25% HNO<sub>3</sub>/DI H<sub>2</sub>O solution prior to use (either apart or pre-assembled). The tubing and valves are rinsed thoroughly with DI H<sub>2</sub>O and dried with high-purity N<sub>2</sub> prior to system setup.

NOTE 7: A different digestion solution may be used, depending on possible interferences with a given analysis technique.

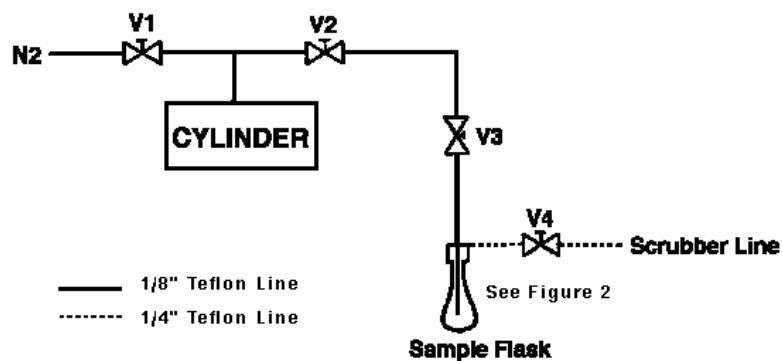
NOTE 8: All wetted surfaces, including P<sub>2</sub>O<sub>5</sub> hygrometer and sample system, are to be of 316 stainless steel or other suitable material.



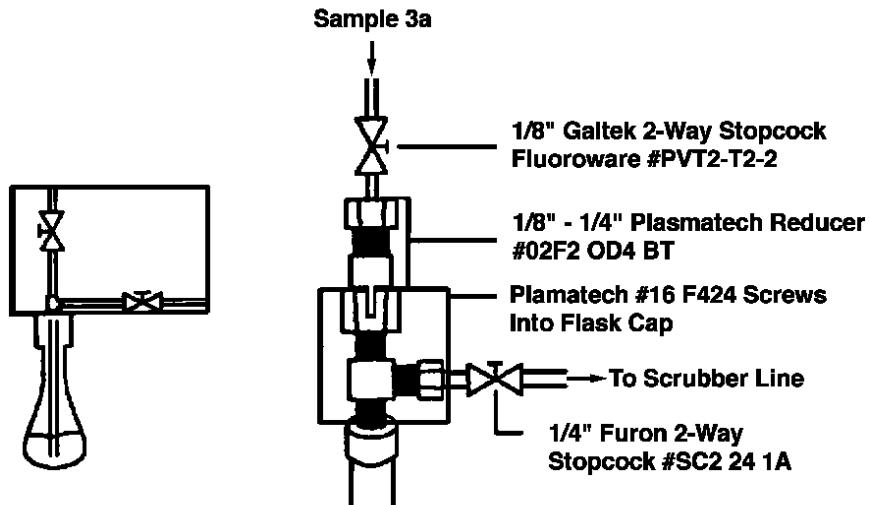
**Figure 1**  
**Carbon Monoxide, Carbon Dioxide, and Hydrocarbons Determination**



**Figure 2**  
Oxygen and Nitrogen Determination



**Figure 3**  
Metals Setup (Liquid Phase Analysis)



**Figure 4**

**NOTICE:** This specification does not purport to address safety issues, if any, associated with its use. It is the responsibility of the user of this specification to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. SEMI makes no warranties or representations as to the suitability of the specification set forth herein for any particular application. The determination of the suitability of the specification is solely the responsibility of the user. Users are cautioned to refer to manufacturer's instructions, product labels, product data sheets, and other relevant literature respecting any materials or equipment mentioned herein. This specification are subject to change without notice.

The user's attention is called to the possibility that compliance with this specification may require use of copyrighted material or of an invention covered by patent rights. By publication of this specification, SEMI takes no position respecting the validity of any patent rights or copyrights asserted in connection with any item mentioned in this specification. Users of this specification are expressly advised that determination of any such patent rights or copyrights, and the risk of infringement of such rights, are entirely their own responsibility.

# SEMI C3.56-0600

## SPECIFICATION FOR DIBORANE MIXTURES

This specification was technically approved by the Global Gases Committee and is the direct responsibility of the European Gases Committee. Current edition approved by the European Regional Standards Committee on April 4, 2000. Initially available at [www.semi.org](http://www.semi.org) May 2000; to be published June 2000.

### 1 Purpose

1.1 To define the specification and analytical methods and validate the specifications for diborane mixtures.

### 2 Scope

2.1 Diborane is not used as a pure gas but as a mixture with balance gases of N<sub>2</sub>, H<sub>2</sub>, Ar, He, or SiH<sub>4</sub>.

2.2 The quality of the mixture is affected by a number of factors which include:

- the purity of the gases used for mixture preparation;
- component filling precision;
- the cylinder preparation process and *in-situ* reactions of diborane with the internal surface of the cylinder.

2.2.1 Furthermore, the elapsed time after filling is important due to the chemical instability, and hence decomposition, of the diborane (see Appendix 1).

2.2.2 All component gases shall adhere to the appropriate SEMI specification, if available.

2.3 The quality of the final mixture can be checked after manufacturing by analyzing each cylinder for the concentration of diborane and for key impurities (tracers), namely H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>.

2.4 This specification does not purport to address safety issues, if any, associated with its use. It is the responsibility of the users of this specification to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

### 3 Referenced Standards

#### 3.1 DIN Standard<sup>1</sup>

DIN 50457-1

NOTE 1: As listed or revised, all documents cited shall be the latest publications of adopted standards.

### 4 Specifications

#### 4.1 Mixing Tolerances

Concentration of Diborane	Preparation Tolerance Level
10–999 ppm	± 20%
0.1–10%	± 5%

#### 4.2 Analytical precision: Determination of Diborane Content

Concentration of Diborane	Analytical Precision
10–99 ppm	± 3%
100–999 ppm	± 2%
0.1–10%	± 2%

N.B. Analytical precision is based on at least 6 replicate determinations

#### 4.3 Impurities

4.3.1 In the final mixture the concentration of impurities should fulfill the following condition:

$$c_i(\text{mix}) = \left[ \frac{x_{(\text{diborane})}}{100} \bullet c_i(\text{diborane}) \right] + \left[ \frac{x_{(\text{main})}}{100} \bullet c_i(\text{main}) \right]$$

c<sub>i</sub>(mix) — concentration of impurity i in the mixture (ppm)

c<sub>i</sub>(diborane) — maximum concentration of impurity i in diborane (ppm)

c<sub>i</sub>(main) — maximum concentration of impurity i in the balance gas (ppm)

x<sub>(diborane)</sub> — concentration of diborane in the mixture (%)

x<sub>(main)</sub> — concentration of balance gas in the mixture (%)

### 5 Analytical Procedure for the Determination of Diborane Concentration

NOTE 2: This procedure is for the determination of the diborane content using a Fourier Transform Infrared analyzer.

5.1 Detection limit — 2 ppm (mole/mole)

1 Deutsches Institut für Normung e.V., BeuthVerlag GmbH,  
burggrafenstrasse 4-10, D10787 Berlin, Germany, [www.din.de](http://www.din.de)

## 5.2 Instrument parameters

### 5.2.1 Cell path length

5.2.1.1 10 cm (mixtures 100 ppm to 10%)

5.2.1.2 10 m (mixtures up to 100 ppm)

Wavenumber — 2444–2739 cm<sup>-1</sup>

Resolution — 4 cm<sup>-1</sup>

### 5.2.2 Sample Flow

5.2.2.1 20 l/h at 10 cm path length

5.2.2.2 40 l/h at 10 m path length

### 5.3 Calibration standard — diborane in hydrogen

NOTE 3: Depending on the concentration of diborane and the storage temperature the standard can be unstable (Section 5). It is recommended to use an appropriate standard with a diborane concentration as low as possible and to store it at low temperature. If there are doubts about the stability of the standard the diborane concentration can be verified by wet chemical methods. (See DIN 50457-1.)

## 5.4 Operating Procedures

5.4.1 Purge the sampling system leading to the cell and the cell with dry nitrogen for 15 minutes and until a zero absorbance is obtained between 2444–2739 cm<sup>-1</sup>. Then purge the cell with the calibration standard and record the absorption of diborane. When a steady absorbance reading is obtained, after approximately 5–10 minutes, the true concentration of the standard shall be recorded. Record the pressure in the gas cell using a calibrated pressure-measuring device.

5.4.2 To determine the concentration of diborane in the mixture set the sample flow through the cell following the same procedures as detailed above. Record the absorption at the same wave number as the calibration standard. Ensure that gas cell pressures are equal during calibration and the determination. Calculate the concentration of diborane. The result must conform to the specification in Section 4 of this standard.

## APPENDIX 1

### STABILITY OF DIBORANE MIXTURES (FOR INFORMATION ONLY)

NOTE: The material in this appendix is an official part of SEMI C3.56 and was approved by full letter ballot procedures on April 4, 2000 by the European Regional Standards Committee.

A1-1 The stability of diborane mixtures in N<sub>2</sub>, Ar, or He depends on the concentration of diborane and on the storage temperature. At ambient temperature best stability is found for mixtures of diborane in hydrogen. No difference in stability could be found for different cylinder materials (steel, stainless steel, aluminum).

A1-2 The following values were measured for different concentrations of diborane at two different storage temperatures:

Storage Temperature	Diborane Concentration (%) in Nitrogen after				
	2	17	45	100	160 Days
8 °C	0.549	0.547	0.547	0.543	0.542
22 °C	0.549	0.544	0.539	0.530	0.526
8 °C	5.05	4.91	4.87	4.85	4.78
22 °C	5.05	4.92	4.83	4.72	4.49
8 °C	10.51	10.45	10.43	10.19	10.00
22 °C	10.59	10.30	10.08	9.44	8.85

A1-3 Based on these results it is recommended to keep mixtures at low temperature.

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## SEMI C3.34-1102

# SPECIFICATION FOR DISILANE ( $\text{Si}_2\text{H}_6$ ) IN CYLINDERS, 97% QUALITY

This specification was technically approved by the Global Gases Committee and is the direct responsibility of the North American Gases Committee. Current edition approved by the North American Regional Standards Committee on August 29, 2002. Initially available at [www.semi.org](http://www.semi.org) September 2002; to be published November 2002. Originally published in 1989; previously published in 1992.

## 1 Purpose

1.1 The purpose of this document is to provide a specification for Disilane ( $\text{Si}_2\text{H}_6$ ) used in the semiconductor industry.

## 2 Scope

2.1 This document covers requirements for Disilane ( $\text{Si}_2\text{H}_6$ ) used in the semiconductor industry.

2.2 If analytical methods are not complete, the requirements are presented as a guideline.

2.3 This standard does not purport to address safety issues, if any, associated with its use. It is the responsibility of the user of these standards to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

## 3 Description

3.1 Disilane is a pyrophoric, highly flammable, noncorrosive, colorless gas. It is toxic and a powerful irritant.

## 4 Referenced Standards

### 4.1 SEMI Standards

SEMI C1 — Specifications for Reagents

SEMI C3 — Specifications for Gases

### 4.2 Other References

R.J. Bogaert, R.E. Rocheleau and B.N. Baron "Gas Chromatographic Determination of Silanes" J. of Chrom. Science Vol. 24, March 86.

NOTE 1: As listed or revised, all documents cited shall be the latest publications of adopted standards.

## 5 Terminology

5.1 Terminology appropriate to this standard is defined in SEMI C3.

## 6 Specifications

QUALITY: 97%

<i>Impurities</i>	<i>Maximum Acceptable Level (ppm)*</i>
Argon (Ar) + Oxygen ( $\text{O}_2$ )	1
Carbon dioxide ( $\text{CO}_2$ )	1
Carbon monoxide (CO)	1
Chlorosilanes (Total hydrolyzable chlorides, reported as $\text{Cl}^-$ )	5
Chromium (Cr)	**
Disiloxane ( $\text{H}_3\text{SiOSiH}_3$ )	5
Hydrogen ( $\text{H}_2$ )	500
Iron (Fe)	**
Monoethylsilane	50
Nickel (Ni)	**
Nitrogen ( $\text{N}_2$ )	10
Silane ( $\text{SiH}_4$ )	2.5%
Total methane, ethane, propane	10
Total trisilane and tetrasilane	500
Water ( $\text{H}_2\text{O}$ )	1
TOTAL SPECIFIED IMPURITIES (excluding chloride, chromium, iron and nickel)	2.6082%

\* An analysis of significant figures has not been considered. The number of significant figures will be based on analytical accuracy and the precision of the provided procedure.

\*\* To be determined between supplier and user.

NOTE 2: This specification applies to the gas phase of the cylinder as received.

## 7 Physical Constants (for information only)

	<i>Metric Units</i>	<i>US Units</i>
Molecular weight	62.22	62.22
Boiling point at 1 atm	-14.8°C	5.4°F
Freezing point	-132.5°C	-206.5°F
Vapor density (air = 1)	2.38	2.38

## 8 Analytical Procedures

8.1 *Carbon Monoxide and Carbon Dioxide* — This procedure is for the determination of carbon monoxide and carbon dioxide in disilane using a gas

chromatograph with a methanizer and a flame ionization detector. (See Figure 1, Notes 3 and 4.)

**NOTE 3:** An optional temperature ramping during vent will shorten the analysis time.

**NOTE 4:** Carrier gases should contain less than 0.1 ppm carbon monoxide and less than 0.1 ppm carbon dioxide.

**8.1.1 Detection Limit** — 0.1 ppm for each impurity.

#### **8.1.2 Instrument Parameters**

**8.1.2.1 Column:** Porapak QS 3 m (10 ft) by 1.6 mm (1/16 in) ID ss or equivalent.

**8.1.2.2 Carrier Flow:** 30 mL/min helium.

**8.1.2.3 Sample Volume:** 1.5 mL.

**8.1.2.4 Support Gases:** As specified by the instrument manufacturer.

**Hydrogen:** 20–30 mL per min added to the carrier gas between the column outlet and the methanizer inlet.

**Air:** 500 mL/min.

**8.1.2.5 Temperatures:**

Detector	110°C
Injector	60°C
Oven	60°C
Methanizer	370°–400°C

**8.1.3 Calibration Standards** — 1–10 ppm carbon monoxide, 1–10 ppm carbon dioxide, balance helium.

#### **8.1.4 Operating Procedure**

**8.1.4.1** Inject the calibration standard into the column using a gas sampling valve. Record the retention times and peak areas. The order of elution is carbon monoxide, carbon dioxide. Repeat this operation.

**8.1.4.2** Inject the sample to be tested in same manner as the calibration standard and vent after elution of carbon dioxide is completed, in case any silane is present. Record the retention times and peak areas.

**8.1.4.3** Repeat Section 8.1.4.1.

**8.1.4.4** Compare the average peak areas of the calibration standard to that of the disilane sample being tested. Calculate the concentrations of carbon monoxide and carbon dioxide using the formula below. The results may not exceed the specifications in Section 7 of this standard.

$$\frac{\text{Sample Peak Area}}{\text{Standard Peak Area}} \times \frac{\text{Concentration of Standard}}{\text{Concentration of Sample}} = \frac{\text{Concentration of Sample}}{\text{Concentration of Standard}}$$

**8.2 Methane, Ethane, Propane, and Silane** — This procedure is for the determination of hydrocarbons

(methane, ethane, and propane) and silane in disilane using a gas chromatograph with a thermal conductivity detector.

**8.2.1 Detection Limit** — 3 ppm for each impurity.

#### **8.2.2 Instrument Parameters**

**8.2.2.1 Column:** Porapak QS 3 m (10 ft) by 1.6 mm (1/16 in) ID ss or equivalent.

**8.2.2.2 Carrier Flow:** 25 mL/min helium.

**8.2.2.3 Sample Volume:** 1 mL.

**8.2.2.4 Temperatures:**

Detector	80°C
Injector	60°C
Oven	60°C

**8.2.3 Calibration Standards** — 10–50 ppm methane, 5–10 ppm ethane, 5–10 ppm propane, 0.1–1% silane, balance helium.

#### **8.2.4 Operating Procedure**

**8.2.4.1** Inject the calibration standard into the column using a gas sampling valve. Record the retention times and peak areas. Order of elution is methane, silane, ethane, propane.

**8.2.4.2** Inject the sample to be tested in same manner as the calibration standard. Record the retention times and peak areas.

**8.2.4.3** Repeat Section 8.2.4.1.

**8.2.4.4** Compare the average peak areas of the calibration standard to that of the disilane sample being tested. Calculate the concentrations of methane, silane, ethane, and propane, using the formula below. The results may not exceed the specification in Section 7 of this standard.

$$\frac{\text{Sample Peak Area}}{\text{Standard Peak Area}} \times \frac{\text{Concentration of Standard}}{\text{Concentration of Sample}} = \frac{\text{Concentration of Sample}}{\text{Concentration of Standard}}$$

**8.3 Hydrogen, Nitrogen, and Argon** — This procedure is for the determination hydrogen, nitrogen, and argon in disilane using a gas chromatograph with a helium ionization detector.

**8.3.1 Detection Limit** — 100 ppb for hydrogen and argon, 500 ppb for nitrogen.

### 8.3.2 Instrument Parameters

#### 8.3.2.1 Columns:

Column 1:	Porapak QS 2.5 m (8 ft) by 3.2 mm (1/8 in) OD ss or equivalent.
Column 2:	5A Molecular sieve, 3 m (10 ft) by 3.2 mm OD ss or equivalent.

8.3.2.2 Carrier Flow: 25 mL/min helium.

8.3.2.3 Sample Volume: 3 mL.

8.3.2.4 Temperatures:

Detector	100°C
Injector	30°C
Oven	30°C

8.3.3 Calibration Standards — 1–10 ppm nitrogen, 1–10 ppm argon, 10–100 ppm hydrogen, balance helium.

#### 8.3.4 Operating Procedure

8.3.4.1 Determination of the backflush time: Inject a methane sample (1–1000 ppm, balance helium) using a 10 port gas valve and backflush at different times. Select the backflush time so that the methane peak is split by the backflush.

8.3.4.2 Inject the calibration standard into the column using a gas sampling valve. Backflush at the time determined in Section 8.3.4.1. Record retention times and peak areas. Order of elution is hydrogen, argon, nitrogen.

8.3.4.3 Inject the sample to be tested in same manner as the calibration standard. Backflush at the time determined in Section 8.3.4.1. Record the retention times and peak areas.

8.3.4.4 Repeat Section 8.3.4.2.

8.3.4.5 Compare the average peak areas of the calibration standard to that of the disilane sample being tested. Calculate the concentrations of hydrogen, nitrogen and argon using the formula below. The results may not exceed the specifications in Section 7 of this standard.

$$\frac{\text{Sample Peak Area}}{\text{Standard Peak Area}} \times \frac{\text{Concentration of Standard}}{\text{Concentration of Sample}} = \text{Concentration of Sample}$$

8.4 Disiloxane, Monoethylsilane, Trisilane, and Tetrosilanes — This procedure is for the determination of disiloxane, monoethylsilane, trisilane, and tetrosilanes in disilane using a gas chromatograph with a thermal conductivity detector.

8.4.1 Detection Limits — 5 ppm for disiloxane and 10 ppm for each of the other impurities.

#### 8.4.2 Instrument Parameters

8.4.2.1 Column: 30% DC 200 on Chromosorb P, 80/100 mesh, 10 m (33 ft) by 3.2 mm (1/8 in) ss or equivalent.

8.4.2.2 Carrier Flow: 20 mL/min helium.

8.4.2.3 Sample Volume: 1 mL.

8.4.2.4 Temperatures:

Detector	120°C
Injector	60°C
Oven	60°C for 25 min then 10°C/min to 120°C

8.4.3 Calibration Standard — 100 ppm each of trisilane, i-tetrasilane, and n-tetrasilane, and 10 ppm each disiloxane and monoethylsilane in helium. If one or several components cannot be obtained, use a 100 ppm monosilane standard and apply the following correction factors using the formula below (See Reference 1).

Trisilane CF = 0.54

i-tetrasilane CF = 0.42

n-tetrasilane CF = 0.41

Correction factors for disiloxane and monoethylsilane are not available. Use the same as disilane CF = 0.69. concentration of impurity = calculated concentration, using silane standard,  $\times$  CF.

#### 8.4.4 Operating Procedure

8.4.4.1 Inject the calibration standard into the column using a gas sampling valve. Record retention times and peak areas. Order of elution is disiloxane, disilane, monoethylsilane, trisilane, i-tetrasilane, and n-tetrasilane.

8.4.4.2 Inject the sample to be tested in same manner as calibration standard. Record the retention times and peak areas.

8.4.4.3 Repeat Section 8.4.4.1.

8.4.4.4 Compare the average peak areas of the calibration standard to that of the disilane sample being tested. Calculate the concentrations of disiloxane, disilane, monoethylsilane, trisilane, i-tetrasilane, and n-tetrasilane, using the formula below. If necessary, correct the results using the specified correction factors in Section 8.4.3. The results may not exceed the specifications in Section 7 of this standard.

$$\frac{\text{Sample Peak Area}}{\text{Standard Peak Area}} \times \frac{\text{Concentration of Standard}}{\text{Concentration of Sample}} = \frac{\text{Concentration of Sample}}{\text{Concentration of Sample}}$$

**8.5 Water** — This procedure is for the determination of moisture in disilane using a continuous flow electrolysis of water in a phosphorus pentoxide ( $P_2O_5$ ) cell.

NOTE 5: Direct gases for moisture measurement to the analyzer with stainless steel lines which have been purged.

**8.5.1 Detection Limit** — 1 ppmv

**8.5.2 Flow Requirement** — Set the sample flow rate and pressure in accordance with manufacturer's instructions.

#### **8.5.3 Operating Procedure**

**8.5.3.1** Direct samples of three standards, independently verified with a dewpoint/frostpoint hygrometer, spanning the range of moisture content of interest to the analyzer. After a stable reading is obtained, record the instrument's response to each standard.

**8.5.3.2** Obtain a representative sample of the gas to be analyzed and direct it to the unit as with the standards. After a stable reading is obtained, record the instrument's response.

**8.5.3.3** Construct calibration curve from the standard data and determine the moisture content in sample gas. The result may not exceed the specification in Section 7 of this standard.

**8.6 Total Chlorides** — This procedure is for the determination of total hydrolyzable chlorides in disilane by titration of a hydrolyzed sample of disilane. (See Figure 2.)

**8.6.1 Detection Limit** — 0.5 ppm.

#### **8.6.2 Instrument Parameters**

##### **8.6.2.1 Equipment**

1. Safety purge regulator with proper fittings.
2. Flow meter capable of measuring 0.25 standard liters per minute (0.5 SCF/hour) (Brooks or equivalent).
3. One cylinder of nitrogen with regulator.
4. One ice bath.
5. Three magnetic stirring bars.
6. Two 2000 mL heavy-duty sidearm flasks (Fisher Cat. No. 10-181G or equivalent).
7. One #9 one-hole rubber stopper.
8. One #9 two-hole rubber stopper.
9. Two borosilicate glass tubes with fritted cylinders (Fisher Cat. No. 11.138B or equivalent).

10. One gas washing bottle with fritted cylinder, 125 mL cap. (Fisher Cat. No. 03-040A or equivalent).

11. One buret, 50 mL capacity with PTFE stopcock (Fisher Cat. No. 03-700-22C or equivalent).

12. One buret stand (Fisher Cat. No. 14-688 or equivalent).

13. Miscellaneous clamps, support stands, and rubber hose.

14. Two 250 mL Erlenmeyer flasks.

#### **8.6.3 Reagents**

1. Potassium hydroxide flakes, technical (Fisher Cat. No. P-246 or equivalent).
2. Mercuric nitrate crystal (Fisher Cat. No. M-168 or equivalent).
3. Sodium chloride crystal (Fisher Cat. No. S-271 or equivalent).
4. Diphenyl carbazole (Fisher Cat. No. D-86 or equivalent).
5. Bromophenol blue (Fisher Cat. No. B-392 or equivalent).
6. Nitric acid (Fisher Cat. No. AA-200 or equivalent).
7. Ethanol, denatured (Fisher Cat. No. AA-407 or equivalent).

#### **8.6.4 Operating Procedure**

**8.6.4.1** Fill each 2000 mL sidearm flask with about 1700 mL of 15% potassium hydroxide solution (15 g KOH per each 100 mL water).

**8.6.4.2** Fill the gas washing bottle with about 75 mL of deionized water that has been degassed.

**8.6.4.3** Assemble apparatus as shown in Diagram A and purge entire system with nitrogen for 30 minutes.

**8.6.4.4** Pass 30 liters (approximately one cubic foot) of disilane through the system at a rate of 0.25 liters per minute. Record the volume of the disilane sample.

**8.6.4.5** Stop disilane flow and purge system for 30 minutes.

**8.6.4.6** Remove gas washing bottle from system and transfer contents quantitatively and with the aid of three 25 mL deionized water washings, to a 250 mL Erlenmeyer flask.

**8.6.4.7** Add a few drops of indicator solution (5 g diphenyl carbazole plus 0.5 g bromophenol blue dissolved in 750 mL ethanol, plus 250 mL deionized water).

**8.6.4.8** Add, in a drop-wise fashion, sufficient 0.2N  $HNO_3$  (13 mL conc.  $HNO_3$ , diluted to 1 L in deionized water) in order to just turn the solution to yellow from purple.

8.6.4.9 Titrate with a solution of 5 g. mercuric nitrate  $\text{Hg}(\text{NO}_3)_2$ , (diluted to 1000 mL in deionized water; then 50 mL diluted to 500 mL in deionized water) which has been previously standardized to 5.0 mL of a sodium chloride solution (approximately 165 ng NaCl, accurately weighed, dissolved in 100 mL deionized water).

#### 8.6.5 Calibration

8.6.5.1 Run titration blank consisting of 150 mL deionized water.

8.6.5.2 Calculate the concentration of chloride, using the formula below. The result may not exceed the specification in Section 8 of this standard.

$$\frac{\text{mL sample - mL blank}}{\text{mL standard - mL blank}} \times \frac{\text{wt. of NaCl(g)}}{100.0 \text{ mL}} \times$$

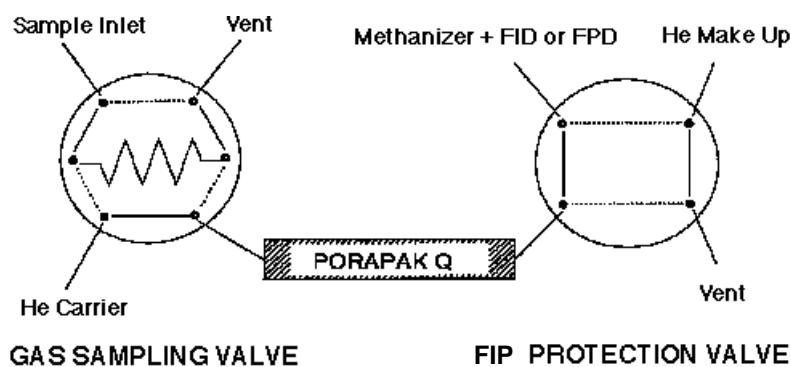
$$\frac{60.66\% \text{ Cl}^-}{100\% \text{ NaCl}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{.005 \text{ L}}{35.453 \text{ g/mole}} \times$$

$$\frac{0.082 \text{ atm L/mole K}}{1 \text{ atm}} \times \frac{294.26 \text{ }^\circ\text{K}}{\text{volume of gas samples}} \times$$

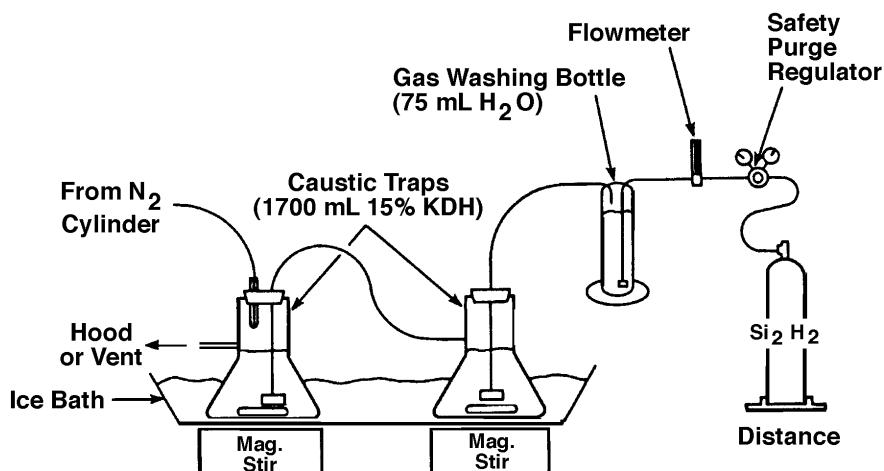
$$1 \times 10^6 \text{ ppm} = \text{ppm Cl}^-$$

8.6.6 Final Calculation — Convert the results from ppm to ppm-wt using the formula below. The result may not exceed the specification in Section 7 of this standard.

$$\text{ppm-wt} = \text{ppm (mole/mole)} \times \frac{35.45}{62.22}$$



**Figure 1**  
**G.C. Configuration**



**Notes:**

1. Bleed nitrogen into system at gently rate.
2. Stirrers should turn at a moderate rate.

**Figure 2**  
**Chloride Scrubbing Apparatus**

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# SEMI C3.20-92 (Reapproved 0999) STANDARD FOR HELIUM (He), IN CYLINDERS, 99.9995% QUALITY

This standard was technically reapproved by the Global Gases Committee and is the direct responsibility of the North American Gases Committee. Current edition approved by the North American Regional Standards Committee on April 15, 1999. Initially available at www.semi.org August 1999; to be published September 1999. Originally published in 1982; previously published in 1992.

## 1 Description

1.1 Helium is a rare gas or cryogenic liquid that is inert, colorless, odorless, and tasteless.

## 2 Specifications

QUALITY: 99.9995%

<i>Impurities</i>	<i>Maximum Acceptable Level (ppm)*</i>
Carbon monoxide and carbon dioxide (CO + CO <sub>2</sub> )	1
Nitrogen (N <sub>2</sub> )	2
Oxygen (O <sub>2</sub> )	0.5
Total Hydrocarbons expressed as Methane (THC)	0.5
Water (H <sub>2</sub> O) (v/v)	0.5
TOTAL SPECIFIED IMPURITIES	4.5

\* An analysis of significant figures has not been considered. The number of significant figures will be based on analytical accuracy and the precision of the provided procedure.

## 3 Physical Constants (for information only)

	<i>Metric Units</i>	<i>US Units</i>
Molecular weight	4.003	4.003
Boiling point at 1 atm	-268.9°C	-452.0°F
Density of gas at 21.1°C (70°F) and 1 atm	0.1656 kg/m <sup>3</sup>	0.01034 lb/ft <sup>3</sup>
Specific gravity of gas at 21.1°C and 1 atm (air = 1)	0.138	0.138
Density of liquid at boiling point	124.9 kg/m <sup>3</sup>	7.798 lb/ft <sup>3</sup>

## 4 Analytical Procedures (See Notes 1, 2)

4.1 *Carbon Monoxide and Carbon Dioxide* — This procedure is for the determination of carbon monoxide and carbon dioxide in helium using a gas chromatograph with a flame ionization detector and methanizer.

4.1.1 *Detection Limit* — 100 ppb (mole/mole).

### 4.1.2 Instrument Parameters

#### 4.1.2.1 Column:

Porapak T or Q, 3 m (9.8 ft) by 3 mm (1/8 in) ss;

or

Chromosorb 102, 2 m (6.6 ft) by 3 mm ss;

or equivalent.

#### 4.1.2.2 Carrier Flow: 30 mL/min helium m.

#### 4.1.2.3 Sample Volume: 0.5 to 2.0 mL.

#### 4.1.2.4 Temperatures:

Detector	280°C
Column Oven	60°C
Methanizer	350°C

4.1.3 *Calibration Standards* — 1-10 ppm (mole/mole) carbon monoxide, 1-10 ppm (mole/mole) carbon dioxide, balance helium.

#### 4.1.4 Operating Procedure

4.1.4.1 Inject the calibration standard into the column using a gas sampling valve. Record the retention times and peak areas. Order of elution is carbon monoxide, carbon dioxide.

4.1.4.2 Inject the sample to be tested in same manner as the calibration standard. Record the retention times and peak areas.

4.1.4.3 Repeat 4.1.4.1.

4.1.4.4 Compare the average peak areas of the calibration standard to that of the helium sample being tested. Calculate the concentrations of carbon monoxide and carbon dioxide, using the formula below. The result may not exceed the specification in Section 2 of this Standard.

$$\frac{\text{Sample Peak Area}}{\text{Standard Peak Area}} \times \frac{\text{Concentration of Standard}}{\text{Concentration of Sample}} = \text{Concentration of Sample}$$

4.2 *Nitrogen* — This procedure is for the determination of nitrogen in helium using a gas chromatograph with a helium ionization detector.

4.2.1 Detection Limit — 500 ppb.

#### 4.2.2 Instrument Parameters

4.2.2.1 Column: 5A molecular sieve, 1.9 m (6 ft) by 3.2 mm (1/8 in) ss, or equivalent.

4.2.2.2 Carrier Flow: 30 mL/min helium.

4.2.2.3 Sample Volume: 3.0 mL.

4.2.2.4 Temperatures:

Detector	125°C
Column Temperature	65°C

4.2.3 Calibration Standard — 5-15 ppm nitrogen in helium.

#### 4.2.4 Operating Procedure

4.2.4.1 Inject the calibration standard into the column using a gas sampling valve. Record the retention time and peak area.

4.2.4.2 Inject the sample to be tested in same manner as the calibration standard. Record the retention time and peak area.

4.2.4.3 Repeat 4.2.4.1.

4.2.4.4 Compare the average peak area of the calibration standard to that of the helium sample being tested. Calculate the concentration of nitrogen, using the formula below. The result may not exceed the specification in Section 2 of this Standard.

$$\frac{\text{Sample Peak Area}}{\text{Standard Peak Area}} \times \frac{\text{Concentration of Standard}}{\text{Concentration of Sample}} = \text{Concentration of Sample}$$

4.3 Oxygen — This procedure is for the determination of oxygen in helium using a continuous flow analyzer using an electrochemical method.

4.3.1 Detection Limit — 100 ppb (mole/mole).

4.3.2 Flow Rate — Set sample flow rates in accordance with the instrument manufacturer's instructions.

4.3.3 Calibration Standard — 1-10 ppm (mole/mole) oxygen in helium or in accordance with the instrument manufacturer's instructions.

#### 4.3.4 Operating Procedure

4.3.4.1 Do not change the initial sample flow setting once established.

4.3.4.2 Introduce helium sample and record oxygen reading. The result may not exceed the specification in Section 2 of this Standard.

4.4 Water — This procedure is for the determination of trace moisture (water) in helium using a continuous flowing piezoelectric hygrometer. (See Note 3.)

4.4.1 Detection Limit — 0.1 ppm (vol / vol) or -90°C (-130°F).

4.4.2 Flow Requirements — Set the sample pressure and flow rate in accordance with the instrument manufacturer's instructions.

4.4.3 Calibration Standards — Construct a calibration curve which contains at least three points covering the range of interest. Verify the standards employed independently by another analytical method.

#### 4.4.4 Operating Procedure

4.4.4.1 Obtain a continuous flow of sample gas from the source using a clean and passivated 316 stainless steel line which has been purged dry after exposure to ambient moisture.

4.4.4.2 After prepurging with a dry gas, allow the sample gas to flow through the sampling system and the piezoelectric hygrometer until a stable reading is obtained. Determine the concentration of moisture by comparing the reading to the calibration curve obtained in 4.4.3. The result may not exceed the specification in Section 2 of this Standard.

4.5 Total Hydrocarbons — This procedure is for the determination of total hydrocarbons in helium using a continuous flow flame ionization detector-equipped total hydrocarbon analyzer. (See Notes 4, 5, 6.)

4.5.1 Detection Limit — 0.1 ppm (mole/mole).

#### 4.5.2 Flow Requirements

4.5.2.1 High purity, hydrocarbon-free (less than 1.0 ppm) hydrogen: 35-40 mL/min or 40% hydrogen in either helium or nitrogen matrix at 75-80 mL/min.

4.5.2.2 Dry, hydrocarbon-free (less than 1.0 ppm) air: 350-400 mL/min.

4.5.2.3 Set sample flow rates in accordance with instrument manufacturer's instructions.

#### 4.5.3 Calibration Standards

4.5.3.1 Helium with known quantity of hydrocarbons at 0.5 ppm level.

4.5.3.2 The span gas not exceeding 5 times the concentration of the specification.

#### 4.5.4 Operating Procedure

4.5.4.1 Do not change the initial flow settings for hydrogen, air and sample once established.

4.5.4.2 Introduce the zero helium with known quantity of hydrocarbons and, using the 0-10 ppm range, set the needle (or output) to read the correct level using the zero adjust knob.

4.5.4.3 Introduce the span gas standard in helium and, using the span adjust knob, set the needle (or output reading) to match the level of hydrocarbons in the span gas.

4.5.4.4 Introduce helium sample into the analyzer and read the quantity of hydrocarbons on the analyzer. The result may not exceed the specification in Section 2 of this Standard.

#### 4.6 Notes

NOTE 1: Introduce the calibration standard as many times as necessary to achieve the desired precision.

NOTE 2: All gases used in the analysis of the sample should contain not more than 10% of the specified value of the component of interest unless otherwise specified.

NOTE 3: The sampling system and hygrometer must be designed to operate under the sample pressure, or the sample pressure must be reduced (by a regulator with a diaphragm of stainless steel or other suitable material) to accommodate the pressure restrictions of the analytical hygrometer.

NOTE 4: The 0-1 range may be used provided that zero and span gas standards in helium with known levels of hydrocarbons between 0-1 ppm are used in the calibration of the analyzer.

NOTE 5: As the flow rate and heat capacity of the matrix gas affect the instrument output, the zero gas matrices must coincide with that of the sample gas.

NOTE 6: The effective response of a flame ionization detector-equipped total hydrocarbon analyzer to different hydrocarbons can vary and must be approximated. However, the response of the most common hydrocarbon impurities in helium can be accurately totaled and compared to methane.

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The user's attention is called to the possibility that compliance with this standard may require use of

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# SEMI C3.37-0701

## SPECIFICATION FOR HEXAFLUOROETHANE (C<sub>2</sub>F<sub>6</sub>), 99.97% QUALITY

This specification was technically approved by the Global Gases Committee and is the direct responsibility of the North American Gases Committee. Current edition approved by the North American Regional Standards Committee on April 30, 2001. Initially available at www.semi.org May 2001; to be published July 2001. Originally published in 1989; previously published in 1993.

### 1 Description

1.1 Hexafluoroethane is one of the most stable of all organic compounds. It is inert, colorless, nonflammable, odorless and tasteless.

### 2 Specifications

QUALITY: 99.97%

Impurities	Maximum Impurities Acceptable (ppm)*
Carbon Dioxide (CO <sub>2</sub> )	1
Carbon Monoxide (CO)	1
Nitrogen (N <sub>2</sub> )	100
Other Halogenated Hydrocarbons (CF <sub>3</sub> Cl, CF <sub>3</sub> H, CF <sub>2</sub> HCl, C <sub>2</sub> F <sub>5</sub> Cl)	50
Oxygen (O <sub>2</sub> )	25
Water (H <sub>2</sub> O) (v/v)	40
TOTAL LISTED IMPURITIES	217

\*An analysis of significant figures has not been considered. The number of significant figures will be based on analytical accuracy and the precision of the provided procedure.

### 3 Chemical Specification

Total Acidity	0.1 ppmw max.
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### 4 Physical Constants (for information only)

	Metric Units	US Units
Molecular weight	138.01	138.01
Boiling point at 1 atm	-78.2°C	-108.8°F
Density of gas at 24°C (75°F) and 1 atm	5.734 kg/m <sup>3</sup>	0.357 lb/ft <sup>3</sup>
Specific gravity of gas at 24°C and 1 atm	4.823	4.823
Density of liquid at -80.0°C	1611 kg/m <sup>3</sup>	100.6 lb/ft <sup>3</sup>

### 5 Analytical Procedures (See Notes 1, 2, 3, and Figure 1)

5.1 Oxygen, Nitrogen, Carbon Monoxide, and Carbon Dioxide — This procedure is for the determination of oxygen, nitrogen, carbon monoxide, and carbon dioxide in hexafluoroethane using a gas chromatograph with an ultrasonic detector.

5.1.1 *Detection Limit* — 0.5 ppm (mol/mol) for each impurity.

5.1.2 *Instrument Parameters*

5.1.2.1 *Columns:*

Column 1:	Haysep D, 100/120 mesh, 4.6 m (15 ft) by 3.2 mm (1/8 in) OD ss, or equivalent.
Column 2:	Porapak QS, 100/120 mesh, 2.1 m (7 ft) by 3.2 mm (1/8 in) OD ss, or equivalent.
Column 3:	Porapak QS, 100/120 mesh, 3.6 m (2 ft) by 3.2 mm (1/8 in) OD ss, or equivalent.
Column 4:	Haysep D, 100/120 mesh, 4.6 m (15 ft) by 3.2 mm (1/8 in) OD ss, or equivalent.
Column 5:	Molecular Sieve 13x, 45/60 menh, 2.1 m (7 ft) by 3.2 mm (1/8 in) OD ss, or equivalent.

5.1.2.2 *Carrier Flow:* 16 mL/min helium

5.1.2.3 *Sample Volume:* 1.0 and 2.0 mL

5.1.2.4 *Temperatures:*

Detector	120°C
Column 1, 2 and 5	50°C
Column 3 and 4	90°C
Valve	90°C

5.1.2.5 *Time Table* — Determine the times for valve switching and signal changes, and enter into the run table.

An example run table follows:

Valve	On	Off
1	0.01	*
2	9.20	*
3	0.01	12.00

\* Valve left on until end of run.

5.1.3 *Calibration Standard* — 1–5 ppm (mol/mol) each carbon dioxide, nitrogen, oxygen and carbon monoxide, balance helium.

5.1.4 *Operating Procedure*

5.1.4.1 Inject a sample of the calibration standard into the column using a gas sampling valve. Record retention times and peak areas. The approximate retention times are: oxygen 11.1 minutes, nitrogen 11.6

minutes, carbon monoxide 14.5 minutes and carbon dioxide 15.9 minutes.

5.1.4.2 Analyze the hexafluoroethane sample to be tested in the same manner as in 5.1.4.1

5.1.4.3 Repeat 5.1.4.1.

5.1.4.4 Calculate the concentration of oxygen, nitrogen, carbon monoxide and carbon dioxide in the sample, using the formula below. The result may not exceed specification in Section 2 of this Standard.

$$\frac{\text{Sample Peak Area}}{\text{Standard Peak Area}} \times \frac{\text{Concentration of Standard}}{\text{Concentration of Sample}} = \frac{\text{Concentration of Sample}}{\text{Concentration of Standard}}$$

5.2 *Halogenated Hydrocarbons* — This procedure is for the determination of halogenated hydrocarbons in hexafluoroethane using a gas chromatograph with a flame ionization detector.

5.2.1 *Detection Limit* — 0.5 ppm (mol/mol).

#### 5.2.2 *Instrument Parameters*

5.2.2.1 Column: 1% SP-1000 on Carbo pak B, 60/80 mesh, 7.3 m (24 ft) by 3.2 mm (1/8 in) OD ss, or equivalent.

5.2.2.2 Carrier Flow: 40 mL/min helium

5.2.2.3 Support Gases: Set the flow rates as specified by the instrument manufacturer.

5.2.2.4 Sample Volume: 2.0 mL

#### 5.2.2.5 Temperatures:

Detector	250°C
Initial Oven	35°C
Pre-Program Hold	7 min
Temperature Rise	10°C/min
Final Oven	150°C

5.2.3 *Calibration Standard* — 5 ppm (mol/mol) each CF<sub>3</sub>H, C<sub>2</sub>F<sub>6</sub>, CF<sub>3</sub>Cl, CF<sub>2</sub>HCl, C<sub>2</sub>F<sub>5</sub>Cl balance helium.

#### 5.2.4 *Operating Procedure*

5.2.4.1 Inject a sample of the calibration standard into the column using a gas sampling valve. Record retention times and peak areas. The order of elution is CF<sub>3</sub>H, C<sub>2</sub>F<sub>6</sub>, CF<sub>3</sub>Cl, CF<sub>2</sub>HCl, C<sub>2</sub>F<sub>5</sub>Cl.

5.2.4.2 Analyze the hexafluoroethane sample to be tested in the same manner as in 5.2.4.1.

5.2.4.3 Repeat 5.2.4.1.

5.2.4.4 Calculate the concentration of each impurity in the sample using the formula below. Total the amounts of chlorofluorocarbons and hydrofluorocarbons. The

result may not exceed the specification in Section 2 of this Standard.

$$\frac{\text{Sample Peak Area}}{\text{Standard Peak Area}} \times \frac{\text{Concentration of Standard}}{\text{Concentration of Sample}} = \frac{\text{Concentration of Sample}}{\text{Concentration of Standard}}$$

5.3 *Water (See Note 4)* — This procedure is for the determination of trace moisture (water) in hexafluoroethane, using a continuous flowing electrolytic hygrometer.

5.3.1 *Detection Limit* — 1.0 ppm (ppmw). This is equivalent to a frostpoint of -76°C (-105°F).

5.3.2 *Sample Pressure and Flow* — Set in accordance with instrument manufacturer's instructions.

5.3.3 *Operation Check* — The instrument should be checked periodically for correct operation. A gas containing a known amount of moisture should be passed through the instrument. Agreement between the hygrometer and the standard should be within their relative accuracies.

#### 5.3.4 *Operating Procedure*

5.3.4.1 Obtain a continuous flow sample of the hexafluoroethane source, using a clean, electropolished or passivated (see Note 5) stainless steel line which has been purged dry after exposure to ambient moisture.

5.3.4.2 After purging with a dry gas, allow the sample gas to flow through the sampling system and hygrometer until a stable reading is obtained. The reading may not exceed specification in Section 2 of this Standard.

#### 5.4 *Notes*

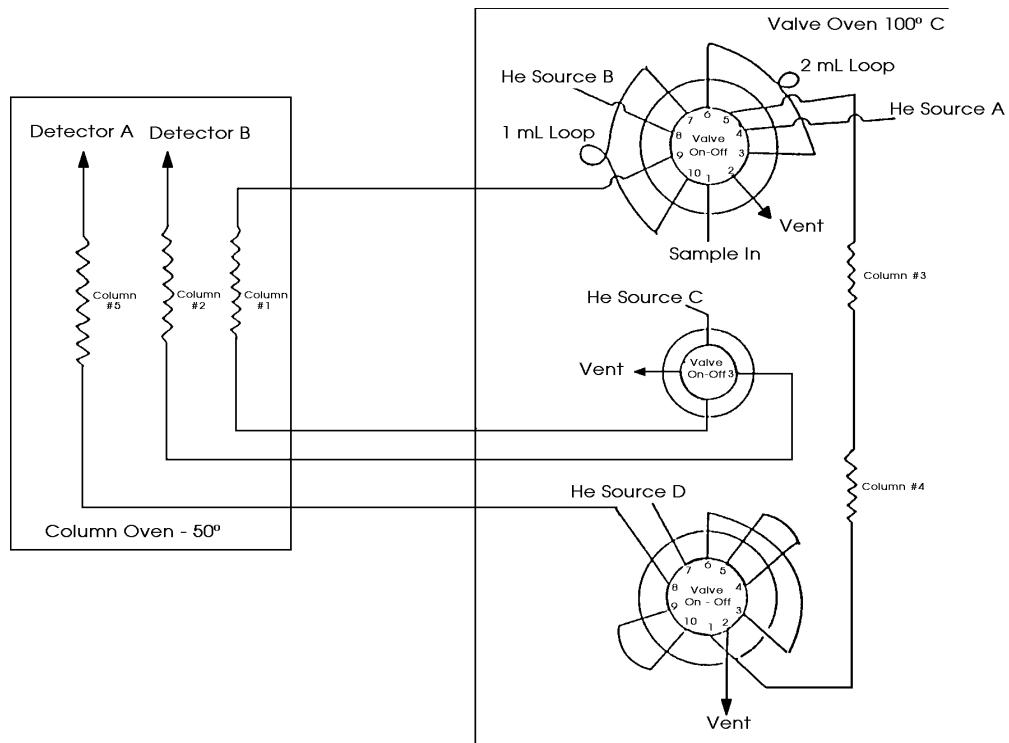
NOTE 1: Introduce the calibration standard as many times as necessary to achieve the desired precision.

NOTE 2: All gases used in the analysis of the sample should not contain more than 10% of the specified value of the component of interest, unless otherwise stated.

NOTE 3: Samples of hexafluoroethane should be equilibrated at no less than 22°C (72°F) for at least 24 hours prior to analysis to ensure that the material, whose critical temperature is 20°C (68°F), is single phase.

NOTE 4: The sampling system and hygrometer must be designed to operate at the sample pressure, or the sample pressure must be reduced (by a regulator with a stainless steel diaphragm) to accommodate the pressure restrictions of the hygrometer.

NOTE 5: A passivation procedure is described in *Metals Handbook*, Eighth Edition, Volume 2, ASM International, Metals Park, Ohio.



**Figure 1**  
**Configuration for the Analysis of O<sub>2</sub>, N<sub>2</sub>O<sub>2</sub> in C<sub>2</sub>F<sub>6</sub>**

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## SEMI C3.47-1101

# SPECIFICATION FOR HYDROGEN BROMIDE (HBr), 99.98% QUALITY

This specification was technically approved by the Global Gases Committee and is the direct responsibility of the North American Gases Committee. Current edition approved by the North American Regional Standards Committee on August 27, 2001. Initially available at [www.semi.org](http://www.semi.org) September 2001; to be published November 2001. Originally published in 1993; previously published in 1995.

## 1 Description

1.1 Hydrogen Bromide is an irritating and corrosive gas with a sharp, penetrating, suffocating odor. It is colorless and nonflammable, but fumes in moist air.

## 2 Specifications

QUALITY: 99.98%, ASSAY (Total Acidity): 98% min

Impurities	Maximum Impurities Acceptable (ppm)*
Carbon Dioxide (CO <sub>2</sub> )	50
Carbon Monoxide (CO)	5
Hydrogen Chloride (HCl)	**
Methane (CH <sub>4</sub> )	15
Oxygen (O <sub>2</sub> ) + Nitrogen (N <sub>2</sub> )	50
Water (H <sub>2</sub> O) (v/v)	5
TOTAL LISTED IMPURITIES (excluding metals)	125

Impurities	Maximum Impurities Acceptable (ppm)*
Iron (Fe)	1 (by weight, vapor phase)

\* An analysis of significant figures has not been considered. The number of significant figures will be based on analytical accuracy and the precision of the provided procedure.

\*\* To be analyzed and reported (typically 500 ppm).

## 3 Physical Constants (for information only)

	Metric Units	U.S. Units
Molecular Weight	80.92	80.92
Boiling Point at 1 atm	-66.7°C	-88.1°F
Density of gas at 70°F (21.1°C) and 1 atm	3.333 g/L	0.208 lb/ft <sup>3</sup>
Specific gravity of gas	2.7	2.7
Critical Pressure	85.16 bar	1234.8 psia
Critical Temperature	90°C	193.6°F

## 4 Analytical Procedures

4.1 *Nitrogen, Oxygen, Carbon Monoxide, Methane, and Carbon Dioxide* — This procedure is for the determination of nitrogen, oxygen + argon, carbon monoxide, methane, and carbon dioxide using a gas chromatograph with a discharge ionization detector.

### 4.1.1 Detection Limits

- N<sub>2</sub> < 10 ppb
- O<sub>2</sub> + Ar < 20 ppb
- CO < 20 ppb
- CH<sub>4</sub> < 10 ppb
- CO<sub>2</sub> < 10 ppb

4.1.2 *Instrument Parameters* — All components are analyzed using two columns and two detectors with a single injection. (See Figure 1.)

#### 4.1.2.1 Columns:

- HayeSep Db 2.0 m (6 ft.) by 3.2 mm (1/8") O.D. by 2.2 mm (0.085") I.D.
- Molecular Sieve 5A 2.0 m (6 ft) by 3.2 mm (1/8") O.D by 2.2 mm (0.085") I.D. ss or equivalent (60/80 mesh)

4.1.2.2 *Carrier Flow* — 40 mL/min He

4.1.2.3 *Sample Volume* — 1.0 mL

4.1.2.4 *Temperatures*:

Detector	100°C
Column 1	40°C
Column 2	100°C

4.1.3 *Calibration Standards* — 5 ppm of each compound of interest including nitrogen, oxygen, carbon monoxide, methane, and carbon dioxide in helium.

#### 4.1.4 Operating Procedures

4.1.4.1 Inject a sample of the calibration standard into the HayeSep column using a gas sample valve. Allow the effluent of HayeSep column to enter the Molecular Sieve column until after CO has eluted. Switch the switching valve to allow the methane and CO<sub>2</sub> to elute directly into detector A while oxygen, nitrogen, and CO separate on the molecular sieve column and elute into detector B. Record retention times and peak areas for all peaks. The order of elution from the HayeSep column to detector A is methane and CO<sub>2</sub>. The order of elution on the molecular sieve column to detector B is oxygen, nitrogen, and CO.

4.1.4.2 Analyze the HBr sample to be tested in the same manner.

4.1.4.3 Analyze the calibration standard again.

4.1.4.4 Compare the average peak area of the calibration standard to that of the HBr sample being tested. Calculate the concentration of impurities, using the formula below. The result may not exceed the specification in Section 2 of this standard.

$$\frac{\text{Sample Peak Area}}{\text{Standard Peak Area}} \times \frac{\text{Concentration of Standard}}{\text{Concentration of Sample}} = \frac{\text{Concentration of Sample}}{\text{Concentration of Standard}}$$

4.2 *Water* — This procedure is for the determination of trace moisture (water) in hydrogen bromide gas using a continuous flowing, cooled surface condensation point hygrometer.

NOTE 1: The National Institute of Standards and Technology (NIST) provides calibration services for the thermometer used in condensation point hygrometers.

NOTE 2: This method is not applicable if other constituents in the gas will condense before the moisture condensation i.e., excessive carbon dioxide and/or oil contamination.

NOTE 3: The sampling system and hygrometer must be designed to operate under the sample pressure, or the sample pressure must be reduced to accommodate the pressure restrictions of the analytical hygrometer using a regulator with a stainless steel diaphragm.

4.2.1 *Detection Limit* — 2.0 ppm.

#### 4.2.2 *Flow Requirements:*

4.2.2.1 Sample flow rate and pressure will be set in accordance with the instrument manufacturer's instructions.

4.2.2.2 Gas must flow past the chilled mirror where optic means are provided to detect the deposit (condensation) and to read the thermometer measuring the temperature of the mirror.

#### 4.2.3 *Calibration*

4.2.3.1 A calibration thermometer designed to indicate temperatures in the -89°C (-121°F) range is required.

4.2.3.2 A calibration curve representing water added to dried hydrogen bromide vs condensation point is required. This can be obtained by preparing a standard of water balance nitrogen and mixing it with dry hydrogen bromide using a dynamic gas blender with mass flow controllers or calibrated flow meters. The hydrogen bromide gas can be dried by passing it over an activated molecular sieve (5A) or magnesium perchlorate.

#### 4.2.4 *Operating Procedures*

4.2.4.1 Obtain a continuous flow of sample gas from the source using a clean stainless steel sampling line

which has been purged dry after exposure to ambient moisture.

4.2.4.2 After prepurging with a dry gas, allow the sample gas to flow through the sampling system and the condensation point hygrometer for one-quarter hour to two hours to allow the entire system to reach equilibrium with regard to moisture content.

4.2.4.3 After equilibrium has been reached, cool the mirror to determine the actual condensation point of the sample. Follow the manufacturer's recommendations to create the temperatures needed.

4.2.4.4 Continue to verify the condensation point for at least 30 minutes after a stable reading has been confirmed.

4.2.4.5 Correct the condensation point reading from the measured pressure to 1 atm of pressure. The result may not exceed the specification in Section 2 of this standard.

4.3 *Iron* — This procedure is for the determination of iron in gaseous hydrogen bromide and analyzed by inductively coupled plasma.

#### 4.3.1 *Sampling Apparatus*

- 3 Teflon diaphragm valves (1/4" FNPT) (Fluoroware 201-10 or equivalent)
- 2 Teflon tees (1/4") (Fluoroware UT4FN-1 or equivalent)
- 50 ft. Teflon tubing (1/4") (Fluoroware AT250-047 or equivalent)
- Teflon flow meter (1/4" FNPT calibrated for HBr flow) (Fluoroware FM-4N-1P or equivalent)
- 8 Teflon connectors (1/4" tube to 1/4" MNPT (Fluoroware C4-CFN-1 or equivalent)
- 9 gas washing bottles (375 mL) (Savillex #507 or equivalent with 501-4-2 cap)
- Tee purge assembly (Matheson 4756-330 or equivalent)
- Manual control valve (Matheson 55A-330 or equivalent)
- Cylinder scale that can measure the mass of the cylinder to  $\pm 1$  g accuracy.

4.3.2 *Water* — 18 megaohm-cm DI water is used for all dilution blanks and washings.

4.3.3 *Reagents* — All reagents are of the highest purity available minimizing background metal contamination.

#### 4.3.4 Sampling Gaseous Hydrogen Bromide

4.3.4.1 Assemble sampling apparatus in laboratory hood for safety.

4.3.4.2 Fill gas washing bottles (scrubbers) with 75 mL 18 megaohm-cm DI water.

4.3.4.3 Start nitrogen purge to remove air from system and to check for leaks.

4.3.4.4 Close V4 and nitrogen purge.

4.3.4.5 Close V2.

4.3.4.6 Open V1 and V3.

4.3.4.7 Open V2 and controlling flow rate at 1 L/min taking care not to over-pressurize system.

4.3.4.8 Continue flow through scrubber train #1 until scale shows that approximately 100 grams of HBr have been purged.

4.3.4.9 Open V4 and close V3. Record the weight of HBr cylinder.

4.3.4.10 Collect 100 grams of HBr in scrubber train #2. Close V1 and record weight of HBr sampled.

4.3.4.11 Open nitrogen purge and purge lines, scrubber train #1 and scrubber train #2, before disconnecting scrubbers.

#### 4.3.5 Sample Preparation

4.3.5.1 For each scrubber train, quantitatively wash with DI water and add to 250 mL volumetric.

4.3.5.2 Wash associated tubing of each scrubber train with DI water and add to the 250 mL volumetric.

4.3.5.3 Make up reagent blank of water from the same lot of DI water used in the sampling.

4.3.6 Calibration — Make calibration standards by serial dilution of standard iron solution which is matrix matched traceable to NIST.

4.3.7 Instrument Parameters — Perform analysis on an inductively coupled plasma spectrometer or equivalent technique employing operating procedures suggested by manufacturer. Correct result to ppm (ppmw) basis on HBr used.

4.4 Chloride Ion — This procedure is for the determination of chloride ion in gaseous hydrogen bromide using ion chromatography.

4.4.1 Detection Limit — 5 ppb wt/vol.

4.4.2 Sample was prepared as in Section 4.3.5. The 250 mL aqueous sample was diluted further 500 to 1, by diluting one milliliter of 250 mL aqueous sample with DI water in a 500 mL volumetric flask.

#### 4.4.3 Instrument Parameters

##### 4.4.3.1 Flow:

- Eluent 10 mM NaOH at 1 cc/min.
- Regenerate 25 mM H<sub>2</sub>SO<sub>4</sub> at 7 psi.

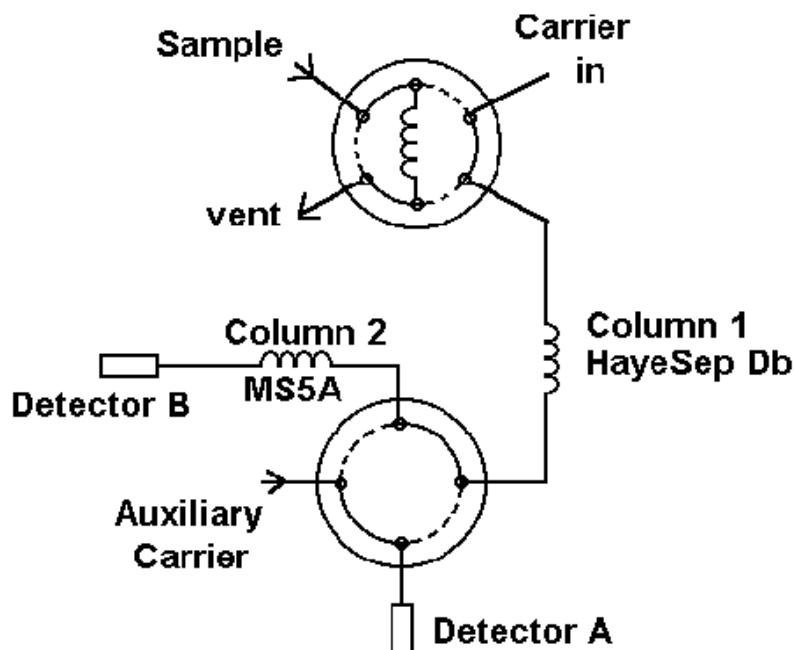
4.4.3.2 Column — AS5A with AG5A guard column

4.4.3.3 Sample Size — 25 microliters.

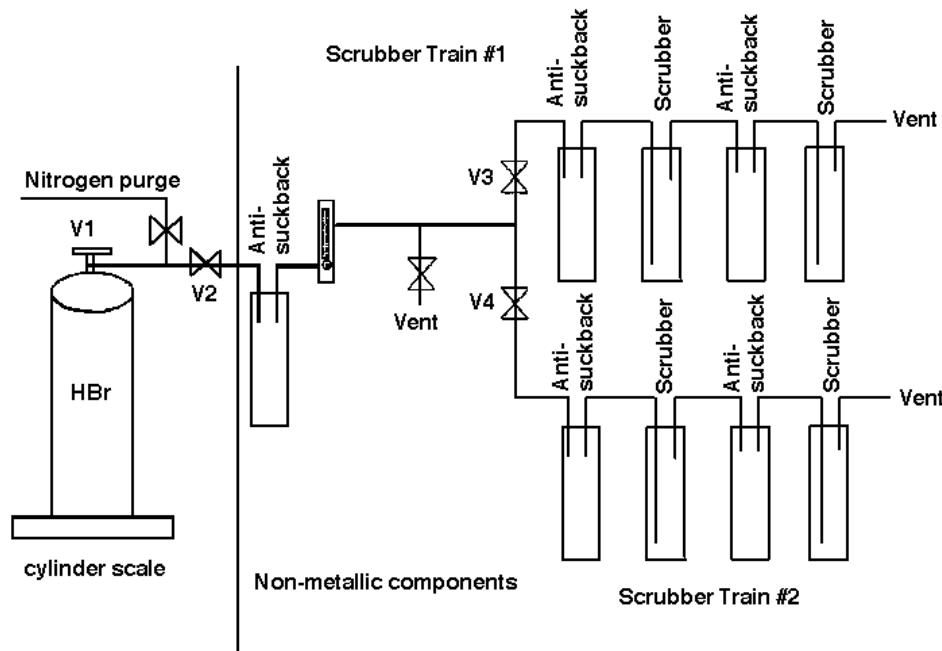
4.4.3.4 Program — Boost eluent concentration to 100 mM NaOH after elution of chloride peak (4.3 min). Continue 100 mM eluent flow for 7 minutes to elute bromide peak. Return to 10 mM NaOH at 12 minutes. Allow to equilibrate for 6 minutes.

4.4.4 Calibration — A multi-point calibration curve is constructed in the range of 10 ppb to 250 ppb (wt/vol) employing standards traceable to NIST.

4.4.5 Use procedures provided by manufacturer of ion chromatograph. Correct results and calculate them to pure HBr on a weight/weight basis.



**Figure 1**  
Column Configuration for the Analysis of CO, CO<sub>2</sub>, and Hydrocarbons



**Figure 2**  
Iron Analysis Sampling Apparatus



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# SEMI C3.35-1101

## SPECIFICATION FOR HYDROGEN CHLORIDE (HCl), 99.997% QUALITY

This specification was technically approved by the Global Gases Committee and is the direct responsibility of the North American Gases Committee. Current edition approved by the North American Regional Standards Committee on August 27, 2001. Initially available at [www.semi.org](http://www.semi.org) September 2001; to be published November 2001. Originally published in 1988; previously published in 1995.

### 1 Description

1.1 Hydrogen chloride is a colorless, pungent, corrosive gas having a suffocating odor. Hydrogen chloride is heavier than air and fumes strongly in moist air. It is very soluble in water and alcohol, and also soluble in ether. While in the cylinder under pressure, hydrogen chloride is in the form of a gas over liquid. As long as liquid is present in the cylinder, the pressure will remain fairly constant. When the liquid phase is exhausted, the cylinder pressure will drop rather rapidly.

### 2 Specifications

QUALITY: 99.997% (See Notes 1, 2, and 3.)

Impurities	Maximum Acceptable Level (ppm)*
Carbon dioxide (CO <sub>2</sub> )	10
Hydrogen (H <sub>2</sub> )	5
Nitrogen (N <sub>2</sub> )	10
Oxygen (O <sub>2</sub> ) + Argon (Ar)	1
Methane and Acetylene	1
Water (H <sub>2</sub> O) (v/v)	1
TOTAL LISTED IMPURITIES (excluding metals)	28

	Maximum Acceptable Level (ppm)*
Iron (Fe)	1 wt. vapor phase

\* An analysis of significant figures has not been considered. The number of significant figures will be based on analytical accuracy and the precision of the procedure provided.

NOTE 1: Due to the reactive nature of the material and the impurities, this product should be used within a period which may be specified by the supplier.

NOTE 2: It is recommended that the user discontinue the use of a cylinder prior to complete consumption of the liquid phase. The content of cylinders should be determined by weight, not pressure.

NOTE 3: This specification applies to the gas phase of the cylinder as received.

### 3 Physical Constants (for information only)

	Metric Units	US Units
Molecular weight	36.465	36.465
Boiling point at 1 atm	-85.°C	-121.°F
Density of gas at 21.1°C (70°F) and 1 atm	1.522 kg/m <sup>3</sup>	0.095 lb/ft <sup>3</sup>
Specific gravity of gas at 0°C (32°F) and 1 atm	1.268	1.268

### 4 Analytical Procedures

4.1 *Carbon Dioxide* — This procedure is for the determination of carbon dioxide in hydrogen chloride using a gas chromatograph with a thermal conductivity detector. A backflush is used to keep the main component from reaching the detector.

4.1.1 *Detection Limit* — 2 ppm.

4.1.2 *Instrument Parameters*

4.1.2.1 Column: Porapak Q, 2.4 m (8 ft) by 6.4 mm (1/4 in) OD ss or equivalent.

4.1.2.2 Carrier Flow: 40 mL/min helium.

4.1.2.3 *Temperatures*:

Detector	50°C
Column Oven	40°C

4.1.2.4 Sample Volume: 10 mL.

4.1.3 *Calibration Standard* — 100 ppm carbon dioxide in helium.

4.1.4 *Operating Procedure*

4.1.4.1 To determine the backflush time, inject the calibration standard, using a gas sampling valve. Record the retention time for carbon dioxide. Choose the backflush time so that the complete carbon dioxide peak is eluted.

4.1.4.2 Inject the calibration standard into the column using a gas sampling valve. Record the retention times and peak areas. Backflush at the time determined in Section 4.1.4.1.

4.1.4.3 Inject the sample to be tested in same manner as the calibration standard. Record the retention times and peak areas. Backflush the main component at the time determined in Section 4.1.4.1.

4.1.4.4 Repeat Section 4.1.4.2.

4.1.4.5 Compare the average peak area of the calibration standard to that of the hydrogen chloride sample being tested. Calculate the concentration of carbon dioxide, using the formula below. The result may not exceed the specification in Section 2 of this Standard.

$$\frac{\text{Sample Peak Area}}{\text{Standard Peak Area}} \times \text{Concentration of Standard} = \text{Concentration of Sample}$$

**4.2 Hydrogen** — This procedure is for the determination of hydrogen in hydrogen chloride using a gas chromatograph with a thermal conductivity detector.

4.2.1 *Detection Limit* — 3 ppm.

4.2.2 *Instrument Parameters*

4.2.2.1 *Columns:*

Column 1:	Ascarite, 0.3 m (1 ft) by 9.6 mm (3/8 in) OD ss or equivalent.
Column 2:	Molecular Sieve 5A, 2.4 m (8 ft) by 6.4 mm (1/4 in) OD ss or equivalent.

4.2.2.2 *Carrier Flow:* 40 mL/min nitrogen.

4.2.2.3 *Temperatures:*

Detector	50°C
Column Oven	40°C

4.2.2.4 *Sample Volume:* 10 mL.

4.2.3 *Calibration Standard* — 50 ppm hydrogen in nitrogen.

4.2.4 *Operating Procedure*

4.2.4.1 Inject the calibration standard using a gas sampling valve. Record the retention time and peak area.

4.2.4.2 Inject the sample to be tested in same manner as the calibration standard. Record the retention time and peak area.

4.2.4.3 Repeat 4.2.4.1.

4.2.4.4 Compare the average peak area of the calibration standard with that of the hydrogen chloride sample being tested. Calculate the concentration of hydrogen using the formula below. The result may not exceed the specification in Section 2 of this standard.

$$\frac{\text{Sample Peak Area}}{\text{Standard Peak Area}} \times \text{Concentration of Standard} = \text{Concentration of Sample}$$

**4.3 Iron** — This procedure is for the determination of iron sampled from gaseous hydrogen chloride and analyzed by inductively coupled plasma.

4.3.1 *Sampling Apparatus*

- 3 Teflon diaphragm valves (1/4" FNPT) (Fluoroware 201-10 or equivalent).
- 2 Teflon tees (1/4") (Fluoroware UT4FN-1 or equivalent).
- 50 ft. Teflon tubing (1/4") (Fluoroware AT250-047 or equivalent).
- Teflon flow meter (1/4" FNPT calibrated for HCl flow) (Fluoroware FM-4N-1P or equivalent).
- 8 Teflon connectors (1/4" tube to 1/4" MNPT) (Fluoroware C4-CFN-1 or equivalent).
- 9 gas washing bottles (375 mL) (Savillex #507 or equivalent with 501-4-2 cap).
- Tee purge assembly (Matheson 4756-330 or equivalent).
- Manual control valve (Matheson 55A-330 or equivalent).
- Cylinder scale that can measure the mass of the cylinder to  $\pm 1$  g accuracy.

**4.3.2 Water** — 18 megohm-cm DI water is used for all dilution blanks and washings.

**4.3.3 Reagents** — All reagents are of the highest purity available minimizing background metal contamination.

4.3.4 *Sampling Gaseous Hydrogen Chloride*

4.3.4.1 Assemble entire sampling apparatus (see Figure 1) in laboratory hood for safety.

4.3.4.2 Fill gas washing bottles (scrubbers) with 75 mL 18 mega-ohm DI water.

4.3.4.3 Start nitrogen purge to remove air from system and to check for leaks.

4.3.4.4 Close V4 and close nitrogen purge.

4.3.4.5 Close V2.

4.3.4.6 Open V1 and V3.

4.3.4.7 Open V2, and, controlling flow rate at 1 L/min., take care not to over-pressurize system.

4.3.4.8 Continue flow through scrubber train #1 until scale shows that approximately 100 grams of HCl have been purged.

4.3.4.9 Open V4 and close V3. Record the weight of HCl cylinder.

4.3.4.10 Collect 100 grams of HCl in scrubber train #2. Close V1 and record weight of HCl sampled.

4.3.4.11 Open nitrogen purge and purge lines, scrubber train #1 and scrubber train #2, before disconnecting scrubbers.

#### 4.3.5 Sample Preparation

4.3.5.1 For each scrubber train, quantitatively wash both scrubbers with DI water and add to 250 mL volumetric flask.

4.3.5.2 Wash associated tubing of each scrubber train with DI water and add to 250 mL volumetric flask.

4.3.5.3 Make up reagent blank of water from the same lot of DI water used in the sampling.

4.3.6 Calibration — Make calibration standards by serial dilution of standard iron solution traceable to NIST.

4.3.7 Instrument Parameters — Perform analysis on an inductively coupled plasma spectrometer employing operating procedures suggested by manufacturer. Correct result to ppm (wt/wt) basis on HCl used.

4.4 Nitrogen — This procedure is for the determination of nitrogen in hydrogen chloride using a gas chromatograph with a thermal conductivity detector.

4.4.1 Detection Limit — 1 ppm.

#### 4.4.2 Instrument Parameters

##### 4.4.2.1 Columns:

Column 1:	Ascarite, 0.3 m (1 ft) by 9.6 mm (3/8 in) OD ss or equivalent.
Column 2:	Molecular Sieve 5A, 2.4 m (8 ft) by 6.4 mm (1/4 in) OD ss or equivalent

4.4.2.2 Carrier Flow: 40 mL/min helium.

##### 4.4.2.3 Temperatures:

Detector	50°C
Column Oven	40°C

4.4.2.4 Sample Volume: 10 mL.

4.4.3 Calibration Standard — 100 ppm nitrogen in helium.

#### 4.4.4 Operating Procedure

4.4.4.1 Inject the calibration standard using a gas sampling valve. Record the retention time and peak area.

4.4.4.2 Inject the sample to be tested in same manner as the calibration standard. Record the retention time and peak area.

4.4.4.3 Repeat Section 4.4.4.1.

4.4.4.4 Compare the average peak area of the calibration standard with that of the hydrogen chloride sample being tested. Calculate the concentration of nitrogen, using the formula below. The results may not exceed the specification in Section 2 of this Standard.

4.5 Oxygen + Argon — This procedure is for the determination of oxygen + argon in hydrogen chloride using a gas chromatograph with a thermal conductivity detector.

4.5.1 Detection Limit — 1 ppm. The oxygen and argon elute simultaneously and are therefore quantified as a sum.

#### 4.5.2 Instrument Parameters

##### 4.5.2.1 Columns:

Column 1:	Ascarite, 0.3 m (1 ft) by 9.6 mm (3/8 in) OD or equivalent.
Column 2:	Molecular Sieve 5A, 2.4 m (8 ft) by 6.4 mm (1/4 in) OD ss or equivalent

4.5.2.2 Carrier Flow: 40 mL/min helium.

##### 4.5.2.3 Temperatures

: Detector	50°C
Column Oven	40°C

4.5.2.4 Sample Volume: 10 mL.

4.5.3 Calibration Standard — 1–5 ppm oxygen in helium.

#### 4.5.4 Operating Procedure

4.5.4.1 Inject the calibration standard into the column using a gas sampling valve. Record the retention time and peak area.

4.5.4.2 Inject the sample to be tested in the same manner as the calibration standard. Record the retention times and peak areas.

4.5.4.3 Repeat Section 4.5.4.1.

4.5.4.4 Compare the average peak area of the calibration standard with that of the hydrogen chloride sample being tested. Calculate the total concentration of oxygen + argon, using the formula below. The result may not exceed the specification in Section 2 of this standard.

$$\frac{\text{Sample Peak Area}}{\text{Standard Peak Area}} \times \frac{\text{Concentration of Standard}}{\text{Concentration of Sample}} = \frac{\text{Concentration of Sample}}{\text{Concentration of Standard}}$$

**4.6 Methane and Acetylene** — This procedure is for the determination of methane and acetylene in hydrogen chloride. Samples from gas phase are analyzed by a gas chromatograph with a flame ionization detector. A backflush is used to keep the main component from the detector. (See Figure 2.)

**4.6.1 Detection Limit** — 0.1 ppm for each impurity.

**4.6.2 Instrument Parameters**

**4.6.2.1 Column:**

Alumina-GC, 60-80 mesh, Chromopack, 1.5 m (5 ft) by 2 mm ID (1/8 in OD) ss;

or

Alumina-GC, 60-80 mesh, Chromopack, 2 m (6.7 ft) by 2 mm ID (1/8 in OD) ss;

or equivalent.

**4.6.2.2 Detector Sensitivity:** 0.012 coulombs/gram.

**4.6.2.3 Carrier Flows (1 and 2):** 30 mL/min helium.

**4.6.2.4 Set the following rates as specified by the instrument manufacturer.**

Support Gases:

Hydrogen Flow:	30 mL/min.
Air Flow:	450 mL/min.

**4.6.2.5 Temperatures:**

Detector	200°C
Column Oven	100°C

**4.6.2.6 Sample Volume:** 0.5 mL.

**4.6.2.7 Sample Flow:** 200 mL/min.

**4.6.3 Calibration Standard** — 5 to 10 ppm each methane and acetylene in nitrogen.

**4.6.4 Operating Procedure**

**4.6.4.1 Install switching valve and columns.**

**4.6.4.2 Adjust carrier gas flows:**

Switching valve in injection position

- Set a flow rate of 30 mL/min, with the regulator T1 measured at the FID outlet.

Switching valve in backflush position

- Set a flow rate of 30 mL/min, with the regulator T2 measured at the FID outlet.
- Set a flow rate of 30 mL/min, with the metering valve, measured at the pre-column outlet.

A last adjustment between the injection and backflush position may be carried out by the FID signal. For this, the baseline is recorded in the injection and backflush position. With the regulator T2, the flow rate is changed so far as there is no offset in the baseline while switching.

**4.6.4.3** Adjust hydrogen and air flows and ignite the burner, following the instrument manufacturer's instructions. Allow the system to stabilize for at least 30 minutes.

**4.6.4.4 Determine backflush time** — Inject calibration standard and leave the switching valve in inject position until all components have been eluted. Determine retention times for methane and acetylene. Choose backflush time so that the acetylene peak is completely registered.

**4.6.4.5 Inject the calibration standard.** Backflush at the time determined in Section 4.6.4.4. Record the retention times and peak areas.

**4.6.4.6 Inject the sample to be tested in the same manner as the calibration standard.** Backflush at the time determined in Section 4.6.4.4. Record the retention times and peak areas.

**4.6.4.7 Repeat Section 4.6.4.5.**

**4.6.4.8 Compare the average peak areas of the calibration standard with those of the hydrogen chloride sample being tested.** Calculate the concentration of each impurity, using the formula below. The results may not exceed the specifications in Section 3 of this standard.

$$\frac{\text{Sample Peak Area}}{\text{Standard Peak Area}} \times \frac{\text{Concentration of Standard}}{\text{Concentration of Sample}} = \text{Concentration of Sample}$$

**4.7 Water** — This procedure is for the determination of trace moisture (water) in hydrogen chloride gas using a continuous flowing, cooled-surface condensation point hygrometer.

**4.7.1 Detection Limit** — 1.0 ppm.

**4.7.2 Flow Requirements**

**4.7.2.1 Set the sample flow rate and pressure in accordance with the instrument manufacturer's instructions.**

**4.7.3 Calibration Standards**

**4.7.3.1** A calibration thermometer designed to indicate temperatures in the -89°C (-121°F) range is required.

NOTE 4: The National Institute of Standards and Technology (NIST) provides calibration services for the thermometers used in condensation point hygrometers.

**4.7.3.2** A calibration curve representing water added to dried hydrogen chloride vs. condensation point is

required. This can be obtained by preparing a standard of water balance nitrogen and mixing it with dry hydrogen chloride using a dynamic gas blender with mass flow controllers or calibrated flowmeters. The hydrogen chloride gas can be dried by passing it over activated molecular sieve (5A) or magnesium perchlorate.

NOTE 5: This method is not applicable if other constituents in the gas will condense before the moisture condensation, e.g., carbon dioxide or oil.

#### 4.7.4 Operating Procedure

4.7.4.1 Obtain a continuous flow of sample gas from the source using a clean stainless steel sampling line which has been purged dry after exposure to ambient moisture.

NOTE 6: The sampling system and hygrometer must be designed to operate under the sample pressure, or the sample pressure must be reduced to accommodate the pressure

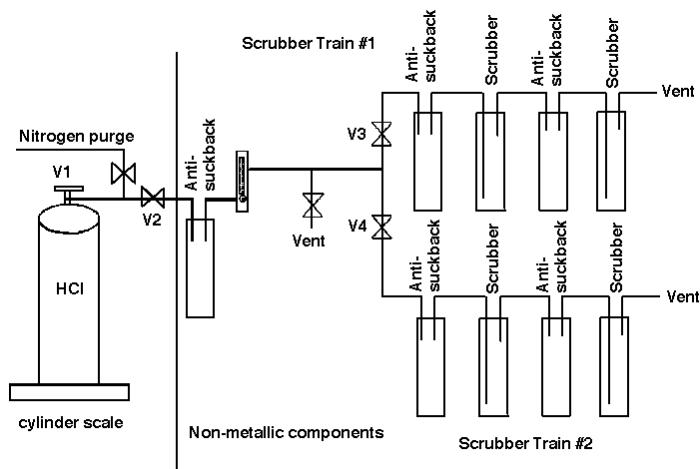
restrictions of the analytical hygrometer using a regulator with a diaphragm of stainless steel or other suitable material.

4.7.4.2 After prepurging with a dry gas, allow the sample gas to flow through the sampling system and the condensation point hygrometer for one-quarter hour to two hours to allow the entire system to reach equilibrium with regards to moisture content.

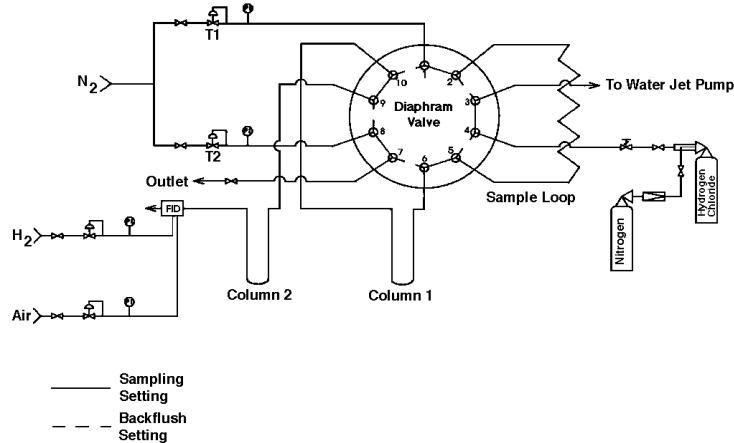
4.7.4.3 After equilibrium has been reached, cool the mirror to determine the actual condensation point of the sample.

4.7.4.4 Continue to verify the condensation point for at least 30 minutes after a stable reading has been confirmed.

4.7.4.5 Correct the condensation point reading from the measured pressure to 1 atm of pressure. The result may not exceed the specification in Section 2 of this standard.



**Figure 1**  
**Metals Analysis Sampling Apparatus Vapor Phase Hydrolysis**



**Figure 2**  
**Column Configuration for the Analysis of Methane, Acetylene**

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# SEMI C3.39-0304

## STANDARD FOR NITROGEN TRIFLUORIDE (NF<sub>3</sub>)

This standard was technically approved by the Global Gases Committee and is the direct responsibility of the North American Gases Committee. Current edition approved by the North American Regional Standards Committee on October 16, 2003. Initially available at [www.semi.org](http://www.semi.org) February 2004; to be published March 2004. Originally published in 1989; last published September 1999.

### 1 Description

1.1 Nitrogen trifluoride is a toxic, odorless, colorless, nonflammable gas. It is a strong oxidizer and supports combustion.

### 2 Specifications

2.1 QUALITY: 99.98%

Impurities	Maximum Acceptable Level (ppm) (see NOTE 1)
Carbon Dioxide (CO <sub>2</sub> )	10
Carbon Monoxide (CO)	10
Carbon Tetrafluoride (CF <sub>4</sub> )	100
Nitrogen (N <sub>2</sub> )	10
Nitrous Oxide (N <sub>2</sub> O)	10
Argon/Oxygen	10
Sulfur Hexafluoride (SF <sub>6</sub> )	10
Water (H <sub>2</sub> O) (v/v)	1
TOTAL IMPURITIES	161 (see NOTE 1)

NOTE 1: An analysis of significant figures has not been considered. The number of significant figures will be based on analytical accuracy and the precision of the provided procedure.

### 3 Chemical Specification

Hydrolyzable Fluorides as HF	1 ppm
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### 4 Physical Constants (for information only)

	Metric Units	US Units
Molecular weight	71.00	71.00
Density of gas at 21.1° C (70° F) and 1 atm	2.94 kg/m <sup>3</sup>	0.1838 lb./ft. <sup>3</sup>

### 5 Analytical Procedures

5.1 *Carbon Tetrafluoride* — This procedure is for the determination of carbon tetrafluoride in nitrogen trifluoride using a gas chromatograph with a thermal conductivity detector. (See Figure 1 and Note 1.)

5.1.1 *Detection Limit* — 1.0 ppm.

#### 5.1.2 Instrument Parameters

5.1.2.1 Column: Super Q (80/100 mesh), 4.9 m (16 ft.) by 1.75 mm (1/16 in.) ID, 3.2 mm (1/8 in.) OD ss or equivalent.

5.1.2.2 Carrier Flow: 19 mL/min helium.

5.1.2.3 Sample Volume: 0.1 mL.

5.1.2.4 Temperatures:

Detector	100° C
Oven	42° C
Gas sampling valve	42° C

5.1.2.5 Valve material: Nitronic-60 or equivalent.

5.1.3 *Calibration Standard* — 100 ppm carbon tetrafluoride, balance helium.

#### 5.1.4 Operating Procedure

5.1.4.1 Inject the calibration standard into the column using a gas sampling valve. Record retention time and peak area.

5.1.4.2 Inject nitrogen trifluoride sample to be tested in the same manner as the calibration standard. Record the retention times and peak areas.

5.1.4.3 Repeat Section 5.1.4.1.

5.1.4.4 Compare the average peak area of the calibration standard to that of the nitrogen trifluoride sample being tested. Calculate the concentration of carbon tetrafluoride, using the formula below. The result may not exceed the specification in Section 2 of this standard.

$$\frac{\text{Sample Peak Area}}{\text{Standard Peak Area}} \times \frac{\text{Concentration of Standard}}{\text{Concentration of Sample}} = \text{Concentration of Sample}$$

5.2 *Carbon Dioxide, Nitrous Oxide, and Sulfur Hexafluoride* — This procedure is for the determination of carbon dioxide, nitrous oxide, and sulfur hexafluoride in nitrogen trifluoride using a gas chromatograph with a thermal conductivity detector. (See Figure 1.)

5.2.1 *Detection Limit* — 1.0 ppm for carbon dioxide, nitrous oxide, and sulfur hexafluoride.

#### 5.2.2 Instrument Parameters

5.2.2.1 Column: Super Q (80/100 mesh), 4.9 m (16 ft.) by 1.75 mm (1/16 in.) ID, 3.2 mm (1/8 in.) OD ss or equivalent.

5.2.2.2 Carrier Flow: 19 mL/min helium.

5.2.2.3 Sample Volume: 1.0 mL.

5.2.2.4 Temperatures:

Detector	100° C
Oven	42° C
Gas sampling valve	42° C

5.2.2.5 Valve Material: Nitronic-60 or equivalent.

5.2.3 *Calibration Standard* — 10 ppm carbon dioxide, 10 ppm nitrous oxide, 10 ppm sulfur hexafluoride, balance helium.

#### 5.2.4 Operating Procedure

5.2.4.1 Inject the calibration standard into the column using a gas sampling valve. Record the retention times and peak areas. The order of elution is carbon dioxide, nitrous oxide, sulfur hexafluoride. (See Figure 1 for valve configuration.)

5.2.4.2 Inject the sample to be tested in the same manner as the calibration standard. Record the retention times and peak areas.

5.2.4.3 Repeat Section 5.4.2.1.

5.2.4.4 Compare the average peak area of the calibration standard to that of the nitrogen trifluoride sample being tested. Calculate the concentration of each impurity using the formula below. The results may not exceed the specifications in Section 2 of this standard.

$$\frac{\text{Sample Peak Area}}{\text{Standard Peak Area}} \times \frac{\text{Concentration of Standard}}{\text{Concentration of Sample}} = \frac{\text{Concentration of Sample}}{\text{Concentration of Standard}}$$

5.3 *Carbon Monoxide* — This procedure is for the determination of carbon monoxide in nitrogen trifluoride using a gas chromatograph with a methanizer and a flame ionization detector. (See Figure 1 and Note 2.)

5.3.1 Detection Limit — 0.1 ppm.

#### 5.3.2 Instrument Parameters

5.3.2.1 Column: Carbosphere (80/100 mesh), 0.74 m (2.4 ft) by 1.75 mm (1/16 in) ID, 3.2 mm (1/8 in) OD ss or equivalent.

5.3.2.2 Carrier Flow: 25 mL/min helium.

5.3.2.3 Sample Volume: 0.5 mL.

5.3.2.4 Fuel gases:

Hydrogen:	Zero grade or better hydrogen at a flow rate of 45 mL/min is added to the carrier gas between the column outlet and the methanizer inlet.
Air:	Zero grade or better air is used at a flow rate of 300 mL/min.

5.3.2.5 Temperatures:

Detector	150° C
Oven	42° C
Methanizer	340° C
Gas sampling valve	70° C

5.3.2.6 Valve Material: Nitronic-60 or equivalent.

5.3.3 *Calibration Standard* — 10 ppm carbon monoxide, balance helium.

#### 5.3.4 Operating Procedure

5.3.4.1 Inject the calibration standard into the column using a gas sampling valve. Record the retention time and peak area.

5.3.4.2 Inject the sample to be tested in the same manner as the calibration standard. Record the retention time and peak area.

5.3.4.3 Repeat Section 5.3.4.1.

5.3.4.4 Compare the average peak area of the calibration standard to that of the nitrogen trifluoride sample being tested. Calculate the concentration of carbon monoxide, using the formula below. The result may not exceed the specification in Section 2 of this standard.

$$\frac{\text{Sample Peak Area}}{\text{Standard Peak Area}} \times \frac{\text{Concentration of Standard}}{\text{Concentration of Sample}} = \frac{\text{Concentration of Sample}}{\text{Concentration of Standard}}$$

5.4 *Oxygen + Argon, Nitrogen* — This procedure is for the determination of oxygen + argon and nitrogen in nitrogen trifluoride using a gas chromatograph with a thermal conductivity detector. (See Figure 2 and Note 1.)

5.4.1 *Detection Limit* — 5 ppm of oxygen + argon and nitrogen.

#### 5.4.2 Instrument Parameters

5.4.2.1 Column: Molecular sieve 13X (80/100 mesh), 6.1 m (20 ft) by 1.75 mm (1/16 in) ID, 3.2 mm (1/8 in) OD ss or equivalent.

5.4.2.2 Carrier Flow: 17 mL/min helium.

5.4.2.3 Sample Volume: 1.0 mL.

5.4.2.4 Temperatures:

Detector	140° C
Filament	240° C
Oven	100° C
Gas sampling valve	60° C

5.4.2.5 Valve Material: Nitronic-60 or equivalent.

5.4.3 *Calibration Standard* — 10 ppm oxygen, 10 ppm nitrogen, balance helium.

#### 5.4.4 Operating Procedure

5.4.4.1 Inject the calibration standard into the column using a gas sampling valve. Record the retention times and peak areas. The order of elution is oxygen + argon (not separated) and nitrogen.

5.4.4.2 Inject the sample to be tested in the same manner as the calibration standard. Record the retention times and peak areas.

5.4.4.3 Repeat Section 5.4.4.1.

5.4.4.4 Compare the average peak area of the calibration standard to that of the nitrogen trifluoride sample being tested. Calculate the concentrations of oxygen + argon and nitrogen, using the formula below. The results may not exceed the specifications in Section 3 of this standard.

$$\frac{\text{Sample Peak Area}}{\text{Standard Peak Area}} \times \frac{\text{Concentration of Standard}}{\text{Concentration of Sample}} = \frac{\text{Concentration of Sample}}{\text{Concentration of Standard}}$$

5.5 Water — This procedure is for the determination of trace moisture (water) in nitrogen trifluoride using a continuous flowing piezoelectric hygrometer. (See Notes 3 and 4.)

5.5.1 Detection Limit — 0.04 ppm (vol/vol) or -95° C (-139° F).

5.5.2 Flow Requirements — Set the sample pressure and flow rate set in accordance with the instrument manufacturer's instructions.

5.5.3 Calibration Standards — Construct a calibration curve which contains at least three points covering the range of interest. Verify the standards employed by another analytical method.

#### 5.5.4 Operating Procedure

5.5.4.1 Obtain a continuous flow of sample gas from the source using a clean and passivated 316 stainless steel line which has been purged dry after exposure to ambient moisture.

5.5.4.2 After prepurging with a dry gas, allow the sample as to flow through the sampling system and the piezoelectric hygrometer until a stable reading is obtained. The result may not exceed the specification in Section 2 of this standard.

5.6 Hydrolyzable Fluorides as HF — This procedure is for the determination of hydrolyzable fluorides in nitrogen trifluoride using fluoride ion selective electrode.

5.6.1 Detection Limit — Detection limits should be checked for any new implementation of a method.

Detection limits below 0.1 ppm have been determined with this method. Detection limits can be improved by increasing the volume of gas sampled.

#### 5.6.2 Equipment

5.6.2.1 mV meter (0.1 mV scale)

5.6.2.2 Reference electrode (single junction type)

5.6.2.3 Fluoride ion selective electrode

5.6.2.4 Magnetic stir bars (PTFE coated)

5.6.2.5 Magnetic stirrer

5.6.2.6 Plastic beakers (See NOTE 5.)

5.6.2.7 PTFE bubblers

5.6.2.8 1000 ml and 100 ml plastic volumetric flasks (see NOTE 5.).

5.6.2.9 0.2 ml and 1 ml plastic volumetric pipettes (see NOTE 5.).

5.6.2.10 Flow controller or flowmeter (0–1000 sccm NF<sub>3</sub>)

#### 5.6.3 Reagents

5.6.3.1 Distilled or deionized water

5.6.3.2 5 N sodium hydroxide

5.6.3.3 0.2 N sodium hydroxide

5.6.3.4 Glacial acetic acid

5.6.3.5 Buffer Solution — To 500 ml distilled or deionized water in a 1000 ml volumetric flask, add 57 ml glacial acetic acid and 58 g of sodium chloride. Adjust the pH to between 5.0–5.5 with 5 M sodium hydroxide. Cool to room temperature. Dilute to one liter with distilled or deionized water.

5.6.4 Calibration Standard — Sodium fluoride standard (10<sup>-3</sup> M F in water, freshly prepared)

#### 5.6.5 Operating Procedure

5.6.5.1 Prepare working standard by adding 100 ml 10<sup>-3</sup> M F to 100 ml buffer solution.

5.6.5.2 Prepare a blank containing 50.0 ml 0.2 N NaOH and 50.0 ml buffer solution in a plastic beaker.

5.6.5.3 While stirring blank gently, record mV reading from the blank once reading is stable.

5.6.5.4 Successively add increments of working standard to the blank to generate a calibration curve. Record stable mV reading after each addition. Table 1 shows recommended increments and resultant concentrations.

**Table 1 Calibration Concentrations**

<i>Added Volume of Working Standard (ml)</i>	<i>Total Volume (ml)</i>	<i>Resulting F<sup>-</sup> Concentration (M)</i>
0.2	100.2	$1.0 \times 10^{-6}$
0.2	100.4	$2.0 \times 10^{-6}$
0.4	100.8	$4.0 \times 10^{-6}$
0.4	101.2	$5.9 \times 10^{-6}$
0.8	102.0	$9.8 \times 10^{-6}$
1.0	103.0	$1.5 \times 10^{-5}$
2.0	105.0	$2.4 \times 10^{-5}$

5.6.5.5 Put 50 ml 0.2 N NaOH into each of two bubblers connected in series.

5.6.5.6 Establish a flow of < 1000 sccm of NF<sub>3</sub> through the bubblers using a suitable flow controller or flowmeter.

5.6.5.7 Sample approximately 15 liters of NF<sub>3</sub>. Record flowrate and time of sampling to determine total volume sampled (flowrate × time). A wet test meter can also be used to measure total volume. The amount of gas sample must be the volume at STP. If the flowmeter or wet test meter is not reference to 0° and 760 torr, use the formula below to correct sample volume.

$$\text{Liters at STP} = \text{Measured Liters} \times \frac{760 \text{ Torr}}{\text{P}} \times \frac{\text{T} + 273}{273 \text{ K}}$$

P: Pressure of sampled gas (mm Hg)

T: Temperature of sampled gas or reference temperature of the flow controller or meter in °C.

5.6.5.8 Transfer contents of each bubbler to individual 100 ml volumetric flasks and add 50 ml Buffer solution to each. Then, if necessary, add deionized or distilled water to bring the volume up to 100 ml.

5.6.5.9 Transfer contents to a plastic beaker.

5.6.5.10 While stirring, measure and record mV

readings for each sample.

5.6.5.11 Determine F<sup>-</sup> concentration in solution using calibration curve generated in Section 5.6.5.4.

5.6.5.12 Calculate gas phase hydrolyzable fluoride concentration using the equation below. Note that the equation assumes the hydrolyzable fluoride is hydrogen fluoride.

$$\text{Gas Phase HF (ppm}_v\text{)} = C \times 0.11 \times \frac{22.4 \text{ l/mole}}{V_s} \times 10^6$$

C: Measured hydrolyzable fluoride concentration (M) determined in Section 5.6.5.11.

V<sub>s</sub>: Volume of NF<sub>3</sub> sampled (liters at STP)

5.6.5.13 The HF concentration of the second bubbler should be insignificant compared to the first bubbler. If significant HF levels are found in the second bubbler, resample with a lower flowrate.

### 5.7 Notes

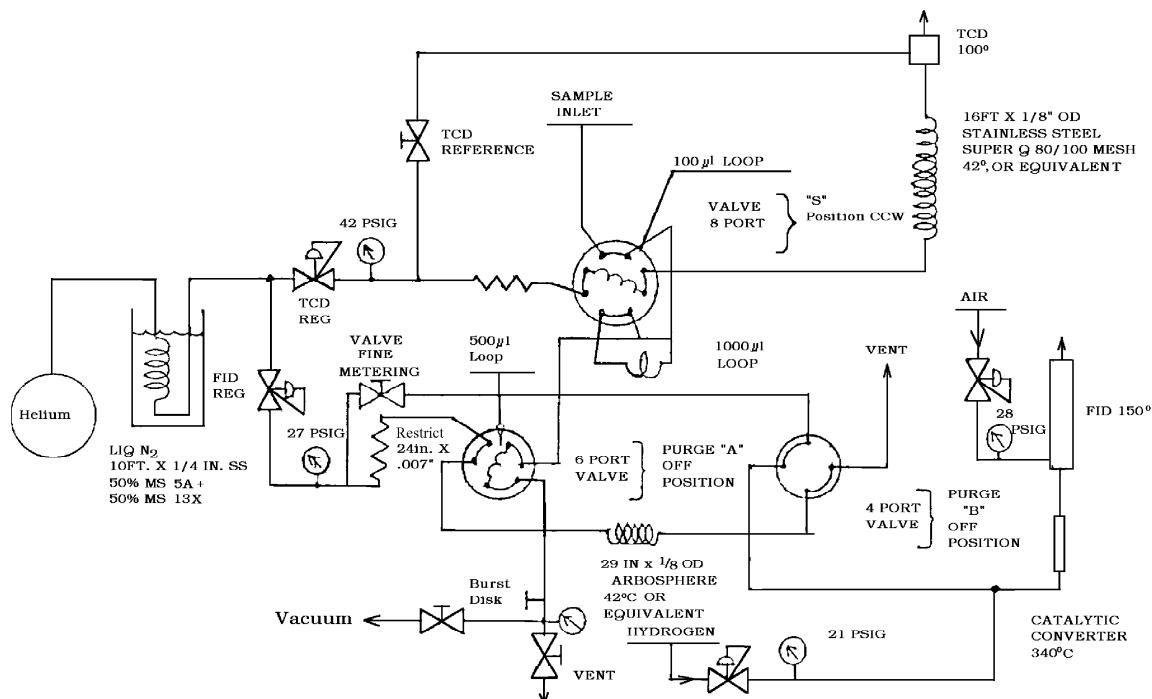
NOTE 1: Pass the carrier gas through a trap (3 m (10 ft.) by 6.4 mm (1/4 in.) OD) containing 50% by volume molecular sieve 5A and 50% by volume molecular sieve 13X submerged in liquid nitrogen.

NOTE 2: The methanizer catalyst can be destroyed by nitrogen trifluoride passing through to at high temperature. After the carbon monoxide peak is detected, the bulk nitrogen trifluoride is bypassed to vent by means of a four-port switching valve installed downstream of the separating column and before the methanizer (see Figure 1).

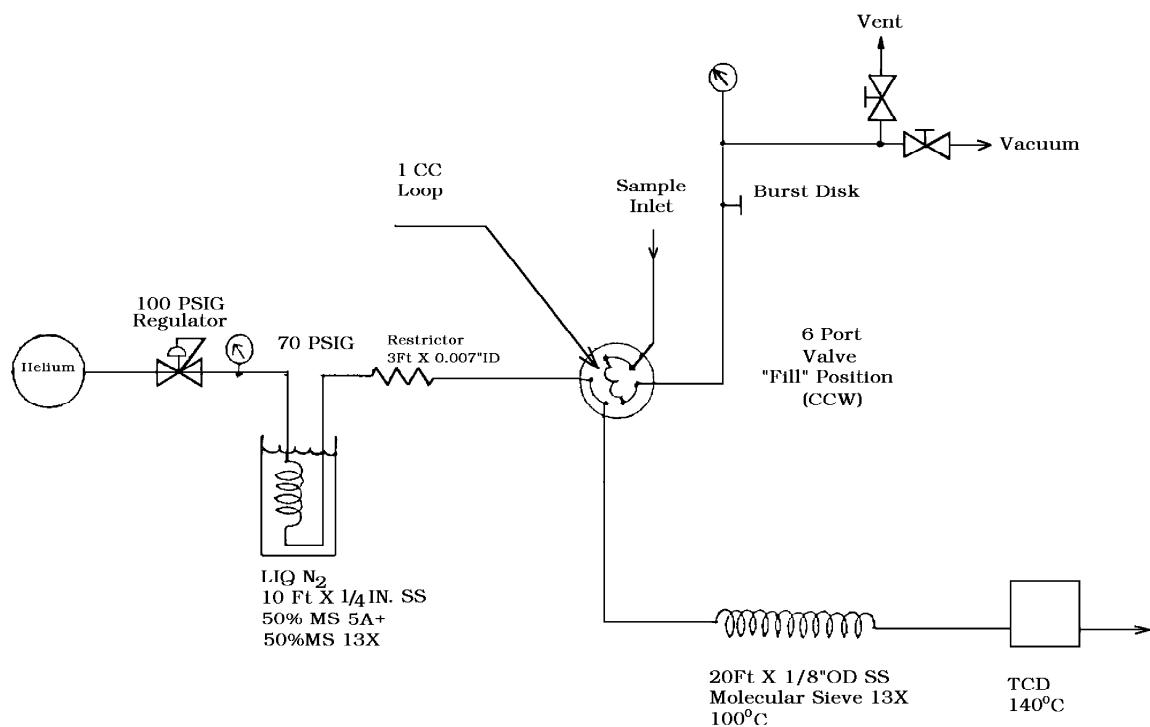
NOTE 3: The sampling system and hygrometer must be designed to operate under the sample pressure, or the sample pressure must be reduced, by a regulator with a diaphragm of stainless steel or other suitable material, to accommodate the pressure restrictions of the analytical hygrometer.

NOTE 4: A passivation procedure is described in the Metals Handbook, 8th ed., Vol. 2, American Society for Metals, Metals Park, OH.

NOTE 5: Polytetrafluoroethylene, polymethylpentene and polypropylene are suitable plastic materials.



**Figure 1**  
Configuration for the Analysis of CF<sub>4</sub>, CO<sub>2</sub>, N<sub>2</sub>O, SF<sub>6</sub>, and CO in NF<sub>3</sub>



**Figure 2**  
Configuration for the Analysis of O<sub>2</sub>/Ar and N<sub>2</sub> in NF<sub>3</sub>



**NOTICE:** This standard does not purport to address safety issues, if any, associated with its use. It is the responsibility of the users of this standard to establish appropriate safety and health practices and determine the applicability of regulatory or other limitations prior to use.

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