

Chromosorb P (80/100), 3 m × 3 mm stainless steel or glass; injection port at 280°C with glass insert; column temperature initially 65°C, programmed at 6°C/min up to 140°C; carrier gas — nitrogen at 40 mL/min; signal adjusted to give an 80% full-scale deflection; and preferably, electronic integration of peak areas. For DDT: Column — 5% silicone gum SESE-30 on Chromosorb® W (60/80), 1.5 × 3 mm, injection port — as above; column temperature — isothermal at 205°C; carrier gas — nitrogen at 75 mL/min, and preferably, electronic integration of peak areas. The order of elution is 2,2,4-trimethylpentane, carbon tetrachloride, benzene, chloroform, 2,2,4-trimethylpentane impurity, 1,2-dichloroethane, chlorobenzene, and dichlorobenzene. The total area under the impurity peaks from the sample should be no greater than that from the blank (extract from second funnel) by more than one-half the total area under the peaks from the standard (third funnel), also corrected for the blank.

**8.3.1 Standard** — Use a syringe to add the volumes of liquid listed in Table 2 into 300 mL of 2,2,4-trimethylpentane. Add 25 mg of DDT to the solution. Dilute to 500 mL with 2,2,4-trimethylpentane. The 2,2,4-trimethylpentane used for both the standard and the analysis should be free from impurities that interfere with the chromatographic analysis.

**8.4 Free Halogen (as Cl<sub>2</sub>)** — Mix 100 mL of sample and 100 mL of freshly boiled water and cool. Add 0.1 mL of 2% potassium iodide reagent solution and 1 mL of carbon disulfide, and mix. The carbon disulfide should not acquire a pink color in one-half minute.

**8.5 Phosphate** — To 170 mL (200 g) of sample, add 10 mL of sodium carbonate reagent solution and evaporate to dryness on a steam bath in a hood. Dissolve the residue in 25 mL of 0.5 N sulfuric acid. Add 1 mL of ammonium molybdate reagent solution and 1 mL of p-(methylamino)phenol solution. Allow to stand at room temperature for 2 hours. Any blue color produced should be no greater than that produced when 0.01 mg of phosphate ion (PO<sub>4</sub>) is treated like the sample.

**8.6 Sulfate** — To 84 mL (100 g) of sample, add 10 mL of sodium carbonate reagent solution and evaporate to dryness in a hood. Dissolve the residue in 10 mL of water and 1 mL of dilute hydrochloric acid (1 + 19); filter, if necessary. Add 1 mL of barium chloride reagent solution, mix, and allow to stand 10 minutes. Any turbidity should be no greater than that produced when 0.05 mg of sulfate ion (SO<sub>4</sub>) is treated as the sample.

**8.7 Sulfite** — Add 1 mL of 10 percent potassium iodide reagent solution, 5 mL of hydrochloric acid, and 2 mL of starch indicator solution to 400 mL of oxygen-

free water. Add 0.01 N iodine until a faint permanent blue color is produced. Add 85 mL of the sample and titrate with 0.01 N iodine to the same endpoint. Not more than 0.20 mL should be required.

**8.8 Arsenic and Antimony (as As)** — To 168 mL (200 g) of sample in a 400 mL beaker, add 10 mL of nitric acid and 5 mL of sulfuric acid, and evaporate to dense fumes of sulfur trioxide in a hood. Cool, cautiously add 10 mL of water, and again evaporate to dense fumes of sulfur trioxide. Cool and cautiously wash into a generator flask with water to make a volume of 35 mL. Proceed as described in the General Method for Arsenic (and Antimony) under SEMI C1, Section 3.4.5, starting with the sentence which begins: "Swirl the flask...." Any red color in the silver diethyldithiocarbamate solution from the sample should be no greater than that of the standard containing 0.001 mg of arsenic (As).

**8.9 Trace Metal Analysis** — The following method has given satisfactory results in determining trace metal impurities at the value specified for each of the following trace metals: aluminum (Al), boron (B), calcium (Ca), chromium (Cr), copper (Cu), gold (Au), iron (Fe), lead (Pb), magnesium (Mg), manganese (Mn), nickel (Ni), potassium (K), sodium (Na), tin (Sn), titanium (Ti), and zinc (Zn). Alternate methods may be used as long as appropriate studies demonstrate recovery between 75 — 125% of a known sample spike for half of the value of each specified item.

#### 8.9.1 Special Reagents

**8.9.1.1 Nitric Acid, Ultra Pure** — Use nitric acid specified for ultra low metal ion content.

**8.9.1.2 2% Nitric Acid Solution** — Dilute 20 mL of ultra pure nitric acid to 1 L using water meeting the criteria for Type E1.1 in ASTM D5127.

#### 8.9.2 Sample Preparation

**8.9.2.1** In a clean environment, place 250 mL of sample in a PTFE evaporating dish. Slowly evaporate on a hot plate, avoiding loss of sample by effervescence or spattering until approximately 2 mL of liquid remains. Note: Evaporation typically requires 2 1/2 to 4 hours. Cool. Transfer quantitatively to a 50 mL volumetric flask using 2% nitric acid for rinsing and dilution to volume. Run a reagent blank.

#### 8.9.3 Analysis

**8.9.3.1** Using the acid sample and reagent blank, analyze group 1 elements by flame atomic absorption spectroscopy and all other elements by plasma emission spectroscopy.

## 9 Grade 2 Procedures

NOTE 2: Each laboratory is responsible for verifying the validity of the method within its own operation.

9.1 *Non-Metal Impurities* — See Section 8, which contains procedures for the following tests:

- Assay
- Color (APHA)
- Free Halogen
- Phosphate
- Sulfate
- Sulfite

### 9.2 Trace Metals Analysis

9.2.1 The following method has given satisfactory results in determining metal ion impurities at the values specified for each of the following metals: aluminum (Al), antimony (Sb), arsenic (As) barium (Ba), beryllium (Be), bismuth (Bi), boron (B), calcium (Ca), chromium (Cr), cobalt (Co), copper (Cu), gallium (Ga), germanium (Ge), gold (Au), iron (Fe), lead (Pb), lithium (Li), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), niobium (Nb), potassium (K), silver (Ag), sodium (Na), strontium (Sr), tantalum (Ta), tin (Sn), titanium (Ti), vanadium (V), zinc (Zn), and zirconium (Zr). Alternate methods may be used as long as appropriate studies demonstrate a recovery between 75–125% of a known sample spike for half of the value of each specified element.

### 9.2.2 Special Reagents

9.2.2.1 *Hydrochloric Acid, Ultrapure* — Use hydrochloric acid specified for low metal ion content.

9.2.2.2 *3.7% Hydrochloric Acid Solution* — Dilute 20 g of ultrapure hydrochloric acid to 200 g using water meeting the criteria for Type E1.1 in ASTM D5127.

9.2.2.3 *Nitric Acid, Ultrapure* — Use nitric acid specified for low metal ion content.

9.2.2.4 *1% Nitric Acid Solution* — Dilute 10 mL of ultrapure nitric acid to 1 L using water meeting the criteria for Type E1.1 in ASTM D5127.

9.2.2.5 *Water* — The water used for all the dilution, calibration and standards should meet at a minimum the criteria for Type E1.1 in ASTM D5127 in regard to cation analysis.

9.2.2.6 *Rhodium Internal Standard* — Make up the internal standard solution to a concentration of 20 µg/mL (ppm) from the appropriate concentrated standard rhodium solution.

### 9.2.3 Sample Preparation

9.2.3.1 In a clean environment, place 2.00 g of sample into a tared FEP bottle (30 mL), dilute with “attainable” water to a final weight of 20.0 g. Add 20 µL of the rhodium internal standard solution. Run a reagent blank.

9.2.3.2 *Vanadium* — In a clean environment, place 20.0 g of sample into a clean PTFE dish. Slowly evaporate on a hot plate to dryness avoiding loss of sample by effervescence or spattering. Dissolve the residue with 5 mL of the 1% nitric acid solution by heating on a hot plate at low temperature for several minutes. Cool to room temperature, dilute to 20 g with 1% nitric acid, add 20 µL of the rhodium internal standard, mix well. Run a reagent blank.

### 9.2.4 Analysis

9.2.4.1 Using the prepared solutions and blanks, analyze sodium, potassium, calcium and iron by graphite furnace atomic absorption (GFAA) and the remaining elements by inductively coupled plasma mass spectrometry (ICP/MS). For calibration, the standards are made up with the 3.7% hydrochloric acid solution and the rhodium internal standard except for the analysis of vanadium which is performed using 1% nitric acid as the matrix. All standards must contain 10 ng/g of rhodium as the internal standard.

## 10 Grade 3 Procedures

10.1 This section does not apply to this chemical.

## 11 Grade 4 Procedures

11.1 This section does not apply to this chemical.

## 12 Grade 5 Procedures

12.1 This section does not apply to this chemical.

## 13 VLSI Grade Procedures

13.1 Specific procedures for this grade do not exist. Refer to Sections 8 and 9 for available procedures.

## 14 Tier A Procedures

14.1 This section does not apply to this chemical.

## 15 Tier B Procedures

15.1 Standardized test methods are being developed for all parameters at the purity levels indicated. Until standardized test methods are published, test methodology shall be determined by user and supplier. The Process Chemicals Committee considers a test method to be valid only if there is a documented recovery study showing a recovery of 75–125%.

Recovery is for a known sample spike at 50% of the specified level.

## 16 Tier C Procedures

16.1 Standardized test methods are being developed for all parameters at the purity levels indicated. Until standardized test methods are published, test methodology shall be determined by user and producer.

The Process Chemicals Committee considers a test method to be valid if there is a documented recovery study showing a recovery of 75–125%. Recovery is for a known sample spike at 50% of the specified level.

## 17 Tier D Procedures

17.1 This section does not apply to this chemical.

**Table 1 Impurity Limits and Other Requirements for Hydrochloric Acid**

Previous SEMI Reference #	C1.7-95	C7.2-94	C11.6-1296	C8.2-92	C12.2-96
	Grade 1	Grade 2	VLSI Grade	Tier B	Tier C
	(Specification)	(Specification)	(Guideline)	(Guideline)	(Guideline)
Assay (HCl)	36.5–38.0%	36.5–38.0 %	36–38%	37.0–38.0%	37.0–38.0%
Color (APHA)	10 max	10 max	10 max	10 max	10 max
Extractable Organic Substances	5 ppm max	--	--	500 ppb max	--
Residue after Ignition (as SO <sub>4</sub> )	--	--	3 ppm max	--	--
Free Halogen (as Cl <sub>2</sub> )	To pass test	To pass test	--	500 ppb max	500 ppb max
Free Chlorine (Cl <sub>2</sub> )	--	--	0.5 ppm max	--	--
Bromide (Br)	--	--	50 ppm max	--	--
Phosphate (PO <sub>4</sub> )	0.05 ppm max	50 ppb max	0.05 ppm max	50 ppb max	50 ppb max
Sulfate (SO <sub>4</sub> )	0.5 ppm max	500 ppb max	0.5 ppm max	100 ppb max	30 ppb max
Sulfite (SO <sub>3</sub> )	0.8 ppm max	800 ppb max	0.7 ppm max	100 ppb max	100 ppb max
Aluminum (Al)	0.3 ppm max	10 ppb max	0.05 ppm max	1 ppb max	100 ppt max
Antimony (Sb)	--	5 ppb max	0.005 ppm max	--	100 ppt max
Arsenic (As)	--	10 ppb max	0.005 ppm max	--	100 ppt max
Arsenic and Antimony (as As)	0.005 ppm max	--	--	1 ppb max	--
Barium (Ba)	--	10 ppb max	0.05 ppm max	1 ppb max	100 ppt max
Beryllium (Be)	--	10 ppb max	0.02 ppm max	1 ppb max	--
Bismuth (Bi)	--	10 ppb max	0.02 ppm max	1 ppb max	--
Boron (B)	0.1 ppm max	10 ppb max	0.02 ppm max	1 ppb max	100 ppt max
Cadmium (Cd)	--	10 ppb max	0.005 ppm max	1 ppb max	--
Calcium (Ca)	0.3 ppm max	10 ppb max	0.2 ppm max	1 ppb max	100 ppt max
Chromium (Cr)	0.2 ppm max	10 ppb max	0.01 ppm max	1 ppb max	100 ppt max
Cobalt (Co)	--	10 ppb max	0.01 ppm max	1 ppb max	100 ppt max
Copper (Cu)	0.1 ppm max	10 ppb max	0.01 ppm max	1 ppb max	100 ppt max
Gallium (Ga)	--	10 ppb max	0.02 ppm max	1 ppb max	--
Germanium (Ge)	--	10 ppb max	--	1 ppb max	--
Gold (Au)	0.3 ppm max	5 ppb max	0.02 ppm max	1 ppb max	--
Indium (In)	--	--	0.02 ppm max	--	--
Iron (Fe)	0.2 ppm max	10 ppb max	0.1 ppm max	1 ppb max	100 ppt max
Lead (Pb)	0.1 ppm max	10 ppb max	0.02 ppm max	1 ppb max	100 ppt max
Lithium (Li)	--	10 ppb max	0.02 ppm max	1 ppb max	--
Magnesium (Mg)	0.3 ppm max	10 ppb max	0.05 ppm max	1 ppb max	100 ppt max
Manganese (Mn)	0.3 ppm max	10 ppb max	0.01 ppm max	1 ppb max	100 ppt max
Mercury (Hg)	--	--	0.02 ppm max	--	--
Molybdenum (Mo)	--	10 ppb max	0.02 ppm max	1 ppb max	--
Nickel (Ni)	0.1 ppm max	10 ppb max	0.01 ppm max	1 ppb max	100 ppt max
Niobium (Nb)	--	10 ppb max	--	1 ppb max	--

Previous SEMI Reference #	C1.7-95	C7.2-94	C11.6-1296	C8.2-92	C12.2-96
	Grade 1 (Specification)	Grade 2 (Specification)	VLSI Grade (Guideline)	Tier B (Guideline)	Tier C (Guideline)
Platinum (Pt)	--	--	0.02 ppm max	--	--
Potassium (K)	0.3 ppm max	10 ppb max	0.05 ppm max	1 ppb max	100 ppt max
Silicon (Si)	--	--	--	1 ppb max	--
Silver (Ag)	--	5 ppb max	0.02 ppm max	1 ppb max	--
Sodium (Na)	0.3 ppm max	10 ppb max	0.1 ppm max	1 ppb max	100 ppt max
Strontium (Sr)	--	10 ppb max	0.02 ppm max	1 ppb max	--
Tantalum (Ta)	--	10 ppb max	--	1 ppb max	100 ppt max
Thallium (Tl)	--	10 ppb max	0.02 ppm max	1 ppb max	--
Tin (Sn)	0.3 ppm max	10 ppb max	0.02 ppm max	1 ppb max	100 ppt max
Titanium (Ti)	0.3 ppm max	10 ppb max	0.05 ppm max	1 ppb max	100 ppt max
Vanadium (V)	--	10 ppb max	0.02 ppm max	1 ppb max	--
Zinc (Zn)	0.3 ppm max	10 ppb max	0.05 ppm max	1 ppb max	100 ppt max
Zirconium (Zr)	--	10 ppb max	0.02 ppm max	1 ppb max	--
Particles in bottles (size, #/mL)	≥ 1.0 µm, 25 max	≥ 0.5 µm, 25 max	≥ 0.5 µm, 250 max	≥ 0.5 µm, 10 max ≥ 0.2 µm, TBD	(See NOTE 1.)

NOTE 1: Due to the limitations of current particle counters, particle size and number are to be agreed upon between supplier and user. See SEMI C1, Section 3.9 for particle counting methodology.

**Table 2 Composition of Standard**

Substance	Amount in 500 mL of 2,2,4-trimethylpentane solution		Concentration in ppm for 5 mL of standard in 100 mL (120 g) of HCl	
	µL	mg		
Benzene	6.8	6		0.5
Chlorobenzene	5.5	6		0.5
1,2-Dichloroethane	20	25		2.0
Chloroform	34	50		4.0
DDT (see NOTE 1)		25		2.0
			Total	9.0
			Allowance for CCl <sub>4</sub>	1.0
			Total	10.0

NOTE 1: 1,1,1-Trichloro-2,2-bis (p-chlorophenyl) ethane, dichlorodiphenyltrichloroethane.

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# SEMI C28-0705

## SPECIFICATIONS FOR HYDROFLUORIC ACID

This specification was technically approved by the global Liquid Chemicals Committee. This edition was approved for publication by the global Audits and Reviews Subcommittee on May 20, 2005. It was available at [www.semi.org](http://www.semi.org) in June 2005 and on CD-ROM in July 2005. Originally published in 1978; previously published July 2004.

**NOTICE:** This document was completely rewritten in 2005.

### 1 Purpose

1.1 The purpose of this document is to standardize requirements for hydrofluoric acid used in the semiconductor industry and testing procedures to support those standards. Test methods have been shown to give statistically valid results.

### 2 Scope

2.1 The scope of this document is all grades of hydrofluoric acid used in the semiconductor industry.

**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.

### 3 Limitations

3.1 None.

### 4 Referenced Standards and Documents

#### 4.1 SEMI Standards

SEMI C1 — Guide for the Analysis of Liquid Chemicals

#### 4.2 ASTM Standards<sup>1</sup>

ASTM D5127 — Standard Guide for Ultra Pure Water Used in the Electronics and Semiconductor Industry

#### 4.3 Other Documents

Dionex Technical Note 45 — Determination of Trace Anions in Concentrated Hydrofluoric Acid

**NOTICE:** Unless otherwise indicated, all documents cited shall be the latest published versions.

### 5 Terminology

5.1 None.

### 6 Physical Property (for information only)

Density at 25°C	1.15 g/mL
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### 7 Requirements

7.1 The requirements for hydrofluoric acid for Grades 1, 2, 3 and 4 are listed in Table 1.

### 8 Grade 1 Procedures

NOTE 1: Each laboratory is responsible for verifying the validity of the method within its own operation.

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8.1 *Assay* — Accurately weigh 1.4–1.5 mL of sample in polyethylene weighing bottle, sample, stopper immediately, and reweigh. To 50 mL of water in a plastic vessel, add the sample (loosen the stopper of the polyethylene bottle, and add both the container and the stopper with the sample). Add 0.1 mL of phenolphthalein indicator solution, and titrate with standardized 1 N sodium hydroxide to a slight, pink color.

$$\% \text{Assay} = \frac{\text{mL} \times \text{N of NaOH} \times 2.001}{\text{Weight of sample (g)}}$$

8.1.1 Alternately, potentiometric end point detection can be used.

8.2 *Chloride* — Add 1.7 mL (2.0 g) of sample to 45 mL of water. Filter, if necessary, through a chloride-free filter. Add 1 mL of nitric acid and 1 mL of silver nitrate reagent solution. Any turbidity produced should be no greater than that produced when 0.01 mg of chloride ion (Cl<sup>-</sup>) is treated as the sample.

8.3 *Nitrate* — Weigh 3.3 g of sample in a white plastic 50 mL beaker and dilute with 4.5 mL of water. To another 50 mL plastic beaker, add 6.5 mL of water and 1 mL of standard nitrate solution containing 0.01 mg of nitrate (NO<sub>3</sub><sup>-</sup>) per mL. To each solution, add 2.5 mL of brucine sulfate reagent solution and cautiously add with stirring 20 mL of sulfuric acid. Allow to stand for 10 minutes. The yellow color in the sample solution should be no greater than that in the standard solution.

8.4 *Phosphate* — Evaporate 9 mL (10 g) of sample to dryness in a platinum or other suitable dish on a steam bath in a hood. Dissolve the residue in 25 mL of 0.5 N sulfuric acid. Add 1 mL of ammonium molybdate reagent solution and 1 mL of p-(methylamino)phenol sulfate reagent solution. Allow to stand for 2 hours at room temperature. Any blue color should be no greater than that produced when 0.01 mg of phosphate ion (PO<sub>4</sub><sup>3-</sup>) is treated like the sample.

8.5 *Sulfate and Sulfite (as SO<sub>4</sub>)* — To 18 mL (20 g) of sample in a platinum or other suitable evaporating dish, add about 10 mg of sodium carbonate and 1 mL of 30 hydrogen peroxide. Evaporate to dryness on a steam bath in a hood, wash down the sides of the dish with a small volume of water, and add 3 mL of perchloric acid. Evaporate to about 1 mL, dilute with about 15 mL of water, and add 0.01 mL of phenolphthalein indicator solution. Neutralize with ammonium hydroxide, dilute with water to 20 mL, and add 2 mL of dilute hydrochloric acid (1 + 19) and 2 mL of barium chloride reagent solution. Any turbidity should not exceed that produced by 0.1 mg of sulfate ion (SO<sub>4</sub><sup>2-</sup>) in an equal volume of solution containing the quantities of reagents used in the test. Compare 10 minutes after adding the barium chloride to the sample and standard solutions.

NOTE 2: For anion determination, alternate method based upon ion chromatography may be used, see ¶10.2.

8.6 *Trace Metal Analysis* — The following method has given satisfactory results in determining trace metal impurities at the value specified for each of the following trace metals: aluminum (Al), antimony (Sb), arsenic (As), barium (Ba), boron (B), cadmium, (Cd), calcium (Ca), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), lithium (Li), magnesium (Mg), manganese (Mn), nickel (Ni), potassium (K), sodium (Na), tin (Sn), titanium (Ti), vanadium (V) and zinc (Zn). An alternate method is described in ¶9.2. Any other alternate methods may be used as long as method validation according to SEMI C1 can be demonstrated.

#### 8.6.1 *Special Reagents*

8.6.1.1 *Nitric Acid, Ultra Pure* — Use nitric acid specified for ultra low metal ion content.

8.6.1.2 *2% Nitric Acid Solution* — Dilute 20 mL of ultra pure nitric acid to 1 L using water meeting the criteria for Type E1.1 in ASTM D5127.

#### 8.6.2 *Sample Preparation*

8.6.2.1 In a clean environment, place 250 g of sample in a PTFE evaporating dish. Slowly evaporate on a hot plate, avoiding loss of sample by effervescence or spattering until approximately 2 mL of liquid remains.

NOTE 3: Evaporation typically requires 2 1/2 to 4 hours.

Cool. Add 1 mL of ultra pure, 70% nitric acid. While maintaining volume, carefully warm several minutes to dissolve any residue. Cool. Transfer quantitatively to a 50 mL volumetric flask using 2% nitric acid for rinsing and dilution to volume. Run a reagent blank.



### 8.6.3 Analysis

8.6.3.1 Using the acid sample and reagent blank, analyze all specified elements by plasma emission spectroscopy or preferably by ICP-MS.

## 9 Grade 2 Procedures

NOTE 4: Each laboratory is responsible for verifying the validity of the method within its own operation.

9.1 *Non-Metal Impurities* — See §8, which contains procedures for the following tests:

- Assay,
- Chloride,
- Nitrate,
- Phosphate, and
- Sulfate and Sulfite (as SO<sub>4</sub>).

### 9.2 Trace Metals Analysis

9.2.1 The following method has given satisfactory results in determining trace metal impurities at the value specified for each of the following trace metals: aluminum (Al), antimony (Sb), arsenic (As), barium (Ba), boron (B), cadmium (Cd), calcium (Ca), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), lithium (Li), magnesium (Mg), manganese (Mn), nickel (Ni), potassium (K), sodium (Na), tin (Sn), titanium (Ti), vanadium (V), and zinc (Zn). Alternate method can be used as long as method validation according to SEMI C1 can be demonstrated.

#### 9.2.2 Special Reagents

9.2.2.1 *Hydrofluoric Acid, Ultra Pure* — Use hydrofluoric acid specified for low metal ion content.

9.2.2.2 *4.9% Hydrofluoric Acid Solution* — Dilute 20 g of ultrapure hydrofluoric acid to 200 g using water meeting the criteria for Type E1.1 in ASTM D5127.

9.2.2.3 *Water* — The water used for all the dilution, calibration and standards should meet at a minimum the criteria for Type E1.1 in ASTM D5127 in regard to cation analysis.

9.2.2.4 *Indium Internal Standard* — Make up a internal standard solution to a concentration of 20 µg/mL (ppm) from the appropriate concentrated indium standard solution.

9.2.3 *Sample Preparation* — In a clean environment, place 2.00 g of sample into a tared FEP bottle (30 mL), dilute with Type E1.1 water to a final weight of 20.0 g. Add 20 µL of the indium internal standard solution. Run a reagent blank.

#### 9.2.4 Analysis

9.2.4.1 Using the prepared solutions and blanks, analyze all the specified elements by inductively coupled plasma mass spectrometry (ICP/MS). For calibration, the standards are made up with the 4.9% hydrofluoric acid solution and the indium internal standard such that the final concentration is 20 ng/g of indium.

NOTE 5: Analysis of dilute hydrofluoric acid requires the use of special hydrofluoric acid resistant sample introduction systems for inductively coupled plasma mass spectrometry. These systems are available from most instrument suppliers.

NOTE 6: Analysis of dilute hydrofluoric acid can produce rapid corrosion of nickel cones commonly used in inductively coupled plasma mass spectrometry, platinum cones should be considered as alternative when performing this analysis.

## 10 Grade 3 Procedures

10.1 Assay — See ¶8.1

10.2 *Chloride, Nitrate, Sulfate, Phosphate*

10.2.1 The above mentioned anions can be determined by ion chromatography using a two dimensional approach. For a detailed procedure, see for example Dionex Technical Note 45. Better results are obtained when using an IonPac ICE-AS1 column instead of the IonPac ICE-AS6 recommended in the TN45. Calibration is preferably done



by the method of standard addition. Alternate method can be used as long as method validation according to SEMI C1 can be demonstrated.

**10.3 Trace Metal Analysis** — The following method has given satisfactory results in determining trace metal impurities at the value specified for each of the following trace metals: aluminum (Al), antimony (Sb), arsenic (As), barium (Ba), boron (B), cadmium (Cd), calcium (Ca), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), lithium (Li), magnesium (Mg), manganese (Mn), nickel (Ni), potassium (K), sodium (Na), tin (Sn), titanium (Ti), vanadium (V), and zinc (Zn). Alternate method can be used as long as method validation according to SEMI C1 can be demonstrated.

#### 10.3.1 Special Reagents

10.3.1.1 *Nitric Acid, Ultra Pure* — Use nitric acid specified for ultra low metal ion content.

10.3.1.2 *3 % Nitric Acid Solution* — In a clean environment, place 15 g of Ultra Pure Nitric Acid ¶10.3.1.1 into a tared clean 500 ml FEP bottle. Dilute to a final weight of 500 g using ultrapure water ¶10.3.1.3.

10.3.1.3 *Water* — The water used for all the dilutions, calibrations and standards should meet at a minimum the criteria for Type E1.2 in ASTM D5127 in regard to cation analysis.

#### 10.3.2 Sample Preparation

10.3.2.1 In a clean environment, place 20 g of sample into a tared clean 120 ml FEP bottle. Dilute to a final weight of 100 g with the 3 % Nitric Acid Solution ¶10.3.1.2.

#### 10.3.3 Analysis

10.3.3.1 Using the prepared solutions, analyze all the specified elements by inductively coupled plasma mass spectrometry (ICP-MS). For calibration, blank and standards are made up with the 3 % Nitric Acid Solution ¶10.3.1.2.

NOTE 7: Analysis of dilute hydrofluoric acid requires the use of special hydrofluoric acid resistant sample introduction systems for inductively coupled plasma mass spectrometry. These systems are available from most instrument suppliers.

NOTE 8: Analysis of dilute hydrofluoric acid can produce rapid corrosion of nickel cones commonly used in inductively coupled plasma mass spectrometry, platinum cones should be considered as alternative when performing this analysis.

NOTE 9: The analytical methodology described in ¶10.3 has been validated using a “Reaction / Collision cell” type ICP-MS. Other instrument type can be used as long as method validation according to SEMI C1 can be demonstrated.

### 11 Grade 4 Procedures

11.1 *Assay* — See ¶8.1.

11.2 *Chloride, Nitrate, Sulfate, Phosphate* — See ¶10.2.

11.3 *Trace Metal Analysis* — See ¶10.3.

### 12 Grade 5 Procedures

12.1 This section does not apply to this chemical.

### 13 Tier A Procedures

13.1 This section does not apply to this chemical.

### 14 Tier B Procedures

14.1 This section does not apply to this chemical

### 15 Tier C Procedures

15.1 This section does not apply to this chemical



## 16 Tier D Procedures

16.1 This section does not apply to this chemical.

**Table 1 Impurity Limits and Other Requirements for Hydrofluoric Acid**

Previous SEMI Reference #	C1.8-95	C7.3-93	C8.3-96	-
	Grade 1 (Specification)	Grade 2 (Specification)	Grade 3 (Specification)	Grade 4 (Specification)
Assay (HF)	48.8–49.2%	48.8–49.2 %	48.90–49.10%	48.90–49.10%
Appearance	Clear and colorless	Clear and colorless	Clear and colorless	Clear and colorless
Chloride (Cl)	5 ppm max	5000 ppb max	200 ppb max	100 ppb max
Nitrate (NO <sub>3</sub> )	3 ppm max	3000 ppb max	100 ppb max	100 ppb max
Phosphate (PO <sub>4</sub> )	1 ppm max	1000 ppb max	100 ppb max	100 ppb max
Sulfate (SO <sub>4</sub> )	--	--	200 ppb max	100 ppb max
Sulfate and Sulfite (as SO <sub>4</sub> )	5 ppm max	5000 ppb max	--	
Aluminum (Al)	0.05 ppm max	10. ppb max	1 ppb max	100 ppt max
Antimony (Sb)	0.03 ppm max	15 ppb max	1 ppb max	100 ppt max
Arsenic (As)	0.03 ppm max	15 ppb max	1 ppb max	100 ppt max
Barium (Ba)	--	10. ppb max	1 ppb max	100 ppt max
Boron (B)	0.05 ppm max	10. ppb max	1 ppb max	100 ppt max
Cadmium (Cd)	--	10. ppb max	1 ppb max	100 ppt max
Calcium (Ca)	0.3 ppm max	10. ppb max	1 ppb max	100 ppt max
Chromium (Cr)	0.01 ppm max	10. ppb max	1 ppb max	100 ppt max
Copper (Cu)	0.05 ppm max	10. ppb max	1 ppb max	100 ppt max
Iron (Fe)	0.2 ppm max	10. ppb max	1 ppb max	100 ppt max
Lead (Pb)	0.1 ppm max	10. ppb max	1 ppb max	100 ppt max
Lithium (Li)	--	5. ppb max	1 ppb max	100 ppt max
Magnesium (Mg)	0.2 ppm max	10. ppb max	1 ppb max	100 ppt max
Manganese (Mn)	0.2 ppm max	10. ppb max	1 ppb max	100 ppt max
Nickel (Ni)	0.1 ppm max	10. ppb max	1 ppb max	100 ppt max
Potassium (K)	0.3 ppm max	10. ppb max	1 ppb max	100 ppt max
Sodium (Na)	0.3 ppm max	10. ppb max	1 ppb max	100 ppt max
Tin (Sn)	0.3 ppm max	10. ppb max	1 ppb max	100 ppt max
Titanium (Ti)	0.3 ppm max	10. ppb max	1 ppb max	100 ppt max
Vanadium (V)	--	10. ppb max	1 ppb max	100 ppt max
Zinc (Zn)	0.3 ppm max	10. ppb max	1 ppb max	100 ppt max
Particles in bottles (size, #/mL)	≥ 1.0 µm, 25 max	≥ 0.5 µm, 25 max	≥ 0.5 µm, 5 max ≥ 0.2 µm, TBD	TBD

**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 or equipment mentioned herein. These standards are subject to change without notice.

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# SEMI C29-0301

## SPECIFICATIONS AND GUIDELINE FOR 4.9% HYDROFLUORIC ACID (10:1 v/v)

These specifications and this guideline were technically approved by the Global Process Chemicals Committee and are the direct responsibility of the North American Process Chemicals Committee. Current edition approved by the North American Regional Standards Committee on October 17, 1999. Initially available at [www.semi.org](http://www.semi.org) February 2001; to be published March 2001. This document replaces SEMI C7.4, C8.4, and C12.3 in their entirety. Originally published in 1990, 1992, and 1995 respectively; previously published June 1999.

### 1 Purpose

1.1 The purpose of this document is to standardize requirements for 4.9% hydrofluoric acid used in the semiconductor industry and testing procedures to support those standards. Test methods have been shown to give statistically valid results. This document also provides guidelines for grades of 4.9% hydrofluoric acid for which a need has been identified. In the case of the guidelines, the test methods may not have been statistically validated yet.

### 2 Scope

2.1 The scope of this document is all grades of 4.9% hydrofluoric acid used in the semiconductor industry.

2.2 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.

### 3 Limitations

3.1 None.

### 4 Referenced Standards

#### 4.1 SEMI Standards

SEMI C28 — Specifications and Guidelines for Hydrofluoric Acid

#### 4.2 ASTM Standards<sup>1</sup>

ASTM D5127 — Standard Guide for Ultra Pure Water Used in the Electronics and Semiconductor Industry

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

### 5 Terminology

5.1 None.

<sup>1</sup> American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, Pennsylvania 19428-2959, USA. Telephone: 610.832.9585, Fax: 610.832.9555. Website: [www.astm.org](http://www.astm.org)

### 6 Physical Property (for information only)

6.1 Not applicable.

### 7 Requirements

7.1 The requirements for 4.9% hydrofluoric acid for Grades 2 and 3 and Tier C are listed in Table 1.

### 8 Grade 1 Procedures

8.1 This section does not apply to this chemical.

### 9 Grade 2 Procedures

NOTE 2: Each laboratory is responsible for verifying the validity of the method within its own operation.

9.1 *Non-Metal Impurities* — See SEMI C28 (Specifications and Guidelines for Hydrofluoric Acid) which contains procedures for the following tests:

Assay

Color (APHA)

Fluosilicic Acid

Chloride

Phosphate

Sulfate and Sulfite (as SO<sub>4</sub>)

Arsenic and Antimony (as As)

9.1.1 *Analysis of Anions and Fluosilicic Acid* — Application of the procedures cited above to dilute hydrofluoric acid requires a tenfold increase in the amount of initial sample weight prior to the evaporation steps given in the procedures.

#### 9.2 Trace Metals Analysis

9.2.1 The following method has given satisfactory results in determining metal ion impurities at the values specified for each of the following metals: aluminum (Al), arsenic (As), antimony (Sb), barium (Ba), beryllium (Be), bismuth (Bi), boron (B), calcium (Ca), chromium (Cr), cobalt (Co), copper (Cu), gallium (Ga), germanium (Ge), gold (Au), iron (Fe), lead (Pb), lithium (Li), magnesium (Mg), manganese (Mn),

molybdenum (Mo), nickel (Ni), niobium (Nb), potassium (K), silver (Ag), sodium (Na), strontium (Sr), tantalum (Ta), tin (Sn), titanium (Ti), vanadium (V), zinc (Zn), and zirconium (Zr). Alternate methods may be used as long as appropriate studies demonstrate a recovery between 75–125% of a known sample spike for half of the value of each specified element.

### 9.2.2 Special Reagents

9.2.2.1 *Hydrofluoric Acid, Ultra Pure* — Use hydrofluoric acid specified for low metal ion content.

9.2.2.2 *4.9% Hydrofluoric Acid Solution* — Dilute 20 g of ultrapure hydrofluoric acid to 200 g using water meeting the criteria for Type E1.1 in ASTM D5127.

9.2.2.3 *Water* — The water used for all the dilution, calibration and standards should meet at a minimum the criteria for Type E1.1 in ASTM D5127 in regard to cation analysis.

9.2.2.4 *Indium Internal Standard* — Make up the internal standard solution to a concentration of 20 µg/mL (ppm) from the appropriate concentrated indium standard solution.

### 9.2.3 Sample Preparation

9.2.3.1 In a clean environment, place 20.0 g of sample into a tared FEP bottle (30 mL). Add 20 µL of the indium internal standard solution. Run a reagent blank.

### 9.2.4 Analysis

9.2.4.1 Using the prepared solutions and blanks, analyze sodium, potassium, calcium and iron by graphite furnace atomic absorption (GFAA) and the remaining elements by inductively coupled plasma mass spectrometry (ICP/MS). For calibration, the standards are made up with the 4.9% hydrofluoric acid solution and a final concentration of 20 ng/g of the indium internal standard.

NOTE 3: Analysis of diluted hydrofluoric acid requires the use of special hydrofluoric acid resistant sample introduction systems for inductively coupled plasma mass spectrometry. These systems are available from most instrument suppliers.

NOTE 4: Analysis of diluted hydrofluoric acid can produce rapid corrosion of nickel cones commonly used in inductively coupled plasma mass spectrometry, platinum cones should be considered as alternative when performing this analysis.

## 10 Grade 3 Procedures

NOTE 5: The analytical procedures associated with this standard are not intended to be the only acceptable procedure or the best procedure available. The published procedures have been found to meet the required criteria for acceptance of an analytical procedure. Alternate procedures may be used if they meet the same criteria as the published procedures.

NOTE 6: Each laboratory is responsible for verifying the validity of each method within its own operation.

10.1 *Non-Metal Impurities* — See SEMI C28, which contains procedures for the following tests:

Assay

Color (APHA)

Fluosilicic Acid

Chlorides

Phosphates

Sulfate and Sulfite (as SO<sub>4</sub>)

10.1.1 *Analysis of Anions and Fluosilicic Acid* — Application of the procedures cited above to dilute hydrofluoric acid requires a tenfold increase in the amount of initial sample weight prior to the evaporation steps given in the procedures.

### 10.2 Trace Metals Analysis

10.2.1 The following method has given satisfactory results in determining metal ion impurities at the values specified for each of the following metals: aluminum (Al), antimony (Sb), arsenic (As), barium (Ba), boron (B), cadmium (Cd), calcium (Ca), chromium (Cr), cobalt (Co), copper (Cu), gold (Au), iron (Fe), lead (Pb), lithium (Li), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), potassium (K), silver (Ag), sodium (Na), strontium (Sr), tin (Sn), titanium (Ti), vanadium (V), and zinc (Zn). Alternate methods may be used as long as appropriate studies demonstrate a recovery between 75–125% of a known sample spike for half of the value of each specified element.

### 10.2.2 Special Reagents

10.2.2.1 *Hydrofluoric Acid, Ultrapure* — Use hydrofluoric acid specified for low metal ion content.

10.2.2.2 *4.9% Hydrofluoric Acid Solution* — Dilute 20 g of ultrapure hydrofluoric acid to 200 g using water meeting the criteria for Type E1.1 in ASTM D5127.

10.2.2.3 *Water* — The water used for all the dilution, calibration, and standards should meet at a minimum the criteria for Type E1.1 in ASTM D5127 in regard to cation analysis.

10.2.2.4 *Indium Internal Standard* — Make up the internal standard solution to a concentration of 20 µg/mL (ppm) from the appropriate concentrated indium standard solution.

### 10.2.3 Sample Preparation

10.2.3.1 In a clean environment, place 20.0 g of sample into a tared FEP bottle (30 mL). Add 20 µL of

the indium internal standard solution. Run a reagent blank.

#### 10.2.4 Analysis

10.2.4.1 Using the prepared solutions and blanks, analyze sodium, potassium, calcium, and iron by graphite furnace atomic absorption (GFAA) and the remaining elements by inductively coupled plasma mass spectrometry (ICP/MS). For calibration, the standards are made up with the 4.9% hydrofluoric acid solution and a final concentration of 20 ng/g of the indium internal standard.

NOTE 7: Analysis of dilute hydrofluoric acid requires the use of special hydrofluoric acid-resistant sample introduction systems for inductively coupled plasma mass spectrometry. These systems are available from most instrument suppliers.

NOTE 8: Analysis of dilute hydrofluoric acid can produce rapid corrosion of nickel cones commonly used in inductively coupled plasma mass spectrometry; platinum cones should be considered as an alternative when performing this analysis.

### 11 Grade 4 Procedures

11.1 This section does not apply to this chemical.

### 12 Grade 5 Procedures

12.1 This section does not apply to this chemical.

### 13 VLSI Grade Procedures

13.1 This section does not apply to this chemical.

### 14 Tier A Procedures

14.1 This section does not apply to this chemical.

### 15 Tier B Procedures

15.1 This section does not apply to this chemical.

### 16 Tier C Procedures

16.1 Standardized test methods are being developed for all parameters at the purity levels indicated. Until standardized test methods are published, test methodology shall be determined by user and producer. The Process Chemicals Committee considers a test method to be valid if there is a documented recovery study showing a recovery of 75–125%. Recovery is for a known sample spike at 50% of the specified level.

### 17 Tier D Procedures

17.1 This section does not apply to this chemical.

**Table 1 Impurity Limits and Other Requirements for 4.9% Hydrofluoric Acid**

Previous SEMI Reference #	C7.4-93	C8.4-0298	C12.3-96
Grade 2	Grade 3	Tier C	
(Specification)	(Specification)	(Guideline)	
Assay (HF)	4.8–5.0 %	4.8–5.0%	4.8–5.0%
Color (APHA)	10 max	10 max	10 max
Fluosilicic Acid ( $H_2SiF_6$ )	10 ppm max	10,000 ppb max	10,000 ppb max
Total Organic Carbon (TOC)	--	--	500 ppb max
Chloride (Cl)	500 ppb max	500 ppb max	100 ppb max
Phosphate ( $PO_4$ )	100 ppb max	100 ppb max	100 ppb max
Sulfate ( $SO_4$ )	--	--	100 ppb max
Sulfate and Sulfite (as $SO_4$ )	500 ppb max	500 ppb max	--
Aluminum (Al)	10 ppb max	1 ppb max	100 ppt max
Antimony (Sb)	--	1 ppb max	100 ppt max
Arsenic (As)	--	1 ppb max	100 ppt max
Arsenic and Antimony (as As)	5 ppb max	--	--
Barium (Ba)	10 ppb max	1 ppb max	--
Beryllium (Be)	5 ppb max	--	--
Bismuth (Bi)	5 ppb max	--	--
Boron (B)	10 ppb max	1 ppb max	100 ppt max
Cadmium (Cd)	10 ppb max	1 ppb max	--
Calcium (Ca)	10 ppb max	1 ppb max	100 ppt max
Chromium (Cr)	10 ppb max	1 ppb max	100 ppt max
Cobalt (Co)	10 ppb max	1 ppb max	--



Previous SEMI Reference #	C7.4-93	C8.4-0298	C12.3-96
	Grade 2 (Specification)	Grade 3 (Specification)	Tier C (Guideline)
Copper (Cu)	10 ppb max	1 ppb max	100 ppt max
Gallium (Ga)	10 ppb max	--	--
Germanium (Ge)	10 ppb max	--	--
Gold (Au)	5 ppb max	1 ppb max	100 ppt max
Iron (Fe)	10 ppb max	1 ppb max	100 ppt max
Lead (Pb)	10 ppb max	1 ppb max	100 ppt max
Lithium (Li)	5 ppb max	1 ppb max	--
Magnesium (Mg)	10 ppb max	1 ppb max	100 ppt max
Manganese (Mn)	10 ppb max	1 ppb max	100 ppt max
Molybdenum (Mo)	10 ppb max	1 ppb max	--
Nickel (Ni)	10 ppb max	1 ppb max	100 ppt max
Niobium (Nb)	10 ppb max	--	--
Potassium (K)	10 ppb max	1 ppb max	100 ppt max
Silver (Ag)	5 ppb max	1 ppb max	--
Sodium (Na)	10 ppb max	1 ppb max	100 ppt max
Strontium (Sr)	10 ppb max	1 ppb max	--
Tantalum (Ta)	10 ppb max	--	--
Thallium (Tl)	10 ppb max	--	--
Tin (Sn)	10 ppb max	1 ppb max	100 ppt max
Titanium (Ti)	10 ppb max	1 ppb max	100 ppt max
Vanadium (V)	10 ppb max	1 ppb max	--
Zinc (Zn)	10 ppb max	1 ppb max	100 ppt max
Zirconium (Zr)	10 ppb max	--	--
Particles in bottles: size, #/mL	≥ 0.5 µm, 25 max	≥ 0.5 µm, 25 max	≥ 0.2 µm, TBD

**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 C30-1101

## SPECIFICATIONS AND GUIDELINES FOR HYDROGEN PEROXIDE

These specifications and guidelines were technically approved by the Global Process Chemicals Committee and are the direct responsibility of the North American Process Chemicals 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. This document replaces SEMI C1.9, C7.5, C8.5, C11.4, and C12.4 in their entirety. Originally published in 1978, 1990, 1992, 1994, and 1995 respectively; previously published March 2001.

### 1 Purpose

1.1 The purpose of this document is to standardize requirements for hydrogen peroxide used in the semiconductor industry and testing procedures to support those standards. Test methods have been shown to give statistically valid results. This document also provides guidelines for grades of hydrogen peroxide for which a need has been identified. In the case of the guidelines, the test methods may not have been statistically validated yet.

### 2 Scope

2.1 The scope of this document is all grades of hydrogen peroxide used in the semiconductor industry.

2.2 The VLSI grade purity level is typically required by semiconductor devices with geometries of 0.8–1.2 microns.

2.3 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 limitations prior to use.

### 3 Limitations

3.1 The specification for VLSI grade hydrogen peroxide is only applicable for materials that remain below 25°C during transport and storage.

### 4 Referenced Standards

#### 4.1 SEMI Standards

SEMI C1 — Specifications for Reagents

#### 4.2 ASTM Standards<sup>1</sup>

ASTM D 5127 — Standard Guide for Ultra Pure Water Used in the Electronics and Semiconductor Industry

NOTE 1: Unless otherwise indicated, all documents cited shall be the latest published versions.

<sup>1</sup> American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, Pennsylvania 19428-2959, USA. Telephone: 610.832.9585, Fax: 610.832.9555 Website: [www.astm.org](http://www.astm.org)

### 5 Terminology

5.1 None.

### 6 Physical Property (for information only)

Density at 25°C	1.11 g/mL
-----------------	-----------

### 7 Requirements

7.1 The requirements for hydrogen peroxide for Grades 1, 2, 3, 4, 5, and VLSI Grade are listed in Table 1.

### 8 Grade 1 Procedures

NOTE 2: When hydrogen peroxide is added to water, there is no spattering. This happens only when the order of addition is reversed.

NOTE 3: Each laboratory is responsible for verifying the validity of the method within its own operation.

8.1 *Assay* — Accurately weigh about 1 mL of sample in a tared 100 mL volumetric flask, dilute to volume with water, and mix thoroughly. Transfer exactly 20.0 mL of this solution to a 250 mL conical flask, add 20 mL of dilute sulfuric acid (1 + 15), and titrate with standardized 0.1 N (0.02 M) potassium permanganate to a pink color that persists for 15 seconds.

$$\% \text{ Assay} = \frac{\text{mL} \times \text{N of KMnO}_4 \times 8.500}{\text{Weight of sample (g)}}$$

8.2 *Color* — Dilute 2.0 mL of platinum-cobalt stock solution (APHA No. 500) to 100 mL with water. Compare this standard (APHA No. 10) with 100 mL of sample in Nessler tubes. View vertically over a white background. The sample must be no darker than the standard.

8.3 *Free Acid* — Dilute 9 mL (10 g) of sample with 90 mL of freshly boiled and cooled carbon dioxide-free water. Add 0.15 mL of methyl red indicator solution and titrate with 0.01 N sodium hydroxide. The volume of sodium hydroxide solution consumed should not be more than 0.6 mL greater than the volume required for a blank test on 90 mL of the water used for dilution.

## 8.4 TOC

### 8.4.1 Equipment

8.4.1.1 TOC analyzer capable of analyzing total organic carbon in water.

8.4.1.2 Platinum sheet 1 × 1 inch, heated in a muffle oven at 800°C for 15 minutes.

### 8.4.2 Special Reagents

8.4.2.1 *Water* — The water used for all of the dilution, calibration, and standards should meet, at a minimum, the criteria for Type E1.1 in ASTM D 5127 in regard to TOC analysis.

8.4.2.2 *1000 mg/mL TOC Standard (prepare fresh weekly)* — Weigh accurately 0.2128 g of potassium acid phthalate into a 100 mL volumetric flask, add water, shake to dissolve, dilute to volume, and mix well. Lower standards (prepare fresh daily) can be made by diluting an aliquot of the 1000 mg/mL to the appropriate volume.

8.4.3 *Sample Preparation* — Weigh 50 g of hydrogen peroxide, to the nearest 0.01 g, into a 400 mL beaker. Add the platinum sheet to the sample, cover the beaker with a Teflon watch glass, and allow the reaction to go overnight (12 hours minimum). Transfer the solution to a 50 mL volumetric flask, and dilute with water meeting the criteria for Type E1.1 in ASTM D 5127 to a final volume of 50 mL.

8.4.4 *Analysis* — Using the prepared solutions, analyze TOC by the total organic carbon analyzer after the instrument has been calibrated with 0, 4, 10, and 20 µg/mL of TOC standards.

8.5 *Chloride* — Dilute 4.5 mL (5 g) of sample with 15 mL of water. Filter, if necessary, through a chloride-free filter. Add 1 mL of nitric acid and 1 mL of silver nitrate reagent solution. Any turbidity produced should be no greater than that produced when 0.01 mg of chloride ion (Cl) is treated as the sample.

8.6 *Sulfate* — To 9 mL (10 g) of sample, add 10 mL of sodium carbonate reagent solution and evaporate to dryness in a hood. Dissolve the residue in 10 mL of water and 1 mL of dilute hydrochloric acid (1 + 19); filter if necessary. Add 1 mL of barium chloride reagent solution, mix, and allow to stand for 10 minutes. Any turbidity developed should be no greater than that produced when 0.05 mg of sulfate ion (SO<sub>4</sub>) is treated as the sample.

8.7 *Phosphate* — Evaporate 4.5 mL (5 g) of sample to dryness on the steam bath and dissolve the residue in 25 mL of 0.5 N sulfuric acid. Add 1 mL of ammonium molybdate reagent solution and 1 mL of p-(methylamino)phenol sulfate reagent solution. Allow to

stand for 2 hours at room temperature. Any blue color should not exceed that produced in a standard of equal volume containing 0.01 mg of phosphate ion (PO<sub>4</sub>) and the quantities of reagents used in the sample.

8.8 *Arsenic and Antimony (as As)* — To 180 mL (200 g) of sample in a 400 mL beaker, add 5 mL of sulfuric acid and evaporate to dense fumes of sulfur trioxide in a hood. Cool, cautiously add 10 mL of water, and again evaporate to dense fumes of sulfur trioxide. Cool, and cautiously wash into a generator flask with water to make a volume of 35 mL. Proceed as described in General Method for Arsenic (and Antimony) under SEMI C1, Section 3.4.5, starting with the first sentence which begins: "Swirl the flask...." Any red color in the silver diethyldithiocarbamate solution from the sample should be no greater than that of the standard containing 0.002 mg of arsenic (As).

8.9 *Trace Metal Analysis* — The following method has given satisfactory results in determining trace metal impurities at the value specified for each of the following trace metals: aluminum (Al), boron (B), calcium (Ca), chromium (Cr), copper (Cu), gold (Au), iron (Fe), lead (Pb), magnesium (Mg), manganese (Mn), nickel (Ni), potassium (K), sodium (Na), tin (Sn), titanium (Ti), and zinc (Zn). Alternate methods may be used as long as appropriate studies demonstrate recovery between 75–125% of a known sample spike for half of the value of each specified element.

### 8.9.1 Special Reagents

8.9.1.1 *Nitric Acid, Ultra Pure* — Use nitric acid specified for ultra low metal ion content.

8.9.1.2 *Hydrochloric Acid, Ultra Pure* — Use hydrochloric acid specified for ultra low metal ion content.

### 8.9.2 Sample Preparation

8.9.2.1 *Sodium and Potassium* — In a clean environment, place 10.0 mL of water in a clean platinum crucible. Slowly add 5.0 mL of hydrogen peroxide. Allow to stand at room temperature until the effervescence ceases (approximately 20 minutes). Swirl. If swirling does not produce any more bubbles, proceed with analysis. If bubbles remain, allow to stand for 5 minutes and repeat the swirl until no bubbles are produced. Run a water blank.

8.9.2.2 *Other Elements* — Two separate samples of hydrogen peroxide are acidified to 2% with hydrochloric acid for the analysis of tin and to 2% with nitric acid for the analysis of (specified elements). Standard additions of tin to the matrix acidified with hydrochloric acid and standard additions of other specified elements to the matrix acidified with nitric acid are added to determine the response for each

element in the peroxide matrix. Aqueous acidified standards for tin in 2% hydrochloric acid and other specified elements in 2% nitric acid should be used to determine instrument responses.

#### 8.9.3 Analysis

8.9.3.1 Using the solution from Section 8.9.2.1, analyze for specified group 1 elements by flame atomic absorption spectroscopy. All other elements analyzed by plasma emission spectroscopy.

### 9 Grade 2 Procedures

NOTE 4: Each laboratory is responsible for verifying the validity of the method within its own operation.

#### 9.1 Non-Metal Impurities

9.1.1 See Section 8, which contains procedures for the following tests:

Assay

Color (APHA)

Free Acid

#### 9.2 TOC

##### 9.2.1 Equipment

9.2.1.1 TOC analyzer capable of analyzing total organic carbon in water.

9.2.1.2 Platinum sheet 1 × 1 inch, heated in a muffle oven at 800°C for 15 minutes.

##### 9.2.2 Special Reagents

9.2.2.1 Water — The water used for all of the dilution, calibration, and standards should meet, at a minimum, the criteria for Type E1.1 in ASTM D 5127 in regard to TOC analysis.

9.2.2.2 1000 mg/mL TOC Standard (*prepare fresh weekly*) — Weigh accurately 0.2128 g of potassium acid phthalate into a 100 mL volumetric flask, add water, shake to dissolve, dilute to volume, and mix well. Lower standards (*prepare fresh daily*) can be made by diluting an aliquot of the 1000 mg/mL to the appropriate volume.

##### 9.2.3 Sample Preparation

9.2.3.1 Weigh 50 g of hydrogen peroxide, to the nearest 0.01 g, into a 400 mL beaker. Add the platinum sheet to the sample, cover the beaker with a Teflon watch glass, and allow the reaction to go overnight (12 hours minimum). Transfer the solution to a 50 mL volumetric flask, dilute with water, meeting the criteria for Type E1.1 in ASTM D 5127, to a final volume of 50 mL.

#### 9.2.4 Analysis

9.2.4.1 Using the prepared solutions, analyze TOC by the total organic carbon analyzer after the instrument has been calibrated with 0, 4, 10, and 20 µg/mL of TOC standards.

#### 9.3 Anions

9.3.1 The following method has given satisfactory results in determining anion impurities at the values specified for each of the following anions: chloride (Cl), phosphate (PO<sub>4</sub>), nitrate (NO<sub>3</sub>), and sulfate (SO<sub>4</sub>). Alternate methods may be used as long as appropriate studies demonstrate a recovery between 75–125% of a known sample spike for half of the value of each specified anion.

##### 9.3.2 Special Reagents

9.3.2.1 Eluent — Prepare an eluent solution that is 2.2 mM sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) and 0.75 mM sodium bicarbonate (NaHCO<sub>3</sub>) in deionized water meeting the criteria for Type E1.1 in ASTM D 5127. Store eluent under a helium gas blanket.

9.3.2.2 Regenerant — Prepare a 0.025 N sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) in deionized water meeting the criteria for Type E1.1 in ASTM D 5127.

9.3.2.3 Potassium Carbonate Solution — Prepare a solution containing 500 mg of reagent grade potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) into 100 mL of water meeting the criteria for Type E1.1 in ASTM D 5127.

##### 9.3.3 Sample Preparation

9.3.3.1 In a clean environment, place 40 g of sample into a clean beaker. Add 1 mL of a 5 mg/mL potassium carbonate solution and evaporate carefully (at 100°C) to a volume of 0.5 mL. Dilute with water meeting the criteria for Type E1.1 in ASTM D 5127 to a final volume of 20 mL.

NOTE 5: For safety purposes, a decomposition aid such as a platinum strip should be used.

##### 9.3.4 Analysis

9.3.4.1 Using the prepared solutions and blanks, analyze chloride, nitrate, phosphate, and sulfate by ion chromatography. Run a reagent blank. Samples and reagent blanks should be prepared and analyzed in triplicate.

9.3.4.2 Columns — Precolumn should be AG4-A (Dionex) or equivalent and Separation column should be AS4-A (Dionex) or equivalent.

#### 9.4 Trace Metals Analysis

9.4.1 The following method has given satisfactory results in determining metal ion impurities at the values

specified for each of the following metals: aluminum (Al), antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), bismuth (Bi), boron (B), calcium (Ca), chromium (Cr), cobalt (Co), copper (Cu), gallium (Ga), germanium (Ge), gold (Au), iron (Fe), lead (Pb), lithium (Li), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), niobium (Nb), potassium (K), silver (Ag), sodium (Na), strontium (Sr), tantalum (Ta), tin (Sn), titanium (Ti), vanadium (V), zinc (Zn), and zirconium (Zr). Alternate methods may be used as long as appropriate studies demonstrate a recovery between 75–125% of a known sample spike for half of the value of each specified element.

#### 9.4.2 Special Reagents

9.4.2.1 *Nitric Acid, Ultra Pure* — Use nitric acid specified for low metal ion content.

9.4.2.2 *1% Nitric Acid Solution* — Dilute 10 mL of ultrapure nitric acid to 1 L of water meeting the criteria for Type E1.1 in ASTM D 5127.

9.4.2.3 *Water* — The water used for all the dilution, calibration, and standards should meet, at a minimum, the criteria for Type E1.1 in ASTM D 5127 in regard to cation analysis.

9.4.2.4 *Indium Internal Standard* — Make up the indium internal standard solution to a concentration of 20 µg/mL (ppm) from the appropriate concentrated indium standard solution.

#### 9.4.3 Sample Preparation

9.4.3.1 In a clean environment, place 20 g of sample in a tared FEP bottle, add 20 µL of the indium internal standard.

#### 9.4.4 Analysis

9.4.4.1 Using the prepared solutions and blanks, analyze sodium, potassium, calcium, and iron by graphite furnace atomic absorption (GFAA) and the remaining elements by inductively coupled plasma mass spectrometry (ICP/MS). For calibration, the standards are made up with the 1% nitric acid solution and the indium internal standard such that the final concentration is 20 ng/g of indium. Run a reagent blank.

### 10 Grade 3 Procedures

NOTE 6: The analytical procedures associated with this standard are not intended to be the only acceptable procedure or the best procedure available. The published procedures have been found to meet the required criteria for acceptance of an analytical procedure. Alternate procedures may be used if they meet the same criteria as the published procedures.

NOTE 7: Each laboratory is responsible for verifying the validity of each method within its own operation.

#### 10.1 Non-Metal Impurities

10.1.1 See Section 8, which contains procedures for the following tests:

Assay

Color (APHA)

Free Acid

#### 10.2 TOC

##### 10.2.1 Equipment

10.2.1.1 TOC analyzer capable of analyzing total organic carbon in water.

10.2.1.2 Platinum sheet 1 × 1 inch, heated in a muffle oven at 800°C for 15 minutes.

##### 10.2.2 Special Reagents

10.2.2.1 *Water* — The water used for all of the dilution, calibration, and standards should meet, at a minimum, the criteria for Type E1.1 in ASTM D 5127 in regard to TOC analysis.

10.2.2.2 *1000 µg/mL TOC Standard (prepare fresh weekly)* — Weigh accurately 0.2128 g of potassium acid phthalate into a 100 mL volumetric flask, add water, shake to dissolve, dilute to volume, and mix well. Lower standards (prepare fresh daily) can be made by diluting an aliquot of the 1000 µg/mL to the appropriate volume.

##### 10.2.3 Sample Preparation

10.2.3.1 Weigh 50 g of hydrogen peroxide, to the nearest 0.01 g, into a 400 mL beaker. Add the platinum sheet to the sample, cover the beaker with a Teflon watch glass, and allow the reaction to go overnight (12 hours minimum). Transfer the solution to a 50 mL volumetric flask, dilute with water, meeting the criteria for Type E1.1 in ASTM D 5127 to a final volume of 50 mL.

##### 10.2.4 Analysis

10.2.4.1 Using the prepared solutions, analyze TOC by the total organic carbon analyzer after the instrument has been calibrated with 0, 4, 10, and 20 µg/mL of TOC standards.

#### 10.3 Anions

10.3.1 The following method has given satisfactory results in determining anion impurities at the values specified for each of the following anions: chloride (Cl), phosphate (PO<sub>4</sub>), nitrate (NO<sub>3</sub>), and sulfate (SO<sub>4</sub>). Alternate methods may be used as long as appropriate studies demonstrate a recovery between 75–125% of a known sample spike for half of the value of each specified anion.

### 10.3.2 Special Reagents

10.3.2.1 *Eluent* — Prepare an eluent solution that is 2.2 mM sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and 0.75 mM sodium bicarbonate ( $\text{NaHCO}_3$ ) in deionized water meeting the criteria for Type E1.1 in ASTM D 5127. Store eluent under a helium gas blanket.

10.3.2.2 *Regenerant* — Prepare a 0.025 N sulfuric acid ( $\text{H}_2\text{SO}_4$ ) in deionized water meeting the criteria for Type E1.1 in ASTM D 5127.

10.3.2.3 *Potassium Carbonate Solution* — Prepare a solution containing 500 mg of reagent grade potassium carbonate ( $\text{K}_2\text{CO}_3$ ) in 100 mL of water meeting the criteria for Type E1.1 in ASTM D 5127.

### 10.3.3 Sample Preparation

10.3.3.1 In a clean environment, place 40 g of sample into a clean beaker. Add 1 mL of a 5 mg/mL potassium carbonate solution and evaporate carefully (at 100°C) to a volume of 0.5 mL. Dilute with water meeting the criteria for Type E1.1 in ASTM D 5127 to a final volume of 20 mL.

NOTE 8: For safety purposes, a decomposition aid such as a platinum strip should be used.

### 10.3.4 Analysis

10.3.4.1 Using the prepared solutions and blanks, analyze chloride, nitrate, phosphate, and sulfate by ion chromatography. Run a reagent blank. Samples and reagent blanks should be prepared and analyzed in triplicate.

10.3.4.2 *Columns* — Precolumn should be AG4-A (Dionex) or equivalent, and separation column should be AS4-A (Dionex) or equivalent.

## 10.4 Trace Metals Analysis

10.4.1 The following method has given satisfactory results in determining metal ion impurities at the values specified for each of the following metals: aluminum (Al), antimony (Sb), arsenic (As), boron (B), cadmium (Cd), calcium (Ca), chromium (Cr), cobalt (Co), copper (Cu), gold (Au), iron (Fe), lead (Pb), lithium (Li), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), potassium (K), silver (Ag), sodium (Na), strontium (Sr), tin (Sn), titanium (Ti), vanadium (V), and zinc (Zn). Alternate methods may be used as long as appropriate studies demonstrate a recovery between 75–125% of a known sample spike for half of the value of each specified element.

### 10.4.2 Special Reagents

10.4.2.1 *Nitric Acid, Ultra Pure* — Use nitric acid specified for low metal ion content.

10.4.2.2 *1% Nitric Acid Solution* — Dilute 10 mL of ultrapure nitric acid to 1 L of water meeting the criteria for Type E1.1 in ASTM D 5127.

10.4.2.3 *Water* — The water used for all the dilution, calibration, and standards should meet, at a minimum, the criteria for Type E1.1 in ASTM D 5127 in regard to cation analysis.

10.4.2.4 *Indium Internal Standard* — Make up the indium internal standard solution to a concentration of 20  $\mu\text{g}/\text{mL}$  (ppm) from the appropriate concentrated indium standard solution.

### 10.4.3 Sample Preparation

10.4.3.1 In a clean environment, place 20 g of sample into a tared FEP bottle and add 20  $\mu\text{L}$  of the indium internal standard.

### 10.4.4 Analysis

10.4.4.1 Using the prepared solutions and blanks, analyze sodium, potassium, calcium, and iron by graphite furnace atomic absorption (GFAA) and the remaining elements by inductively coupled plasma mass spectrometry (ICP/MS). For calibration, the standards are made up with the 1% nitric acid solution and the indium internal standard such that the final concentration is 20 ng/g of indium. Run a reagent blank.

## 11 Grade 4 Procedures

NOTE 9: The analytical procedures associated with this standard are not intended to be the only acceptable procedure or the best procedure available. The published procedures have been found to meet the required criteria for acceptance of an analytical procedure. Alternate procedures may be used if they meet the same criteria as the published procedures.

NOTE 10: Each laboratory is responsible for verifying the validity of each method within its own operation.

### 11.1 Non-Metal Impurities

11.1.1 See Section 8, which contains procedures for the following tests:

Assay

### 11.2 TOC

#### 11.2.1 Equipment

11.2.1.1 TOC analyzer capable of analyzing total oxidizable carbon in 31%  $\text{H}_2\text{O}_2$ . Validated instrumentation includes TOC analyzer using a high temperature platinum catalyst.

#### 11.2.2 Special Reagents

11.2.2.1 *Water* — The water used for all of the dilutions, calibrations, and standards should be the

appropriate grade of 18.2 Mohm-cm water that meets the criteria for Type E1.2 in ASTM D 5127.

**11.2.2.2 1000 µg/mL TOC Standard (prepare fresh weekly)** — Weigh accurately 0.2128 g of potassium acid phthalate into a 100 mL volumetric flask, add water, shake to dissolve, dilute to volume, and mix well. Lower standards (prepare fresh daily) can be made by diluting an aliquot of the 1000 µg/mL to the appropriate volume.

### 11.2.3 Analysis

**11.2.3.1 Analyze TOC** by directly injecting the 31% H<sub>2</sub>O<sub>2</sub> into the total oxidizable carbon analyzer after the instrument has been calibrated with 0, 5, 10, and 30 µg/mL of TOC standards.

### 11.3 Anions

**11.3.1** The following method has given satisfactory results in determining anion impurities at the values specified for each of the following anions: chloride (Cl), phosphate (PO<sub>4</sub>), nitrate (NO<sub>3</sub>), and sulfate (SO<sub>4</sub>). Alternate methods may be used as long as validity is demonstrated as defined in SEMI C1, Section 3.14 (Method Validation).

### 11.3.2 Special Reagents

**11.3.2.1 Eluent** — Prepare an eluent solution that is 100 mM potassium hydroxide (KOH) in deionized water meeting the criteria for Type E1.2 in ASTM D 5127. Prepare second solution consisting of deionized water only meeting the criteria for Type E1.2 in ASTM D 5127. Store eluents under a helium gas blanket.

### 11.3.3 Sample Preparation

**11.3.3.1** Prepare the following calibration standards by spiking 31% H<sub>2</sub>O<sub>2</sub> with appropriate amounts of individual anion standards: 0, 5, 15, 30 ppb.

### 11.3.4 Analysis

**11.3.4.1 Gradient** — Using the prepared eluent solutions, design a gradient as follows, flow rate should remain 2ml/min throughout analysis:

Pump	Time (min)	[mM KOH]
isocratic	0.0–2.5	1.0
isocratic	2.5–14	9.0
ramp	14–15	40.0
ramp	15–30	47.0

**11.3.4.2 Columns** — Precolumn should be AG15 (Dionex) or equivalent, separation column should be AS15 (Dionex) or equivalent, concentrator column should be TAC-LP1 (Dionex) or equivalent.

**11.3.4.3 Load 5mL standard then 5mL deionized water meeting the criteria for Type E1.2 in ASTM D 5127 onto concentrator column. Using the prepared solutions, blanks, and prescribed eluent gradient analyze chloride, nitrate, phosphate, and sulfate in neat 31% H<sub>2</sub>O<sub>2</sub> by ion chromatography. Run a reagent blank. Samples and reagent blanks should be prepared and analyzed in triplicate.**

### 11.4 Trace Metals Analysis

**11.4.1** The following method has given satisfactory results in determining metal ion impurities at the values specified for each of the following metals: aluminum (Al), antimony (Sb), arsenic (As), barium (Ba), boron (B), cadmium (Cd), calcium (Ca), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), lithium (Li), magnesium (Mg), manganese (Mn), nickel (Ni), potassium (K), sodium (Na), tin (Sn), titanium (Ti), vanadium (V), and zinc (Zn). Alternate methods may be used as long as validity is demonstrated as defined in SEMI C1, Section 3.14 (Method Validation).

### 11.4.2 Special Reagents

**11.4.2.1 Nitric Acid, Ultra Pure** — Use nitric acid specified for low metal ion content.

**11.4.2.2 1% Nitric Acid Solution** — Dilute 10 mL of ultrapure nitric acid to 1 L of water that meets the criteria for Type E1.2 in ASTM D 5127.

**11.4.2.3 Water** — The water used for all of the dilutions, calibrations, and standards should be the appropriate grade of 18.2 Mohm-cm water meeting the criteria for Type E1.2 in ASTM D 5127.

**11.4.2.4 Indium Internal Standard** — Make up the indium internal standard solution to a concentration of 20 µg/mL (ppm) from the appropriate concentrated indium standard solution.

### 11.4.3 Sample Preparation

**11.4.3.1** In a clean environment, place 200 g of sample into a tared FEP bottle and add 20 µL of the indium internal standard.

### 11.4.4 Analysis

**11.4.4.1** Using the prepared solutions and blanks, analyze the aforementioned metals by GFAA and/or inductively coupled plasma mass spectrometry (ICP-MS). For calibration, the standards are made up with the 1% nitric acid solution and the indium internal standard such that the final concentration is 2 ng/g of indium. Run a reagent blank.

## 12 Grade 5 Procedures

NOTE 11: The analytical procedures associated with this standard are not intended to be the only acceptable procedure or the best procedure available. The published procedures have been found to meet the required criteria for acceptance of an analytical procedure. Alternate procedures may be used if they meet the same criteria as the published procedures.

NOTE 12: Each laboratory is responsible for verifying the validity of each method within its own operation.

### 12.1 Non-Metal Impurities

12.1.1 See Section 8, which contains procedures for the following tests:

Assay

12.2 TOC

#### 12.2.1 Equipment

12.2.1.1 TOC analyzer capable of analyzing total oxidizable carbon in 31% H<sub>2</sub>O<sub>2</sub>. Validated instrumentation includes TOC analyzer using a high temperature platinum catalyst.

#### 12.2.2 Special Reagents

12.2.2.1 Water — The water used for all of the dilutions, calibrations, and standards should be the appropriate grade of 18.2 Mohm-cm water that meets the criteria for Type E1.2 in ASTM D 5127.

12.2.2.2 1000 µg/mL TOC Standard (*prepare fresh weekly*) — Weigh accurately 0.2128 g of potassium acid phthalate into a 100 mL volumetric flask, add water, shake to dissolve, dilute to volume, and mix well. Lower standards (*prepare fresh daily*) can be made by diluting an aliquot of the 1000 µg/mL to the appropriate volume.

#### 12.2.3 Analysis

12.2.3.1 Analyze TOC by directly injecting the 31% H<sub>2</sub>O<sub>2</sub> into the total oxidizable carbon analyzer after the instrument has been calibrated with 0, 5, 10, and 30 µg/mL of TOC standards.

### 12.3 Anions

12.3.1 The following method has given satisfactory results in determining anion impurities at the values specified for each of the following anions: chloride (Cl), phosphate (PO<sub>4</sub>), nitrate (NO<sub>3</sub>), and sulfate (SO<sub>4</sub>). Alternate methods may be used as long as validity is demonstrated as defined in SEMI C1, Section 3.14 (Method Validation).

#### 12.3.2 Special Reagents

12.3.2.1 Eluent — Prepare an eluent solution that is 100 mM potassium hydroxide (KOH) in deionized water meeting the criteria for Type E1.2 in ASTM D

5127. Prepare second solution consisting of deionized water only meeting the criteria for Type E1.2 in ASTM D 5127. Store eluents under a helium gas blanket.

#### 12.3.3 Sample Preparation

12.3.3.1 Prepare the following calibration standards by spiking 31% H<sub>2</sub>O<sub>2</sub> with appropriate amounts of individual anion standards: 0, 5, 15, 30 ppb.

#### 12.3.4 Analysis

12.3.4.1 Gradient — Using the prepared eluent solutions, design a gradient as follows, flow rate should remain 2mL/min throughout analysis:

Pump	Time (min)	[mM KOH]
isocratic	0.0–2.5	1.0
isocratic	2.5–14	9.0
ramp	14–15	40.0
ramp	15–30	47.0

12.3.4.2 Columns — Precolumn should be AG15 (Dionex) or equivalent, separation column should be AS15 (Dionex) or equivalent, concentrator column should be TAC-LP1 (Dionex) or equivalent.

12.3.4.3 Load 5mL standard then 5mL deionized water meeting the criteria for Type E1.2 in ASTM D 5127 onto concentrator column. Using the prepared solutions, blanks, and prescribed eluent gradient analyze chloride, nitrate, phosphate, and sulfate in neat 31% H<sub>2</sub>O<sub>2</sub> by ion chromatography. Run a reagent blank. Samples and reagent blanks should be prepared and analyzed in triplicate.

### 12.4 Trace Metals Analysis

12.4.1 The following method has given satisfactory results in determining metal ion impurities at the values specified for each of the following metals: aluminum (Al), antimony (Sb), arsenic (As), barium (Ba), boron (B), cadmium (Cd), calcium (Ca), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), lithium (Li), magnesium (Mg), manganese (Mn), nickel (Ni), potassium (K), sodium (Na), tin (Sn), titanium (Ti), vanadium (V), and zinc (Zn). Alternate methods may be used as long as validity is demonstrated as defined in SEMI C1, Specifications for Reagents; Section 3.14, Method Validation.

#### 12.4.2 Special Reagents

12.4.2.1 Nitric Acid, Ultra Pure — Use nitric acid specified for low metal ion content.

12.4.2.2 1% Nitric Acid Solution — Dilute 10 mL of ultrapure nitric acid to 1 L of water meeting the criteria for Type E1.2 in ASTM D 5127.

**12.4.2.3 Water** — The water used for all of the dilutions, calibrations, and standards should be the appropriate grade of 18.2 Mohm-cm water that meets the criteria for Type E1.2 in ASTM D 5127.

**12.4.2.4 Indium Internal Standard** — Make up the indium internal standard solution to a concentration of 20 µg/mL (ppm) from the appropriate concentrated indium standard solution.

#### 12.4.3 Sample Preparation

**12.4.3.1** In a clean environment, place 200 g of sample into a tared FEP bottle and add 20 µL of the indium internal standard.

#### 12.4.4 Analysis

**12.4.4.1** Using the prepared solutions and blanks, analyze the aforementioned metals by GF AAS and/or inductively coupled plasma mass spectrometry (ICP-MS). For calibration, the standards are made up with the 1% nitric acid solution and the indium internal

standard such that the final concentration is 2 ng/g of indium. Run a reagent blank.

### 13 VLSI Grade Procedures

13.1 Specific procedures for this grade do not exist. Refer to Sections 8 and 9 for available procedures.

### 14 Tier A Procedures

14.1 This section does not apply to this chemical.

### 15 Tier B Procedures

15.1 This section does not apply to this chemical.

### 16 Tier C Procedures

16.1 This section does not apply to this chemical.

### 17 Tier D Procedures

17.1 This section does not apply to this chemical.

**Table 1 Impurity Limits and Other Requirements for Hydrogen Peroxide**

Previous SEMI Reference #	C1.9-96	C7.5-95	C8.5-0298	--	--	C11.4-94
	Grade 1 (Specification)	Grade 2 (Specification)	Grade 3 (Specification)	Grade 4 (Specification)	Grade 5 (Specification)	VLSI Grade (Guideline)
Assay (H <sub>2</sub> O <sub>2</sub> )	30.0–32.0%	30.0–32.0%	30.0–32.0%	30.0–32.0%	30.0–32.0%	30.0–32.0% or 34.0–36.0%
Color (APHA)	10 max	10 max	10 max	--	--	10 max
Residue after Evaporation	--	--	--	--	--	20 ppm max
Chloride (Cl)	2 ppm max	200 ppb max	200 ppb max	30 ppb max	30 ppb max	0.5 ppm max
Nitrate (NO <sub>3</sub> )	--	400 ppb max	400 ppb max	30 ppb max	30 ppb max	--
Phosphate (PO <sub>4</sub> )	2 ppm max	200 ppb max	200 ppb max	30 ppb max	30 ppb max	1 ppm max
Sulfate (SO <sub>4</sub> )	5 ppm max	200 ppb max	200 ppb max	30 ppb max	30 ppb max	1 ppm max
Total Nitrogen (N)	--	--	--	--	--	2 ppm max
Total Organic Carbon (TOC)	20 ppm max	20,000 ppb max	20 ppm max	--	--	--
Total Oxidizable Carbon (TOC)	--	--	--	10 ppm max	10 ppm max	--
Free Acid	0.6 µeq/g max	0.6 µeq/g max	0.6 µeq/g max	--	--	0.6 µeq/g max
Aluminum (Al)	1 ppm max	10 ppb max	1 ppb max	100 ppt max	10 ppt max	0.2 ppm max
Ammonium (NH <sub>4</sub> )	--	--	--	--	--	2 ppm max
Antimony (Sb)	--	5 ppb max	1 ppb max	100 ppt max	10 ppt max	--
Arsenic (As)	--	5 ppb max	1 ppb max	100 ppt max	10 ppt max	--
Arsenic and Antimony (as As)	0.01 ppm max	--	--	--	--	0.01 ppm max
Barium (Ba)	--	10 ppb max	--	100 ppt max	10 ppt max	0.05 ppm max
Beryllium (Be)	--	10 ppb max	--	--	--	0.01 ppm max
Bismuth (Bi)	--	10 ppb max	--	--	--	0.02 ppm max
Boron (B)	0.1 ppm max	10 ppb max	1 ppb max	100 ppt max	10 ppt max	0.02 ppm max
Cadmium (Cd)	--	10 ppb max	1 ppb max	100 ppt max	10 ppt max	0.01 ppm max
Calcium (Ca)	0.2 ppm max	10 ppb max	1 ppb max	100 ppt max	10 ppt max	0.05 ppm max

Previous SEMI Reference #	C1.9-96	C7.5-95	C8.5-0298	--	--	C11.4-94
	Grade 1 (Specification)	Grade 2 (Specification)	Grade 3 (Specification)	Grade 4 (Specification)	Grade 5 (Specification)	VLSI Grade (Guideline)
Chromium (Cr)	0.05 ppm max	10 ppb max	1 ppb max	100 ppt max	10 ppt max	0.01 ppm max
Cobalt (Co)	--	10 ppb max	1 ppb max	--	--	0.01 ppm max
Copper (Cu)	0.05 ppm max	10 ppb max	1 ppb max	100 ppt max	10 ppt max	0.01 ppm max
Gallium (Ga)	--	10 ppb max	--	--	--	0.02 ppm max
Germanium (Ge)	--	10 ppb max	--	--	--	0.05 ppm max
Gold (Au)	0.3 ppm max	10 ppb max	10 ppb max	--	--	0.02 ppm max
Indium (In)	--	--	--	--	--	0.02 ppm max
Iron (Fe)	0.1 ppm max	10 ppb max	1 ppb max	100 ppt max	10 ppt max	0.05 ppm max
Lead (Pb)	0.3 ppm max	10 ppb max	1 ppb max	100 ppt max	10 ppt max	0.01 ppm max
Lithium (Li)	--	10 ppb max	1 ppb max	100 ppt max	10 ppt max	0.01 ppm max
Magnesium (Mg)	0.1 ppm max	10 ppb max	1 ppb max	100 ppt max	10 ppt max	0.05 ppm max
Manganese (Mn)	0.05 ppm max	10 ppb max	1 ppb max	100 ppt max	10 ppt max	0.01 ppm max
Molybdenum (Mo)	--	10 ppb max	1 ppb max	--	--	0.01 ppm max
Nickel (Ni)	0.05 ppm max	10 ppb max	1 ppb max	100 ppt max	10 ppt max	0.01 ppm max
Niobium (Nb)	--	10 ppb max	--	--	--	--
Platinum (Pt)	--	--	--	--	--	0.02 ppm max
Potassium (K)	1 ppm max	10 ppb max	1 ppb max	100 ppt max	10 ppt max	0.05 ppm max
Silver (Ag)	--	10 ppb max	1 ppb max	--	--	0.02 ppm max
Sodium (Na)	1 ppm max	10 ppb max	1 ppb max	100 ppt max	10 ppt max	0.05 ppm max
Strontium (Sr)	--	10 ppb max	1 ppb max	--	--	0.01 ppm max
Tantalum (Ta)	--	10 ppb max	--	--	--	--
Thallium (Tl)	--	10 ppb max	--	--	--	0.02 ppm max
Tin (Sn)	1 ppm max	10 ppb max	1 ppb max	100 ppt max	10 ppt max	0.02 ppm max
Titanium (Ti)	0.3 ppm max	10 ppb max	1 ppb max	100 ppt max	10 ppt max	0.01 ppm max
Vanadium (V)	--	10 ppb max	1 ppb max	100 ppt max	10 ppt max	0.01 ppm max
Zinc (Zn)	0.1 ppm max	10 ppb max	1 ppb max	100 ppt max	10 ppt max	0.05 ppm max
Zirconium (Zr)	--	10 ppb max	--	--	--	0.01 ppm max
Particles in bottles (size, #/mL)	≥ 1.0 µm, 25 max	≥ 0.5 µm, 25 max	≥ 0.5 µm, 25 max (see NOTE 1)	See NOTE 2.	See NOTE 2.	≥ 0.5 µm, 250 max

NOTE 1: Care must be taken in analyzing particles because of the potential formation of microbubbles.

NOTE 2: Due to the limitations of current particle counters, particle size and number are to be agreed upon between supplier and user. See SEMI C1, Section 3.9 for particle counting methodology.

**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.

The user's attention is called to the possibility that compliance with this standard may require use of copyrighted material or of an invention covered by patent rights. By publication of this standard, SEMI takes no position respecting the validity of any patent rights or copyrights asserted in connection with any item mentioned in this standard. Users of this standard 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 C31-0301

## SPECIFICATION FOR METHANOL

This specification was technically approved by the Global Process Chemicals Committee and is the direct responsibility of the North American Process Chemicals Committee. Current edition approved by the North American Regional Standards Committee on October 17, 1999. Initially available at [www.semi.org](http://www.semi.org) February 2001; to be published March 2001. This document replaces SEMI C1.10 in its entirety. Originally published in 1978; previously published June 1999.

### 1 Purpose

1.1 The purpose of this document is to standardize requirements for methanol used in the semiconductor industry and testing procedures to support those standards. Test methods have been shown to give statistically valid results. This document also provides guidelines for grades of methanol for which a need has been identified. In the case of the guidelines, the test methods may not have been statistically validated yet.

### 2 Scope

2.1 The scope of this document is all grades of methanol used in the semiconductor industry.

2.2 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.

### 3 Limitations

3.1 None.

### 4 Referenced Standards

#### 4.1 SEMI Standards

SEMI C1 — Specifications for Reagents

#### 4.2 ASTM Standards<sup>1</sup>

ASTM D5127 — Standard Guide for Ultra Pure Water Used in the Electronics and Semiconductor Industry

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

### 5 Terminology

5.1 None.

### 6 Physical Property (for information only)

Density at 25°C	0.79 g/mL
Boiling Point	64.5°C

<sup>1</sup> American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, Pennsylvania 19428-2959, USA. Telephone: 610.832.9585, Fax: 610.832.9555. Website: [www.astm.org](http://www.astm.org)

### 7 Requirements

7.1 The requirements for methanol for Grade 1 are listed in Table 1.

### 8 Grade 1 Procedures

NOTE 2: Each laboratory is responsible for verifying the validity of the method within its own operation.

8.1 *Assay* — Analyze the sample by gas chromatography (see SEMI C1, Section 3.1, Guidelines for Assay by Wide Bore Column Gas Chromatography). The parameters cited have given satisfactory results.

Column: 30 meter × 530 micron I.D. fused silica capillary, coated with 5 micron film of DB-1 or equivalent (100% methyl silicone which has been surface bonded and cross linked).

Column Temperature: 40°C isothermal for 5 minutes, then programmed to 200°C at 10°C/min.

Injector Temperature:	150°C
Detector Temperature:	250°C
Sample Size:	0.2 µL splitless
Carrier Gas:	Helium at 3 mL/min
Detector:	Thermal Conductivity
Approximate Retention Times (min):	
Methanol	3.0
Ethanol	4.0
Acetone	4.8

8.2 *Color* — Dilute 2.0 mL of platinum-cobalt stock solution (APHA No. 500) to 100 mL with water. Compare this standard (APHA No. 10) with 100 mL of sample in Nessler tubes. View vertically over a white background. The sample must be no darker than the standard.

8.3 *Acidity* — To 25 mL of water in a glass-stoppered flask, add 10 mL of sample and 0.1 mL of phenolphthalein indicator solution. Add 0.01 N sodium hydroxide until a slight pink color persists after shaking for one-half minute. Add 42 mL (33 g) of the sample, mix well, and titrate with 0.01 N sodium hydroxide until the pink color is reproduced. Not more than 1.0

mL of the sodium hydroxide solution should be required.

**8.4 Alkalinity** — Add 126 mL (100 g) of sample to 25 mL of water and mix well. Add 0.05 mL of methyl red indicator solution. Titrate with 0.01 N hydrochloric acid until a slight pink color is produced. Not more than 1.0 mL of the hydrochloric acid should be required.

**8.5 Residue after Evaporation** — Evaporate 253 mL (200 g) of sample to dryness. Dry at 105°C for 30 minutes, cool in a desiccator, and weigh (see SEMI C1, Section 3.3, Determination of Residue After Evaporation).

**8.6 Water** — Add 50 mL of sample to a dry titration flask and add Karl Fischer (KF) reagent to a visually or electrometrically determined endpoint that persists for 30 seconds. Add 50 mL (40 g) of sample, taking care to protect the sample and contents of the flask from moisture. Stir vigorously and titrate with Karl Fischer reagent to the same endpoint.

$$\% \text{ Water} (\text{H}_2\text{O}) = \frac{\text{mL KF reagent} \times \text{KF factor (g H}_2\text{O/mL)} \times 100}{\text{Weight of sample (g)}}$$

**8.7 Solubility in Water** — Mix 15 mL of sample with 45 mL of water. Allow to stand for 30 minutes. The solution should be as clear as an equal volume of water.

**8.8 Boron** — To 127 mL (100 g) of sample, add 0.10 mL of 10% sodium hydroxide solution, and evaporate to dryness in a nitrogen atmosphere using a covered chamber such as a Thiers assembly (or equivalent). Dissolve the residue with 2 mL of water and 0.10 mL of hydrochloric acid. Transfer to a test tube, cool in an ice bath, and add 10 mL of sulfuric acid. Then add 10 mL of carminic acid solution and remove from the ice bath. Allow to stand for 45 minutes. Prepare a standard containing 0.001 mg of boron treated exactly as the sample. Run a complete blank determination on 2 mL of water. Measure the absorbances of the sample and standard against the blank at 585 nm using 5.00 cm cells. The absorbance of the sample solution should be no greater than that of the standard.

**8.9 Chloride** — To 63 mL (50 g) of sample, add 10 mL of sodium carbonate reagent solution and evaporate to dryness on a steam bath in a hood. Dissolve the residue in 10 mL of water. Add 1 mL of nitric acid and dilute to 20 mL with water. Add 1 mL of silver nitrate reagent solution. Any turbidity produced should be no greater than that produced when 0.01 mg of chloride ion (Cl) is treated as the sample.

**8.10 Phosphate** — To 25 mL (20 g) of sample add 10 mL of sodium carbonate reagent solution and evaporate to dryness on a steam bath in a hood. Dissolve the residue in 25 mL of 0.5 N sulfuric acid. Add 1 mL of ammonium molybdate reagent solution and 1 mL of p-

(methylamino)phenol sulfate reagent solution. Allow to stand at room temperature for 2 hours. Any blue color produced should be no greater than that produced when 0.01 mg of phosphate ion (PO<sub>4</sub>) is treated as the sample.

**8.11 Arsenic and Antimony (as As)** — Evaporate 253 mL (200 g) of sample in a 400 mL beaker to a small volume in a hood. Add 50 mL of water and again evaporate to a small volume. Repeat the evaporation with water addition. Do not allow to go to dryness. Add 5 mL of nitric acid and 5 mL of sulfuric acid and evaporate to dense fumes of sulfur trioxide. Cool, cautiously add 10 mL of water, and again evaporate to dense fumes of sulfur trioxide. Cool, and cautiously wash into a generator flask with water to make a volume of 35 mL. Proceed as described in the General Method for Arsenic (and Antimony) under SEMI C1, Section 3.4.5, starting with the sentence which begins: "Swirl the flask...." Any red color in the silver diethyldithiocarbamate solution from the sample should be no greater than that of the standard containing 0.002 mg of arsenic (As).

## 8.12 Trace Metal Analysis

**8.12.1 Gold (Au)** — Analyze by graphite atomic absorption using the manufacturer's recommended procedure. This technique has been shown to give satisfactory results using a 1:4 dilution and Zeeman background correction. Each laboratory must determine the appropriate dilution and background correction for its instrument to meet the specification limit.

**8.12.2** The following method has given satisfactory results in determining trace metal impurities at the value specified for each of the following trace metals: aluminum (Al), calcium (Ca), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), magnesium (Mg), manganese (Mn), nickel (Ni), potassium (K), sodium (Na), tin (Sn), titanium (Ti), and zinc (Zn). Alternate methods may be used as long as appropriate studies demonstrate recovery between 75 - 125% of a known sample spike for half of the value of each specified item.

### 8.12.3 Special Reagents

**8.12.3.1 Hydrochloric Acid, Ultra Pure** — Use hydrochloric acid specified for ultra low metal ion content.

**8.12.3.2 2% (v/v) Hydrochloric Acid Solution** — Dilute 20 mL of ultra pure 12 M hydrochloric acid to 1 L using water meeting the criteria for Type E1 in ASTM D5127.

### 8.12.4 Sample Preparation

**8.12.4.1** In a clean environment, place 250 g of solvent in a PTFE dish. Slowly evaporate on a hot plate avoiding loss of sample by effervescence or spattering

until approximately 1 mL of liquid remains. Take up liquid and all visible residue (from walls of dish) with 1 mL ultra pure, 12 M hydrochloric acid and continue heating until approximately 0.5 mL of liquid remains. No undissolved particulate matter should be observed. Otherwise repeat the addition of hydrochloric acid until all particulate matter is dissolved. Transfer quantitatively to a 50 mL volumetric flask using 2% (v/v) hydrochloric acid and adjust liquid level to mark. Prepare a reagent blank using the same reagents and in the same manner as for the sample concentration.

#### 8.12.5 Analysis

8.12.5.1 Using the prepared sample and reagent blank, analyze group I elements potassium (K) and sodium (Na) by atomic absorption spectroscopy and all other elements by plasma emission spectroscopy. Apply, if necessary, a reagent blank correction to the final determined value of the sample.

NOTE 3: Due to the uncertainty of acid concentration in the liquid residue the final concentration can be estimated to be approximately 2% (v/v). Standard calibration solutions are to use this same acid concentration.

### 9 Grade 2 Procedures

9.1 This section does not apply to this chemical.

### 10 Grade 3 Procedures

10.1 This section does not apply to this chemical.

### 11 Grade 4 Procedures

11.1 This section does not apply to this chemical.

### 12 Grade 5 Procedures

12.1 This section does not apply to this chemical.

### 13 VLSI Grade Procedures

13.1 This section does not apply to this chemical.

### 14 Tier A Procedures

14.1 This section does not apply to this chemical.

### 15 Tier B Procedures

15.1 This section does not apply to this chemical.

### 16 Tier C Procedures

16.1 This section does not apply to this chemical.

### 17 Tier D Procedures

17.1 This section does not apply to this chemical.

**Table 1 Impurity Limits and Other Requirements for Methanol**

Previous SEMI Reference #	C1.10-96
	Grade 1
	(Specification)
Assay (CH <sub>3</sub> OH)	99.9% min
Color (APHA)	10 max
Acidity	0.3 μeq/g max
Alkalinity	0.1 μeq/g max
Residue after Evaporation	5 ppm max
Water (H <sub>2</sub> O)	0.05% max
Solubility in Water	To pass test
Boron (B)	0.01 ppm max
Chloride (Cl)	0.2 ppm max
Phosphate (PO <sub>4</sub> )	0.5 ppm max
Aluminum (Al)	0.1 ppm max
Arsenic and Antimony (as As)	0.01 ppm max
Calcium (Ca)	0.1 ppm max
Chromium (Cr)	0.1 ppm max
Copper (Cu)	0.1 ppm max
Gold (Au)	0.1 ppm max
Iron (Fe)	0.1 ppm max
Lead (Pb)	0.1 ppm max
Magnesium (Mg)	0.1 ppm max
Manganese (Mn)	0.1 ppm max



Previous SEMI Reference #	C1.10-96
	Grade 1
	(Specification)
Nickel (Ni)	0.1 ppm max
Potassium (K)	0.1 ppm max
Sodium (Na)	0.1 ppm max
Tin (Sn)	0.1 ppm max
Titanium (Ti)	0.1 ppm max
Zinc (Zn)	0.1 ppm max
Particles in bottles: size, #/mL	$\geq 1.0 \mu\text{m}$ , 10 max

**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.

The user's attention is called to the possibility that compliance with this standard may require use of copyrighted material or of an invention covered by patent rights. By publication of this standard, SEMI takes no position respecting the validity of any patent rights or copyrights asserted in connection with any item mentioned in this standard. Users of this standard 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 C32-0699

## SPECIFICATION FOR METHYL ETHYL KETONE

This specification was technically approved by the Global Process Chemicals Committee and is the direct responsibility of the North American Process Chemicals Committee. Current edition approved by the North American Regional Standards Committee on April 23, 1999. Initially available on SEMI OnLine May 1999; to be published June 1999. This document replaces SEMI C1.11 in its entirety. Originally published in 1978.

### 1 Purpose

1.1 The purpose of this document is to standardize requirements for methyl ethyl ketone used in the semiconductor industry and testing procedures to support those standards. Test methods have been shown to give statistically valid results. This document also provides guidelines for grades of methyl ethyl ketone for which a need has been identified. In the case of the guidelines, the test methods may not have been statistically validated yet.

### 2 Scope

2.1 The scope of this document is all grades of methyl ethyl ketone used in the semiconductor industry.

### 3 Limitations

3.1 None.

### 4 Referenced Documents

SEMI C1 — Specifications for Reagents

### 5 Terminology

5.1 None.

### 6 Physical Property (for information only)

Density at 25°C	0.80 g/mL
Boiling Point	79.6°C

### 7 Requirements

7.1 The requirements for methyl ethyl ketone for Grade 1 are listed in Table 1.

### 8 Grade 1 Procedures

8.1 Assay — Analyze the sample by gas chromatography (see SEMI C1, Section 3.1, Guidelines for Assay by Wide Bore Column Gas Chromatography). The parameters cited have given satisfactory results.

Column: 30 meter × 530 micron I.D. fused silica capillary, coated with 5 micron film of DB-1 or equivalent (100% methyl silicone which has been surface bonded and cross linked).

Column Temperature: 40°C isothermal for 5 minutes, then programmed to 200°C at 10°C/min.

Injector Temperature:	150°C
Detector Temperature:	250°C
Sample Size:	0.2 µL splitless
Carrier Gas:	Helium at 3 mL/min
Detector:	Thermal Conductivity
Approximate Retention Times (min):	
Methyl Ethyl Ketone	9.0
2-Butanol	10.5

8.2 *Color* — Dilute 3.0 mL of platinum-cobalt stock solution (APHA No. 500) to 100 mL with water. Compare this standard (APHA No. 15) with 100 mL of sample in Nessler tubes. View vertically over a white background. The sample must be no darker than the standard.

8.3 *Acidity* — To 25 mL of water in a glass-stoppered flask, add 10 mL of sample and 0.1 mL of phenolphthalein indicator solution. Add 0.10 N sodium hydroxide until a slight, pink color persists after shaking for one-half minute. Add 21 mL (17 g) of the sample, mix well, and titrate with 0.01 N sodium hydroxide until the pink color is reproduced. Not more than 3.0 mL of the sodium hydroxide solution should be required.

8.4 *Residue After Evaporation* — Evaporate 63 mL (50 g) of sample to dryness. Dry at 105°C for 30 minutes, cool in a desiccator, and weigh (see SEMI C1, Section 3.3, Determination of Residue After Evaporation).

8.5 *Water* — Add 25 mL of pyridine-dichloromethane mixture (1 + 1) to a dry titration flask and add Karl Fischer (KF) reagent to a visually or electrometrically determined endpoint that persists for 30 seconds. Add 25 mL (20 g) of sample, taking care to protect the sample and contents of the flask from moisture. Stir vigorously and titrate with Karl Fischer reagent to the same endpoint.

$$\text{% Water (H}_2\text{O)} = \frac{\text{mL KF reagent} \times \text{KF factor (g H}_2\text{O/mL)} \times 100}{\text{Weight of sample (g)}}$$

**8.6 Phosphate** — To 12.5 mL (10 g) of sample, add 10 mL of sodium carbonate reagent solution and evaporate to dryness on a steam bath in a hood. Carefully dissolve the residue in 25 mL of 0.5 N sulfuric acid. Add 1 mL of ammonium molybdate reagent solution and 1 mL of p-(methylamino)phenol sulfate reagent solution. Allow to stand at room temperature for 2 hours. Any blue color should be no greater than that produced when 0.01 mg of phosphate ion ( $\text{PO}_4$ ) is treated as the sample.

**8.7 Heavy Metals (as Pb)** — Evaporate 25 mL (20 g) of sample to dryness on a steam bath in a hood. Dissolve the residue in 3 mL of dilute hydrochloric acid (1 + 1) and dilute with water to 15 mL. If necessary, filter through a small filter, and wash the evaporating dish and the filter with 10 mL of water. Dilute to 25 mL with water. For the standard, dilute a solution containing 0.02 mg of lead ion (Pb) and 3 mL of dilute hydrochloric acid (1 + 1) to 25 mL with water. Adjust the pH of both solutions to between 3 and 4 with dilute ammonium hydroxide (10%  $\text{NH}_3$ ) or with acetic acid, and dilute with water to 40 mL. To each solution, add 10 mL of freshly prepared hydrogen sulfide water and compare. The sample solution should be no darker than the standard.

**8.8 Arsenic and Antimony (as As)** — Evaporate 250 mL (200 g) of sample in a 400 mL beaker to a small volume in a hood. Add 50 mL of water and again evaporate to a small volume. Repeat the evaporation with water addition. Do not allow to go to dryness. Add 5 mL of nitric acid and 5 mL of sulfuric acid and evaporate to dense fumes of sulfur trioxide. Cool and cautiously add 10 mL of water, and again evaporate to dense fumes of sulfur trioxide. Cool and cautiously wash into a generator flask with water to make a volume of 35 mL. Proceed as described in the General Method for Arsenic (and Antimony) under SEMI C1, Section 3.4.5, starting with the sentence which begins, "Swirl the flask...." Any red color in the silver diethyldithiocarbamate solution of the sample should be no greater than that of the standard containing 0.002 mg of arsenic (As).

**8.9 Trace Element Contents** — By a suitable emission spectrographic procedure, determine for each of the specified trace elements that its content is not greater than the stated specification limit (see SEMI C1, Section 3.5, Guidelines for Determination of Trace Elements by Emission Spectrography).

## **9 Grade 2 Procedures**

9.1 This section does not apply to this chemical.

## **10 Grade 3 Procedures**

10.1 This section does not apply to this chemical.

## **11 Grade 4 Procedures**

11.1 This section does not apply to this chemical.

## **12 Grade 5 Procedures**

12.1 This section does not apply to this chemical.

## **13 VLSI Grade Procedures**

13.1 This section does not apply to this chemical.

## **14 Tier A Procedures**

14.1 This section does not apply to this chemical.

## **15 Tier B Procedures**

15.1 This section does not apply to this chemical.

## **16 Tier C Procedures**

16.1 This section does not apply to this chemical.

## **17 Tier D Procedures**

17.1 This section does not apply to this chemical.

**Table 1 Impurity Limits and Other Requirements for Methyl Ethyl Ketone**

Previous SEMI Reference #	C1.11-95
	Grade 1
	(Specification)
Assay ( $\text{CH}_3\text{COCH}_2\text{CH}_3$ )	99.5% min
Color (APHA)	15 max
Acidity	0.6 $\mu\text{eq/g}$ max
Residue after Evaporation	20 ppm max
Water ( $\text{H}_2\text{O}$ )	0.2% max

Previous SEMI Reference #	C1.11-95
	Grade 1
	(Specification)
Phosphate (PO <sub>4</sub> )	1 ppm max
Heavy Metals (as Pb)	1 ppm max
Aluminum (Al)	1 ppm max
Arsenic and Antimony (as As)	0.01 ppm max
Barium (Ba)	1 ppm max
Boron (B)	0.2 ppm max
Cadmium (Cd)	1 ppm max
Calcium (Ca)	1 ppm max
Chromium (Cr)	0.5 ppm max
Cobalt (Co)	0.1 ppm max
Copper (Cu)	0.1 ppm max
Gallium (Ga)	0.5 ppm max
Germanium (Ge)	1 ppm max
Gold (Au)	0.5 ppm max
Iron (Fe)	1 ppm max
Lithium (Li)	1 ppm max
Magnesium (Mg)	1 ppm max
Manganese (Mn)	1 ppm max
Nickel (Ni)	0.1 ppm max
Potassium (K)	1 ppm max
Silicon (Si)	1 ppm max
Silver (Ag)	0.5 ppm max
Sodium (Na)	1 ppm max
Strontium (Sr)	1 ppm max
Tin (Sn)	1 ppm max
Zinc (Zn)	1 ppm max

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.

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

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# SEMI C33-0301

## SPECIFICATIONS FOR n-METHYL 2-PYRROLIDONE

These specifications were technically approved by the Global Process Chemicals Committee and are the direct responsibility of the North American Process Chemicals Committee. Current edition approved by the North American Regional Standards Committee on October 17, 1999. Initially available at [www.semi.org](http://www.semi.org) February 2001; to be published March 2001. This document replaces SEMI C1.25, C7.16, and C8.11 in their entirety. Originally published in 1986, 1992, and 1998 respectively; previously published June 1999.

### 1 Purpose

1.1 The purpose of this document is to standardize requirements for n-methyl 2-pyrrolidone used in the semiconductor industry and testing procedures to support those standards. Test methods have been shown to give statistically valid results. This document also provides guidelines for grades of n-methyl 2-pyrrolidone for which a need has been identified. In the case of the guidelines, the test methods may not have been statistically validated yet.

### 2 Scope

2.1 The scope of this document is all grades of n-methyl 2-pyrrolidone used in the semiconductor industry.

2.2 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.

### 3 Limitations

3.1 None.

### 4 Referenced Standards

#### 4.1 SEMI Standards

SEMI C1 — Specifications for Reagents

#### 4.2 ASTM Standards<sup>1</sup>

ASTM D5127 — Standard Guide for Ultra Pure Water Used in the Electronics and Semiconductor Industry

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

### 5 Terminology

5.1 None.

<sup>1</sup> American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, Pennsylvania 19428-2959, USA. Telephone: 610.832.9585, Fax: 610.832.9555. Website: [www.astm.org](http://www.astm.org)

### 6 Physical Property (for information only)

Density at 25°C	1.03 g/mL
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### 7 Requirements

7.1 The requirements for n-methyl 2-pyrrolidone for Grades 1, 2, and 3 are listed in Table 1.

### 8 Grade 1 Procedures

NOTE 2: Due to the uncertainty of acid concentration in the liquid residue, the final concentration can be estimated to be approximately 2% (v/v).

NOTE 3: Each laboratory is responsible for verifying the validity of the method within its own operation.

8.1 *Assay* — Analyze the sample by gas chromatography (see SEMI C1, Section 3.1, Guidelines for Assay by Wide Bore Column Gas Chromatography). The parameters cited have given satisfactory results.

Column: 30 × 530 micron I.D. fused silica capillary, coated with 5 micron film of DB-1 or equivalent (100% methyl silicone which has been surface bonded and cross linked).

Column Temperature:	100°C isothermal
Injector Temperature:	250°C
Detector Temperature:	300°C
Sample Size:	0.2 µL splitless
Carrier Gas:	Helium at 5 mL/min
Detector:	Thermal Conductivity
Approximate Retention Times (min):	
Butyrolactone	15.2
1-Methyl 2-Pyrrolidone	20.2
Methyl Homologue	21.2
Methyl Homologue	23.0

8.2 *Color* — Dilute 10.0 mL of platinum-cobalt stock solution (APHA No. 500) with water. Compare this standard (APHA No. 50) with 100 mL of sample in Nessler tubes. View vertically over a white background. The sample must be no darker than the standard.

8.3 *Water* — Add 25 mL of methanol to a dry titration flask and add Karl Fischer (KF) reagent to a visually or electrometrically determined endpoint that persists for 30 seconds. Add 98 mL (100 g) of sample, taking care to protect the sample and contents of the flask from moisture. Stir vigorously and titrate with Karl Fischer reagent to the same endpoint.

$$\% \text{ Water } (\text{H}_2\text{O}) = \frac{\text{mL KF reagent} \times \text{KF factor (g H}_2\text{O/mL)} \times 100}{\text{Weight of sample (g)}}$$

8.4 *Free Amines* — Weigh 63 mL (65 g) of sample into a 500 mL beaker. Add 100 mL of 2-propanol and mix thoroughly. Into the solution, insert a pH and reference electrodes connected to a pH meter set to the direct voltage mode. Titrate potentiometrically with 0.05 N hydrochloric acid in 2-propanol. Express the result in terms of methylamine:

$$\% \text{ Free Amines as } (\text{CH}_3\text{NH}_2) = \frac{\text{mL} \times \text{N of HCl} \times 3.10}{\text{Weight of sample (g)}}$$

8.5 *Chloride* — In a 50 mL glass-stoppered graduated cylinder, dilute 24.5 mL (25 g) of sample with water to volume. Place a 10 mL aliquot of this solution into a 50 mL Nessler tube and a 30 mL aliquot into a second tube. To the first tube add 0.01 mg of chloride standard and mix. Dilute the contents of each tube to about 45 mL with water, mix, add 1 mL of nitric acid and 1 mL of silver nitrate reagent solution, mix thoroughly, and allow to stand for 10 minutes. Any turbidity produced by the sample should be no greater than that of the 0.01 mg standard.

8.6 *Phosphate* — Add 20 mL (20) of sample to 100 mL of dilute ammonium hydroxide (1 + 4). Prepare a standard containing 0.1 mg of phosphate ion ( $\text{PO}_4^{3-}$ ) in 100 mL of dilute ammonium hydroxide. Proceed as follows with each of the two solutions.

8.6.1 Add, while stirring vigorously, 3.5 mL of a 10% solution of ferric nitrate 9-hydrate. Allow to stand for 15 minutes. If the precipitate has not coagulated by this time, warm gently (avoid boiling). Filter and wash the precipitate on the filter with several portions of quite dilute ammonium hydroxide (1 + 9). Discard the filtrate and washings. Dissolve the precipitate on the filter with 50 mL nitric acid (1 + 3) added in small portions. Catch the filtrate in a 250 mL glass-stoppered conical flask. Add 13 mL of ammonium hydroxide (28-32%  $\text{NH}_3$ ) to the flask while swirling and continue agitation until any precipitate redissolves. Warm the solution to 40°C and add 50 mL of ammonium molybdate-nitric acid reagent solution. Shake vigorously for 5 minutes and allow to stand at 40°C for 2 hours. The precipitate, if any, for the sample should be no greater than that for the standard.

8.6.2 *Ammonium Molybdate-Nitric Acid Reagent Solution* — Mix thoroughly 100 g of molybdate acid, 85%, with 240 mL of water and 140 mL of ammonium hydroxide (28 - 32%  $\text{NH}_3$ ). Filter and add 60 mL of nitric acid. Cool and while stirring continually, pour into a cooled mixture of 400 mL of nitric acid and 960 mL of water. Add 0.1 g of ammonium phosphate, monobasic,  $\text{NH}_4\text{H}_2\text{PO}_4$ , allow to stand 24 hours and filter through glass wool.

8.7 *Arsenic and Antimony (as As)* — Evaporate 20 mL (20 g) of sample in a 150 mL beaker to a small volume on a hot plate. Cool, add carefully 15 mL of nitric acid and 5 mL of sulfuric acid, and evaporate to dense fumes of sulfur trioxide. Add 10 mL of nitric acid and again evaporate to dense fumes. If carbon is still present, cool, add 1 mL of 30% hydrogen peroxide, and evaporate to dense fumes of sulfur trioxide. Repeat this step with hydrogen peroxide addition until carbon has been removed completely. Cool, and cautiously wash the colorless residue into a generator flask with water to make a volume of 35 mL. Proceed as described in the General Method for Arsenic (and Antimony) under SEMI C1, Section 3.4.5, starting with the sentence that begins "Swirl the flask...". Any red color in the silver diethyldithiocarbamate solution of the sample should be no greater than that of the standard containing 0.002 mg of arsenic (As).

8.8 *Trace Metal Analysis* — The following method has given satisfactory results in determining trace metal impurities at the value specified for each of the following trace metals: aluminum (Al), boron (B), calcium (Ca), chromium (Cr), copper (Cu), gold (Au), iron (Fe), lead (Pb), magnesium (Mg), manganese (Mn), nickel (Ni), potassium (K), sodium (Na), tin (Sn), titanium (Ti), and zinc (Zn). Alternate methods may be used as long as appropriate studies demonstrate recovery between 75–125% of a known sample spike for half of the value of each specified item.

#### 8.8.1 Special Reagents

8.8.1.1 *Hydrochloric Acid, Ultra Pure* — Use hydrochloric acid specified for ultra low metal ion content.

8.8.1.2 *Mannitol Powder* — Use mannitol specified for reagent grade (A.C.S.) and determined, via the reagent blank, to be ultra metal ion content.

8.8.1.3 *5% Mannitol Solution* — Dissolve and dilute 5 g of mannitol to 100 mL using water meeting the criteria for Type E1.1 in ASTM D5127.

8.8.1.4 *2% (v/v) Hydrochloric Acid Solution* — Dilute 20 mL of ultra pure, 12 M hydrochloric acid to 1 L using water meeting the criteria for Type E1.1 in ASTM D5127.

### 8.8.2 Sample Preparation

8.8.2.1 In a clean environment, place 250 g of solvent in a PTFE dish. Add 0.5 mL of freshly prepared 5% mannitol solution. Slowly evaporate on a hot plate, avoiding loss of sample by effervescence or spattering until approximately 1 mL of liquid remains. Take up liquid and all visible residue (from walls of dish) with 1 mL ultra pure, 12 M hydrochloric acid and continue heating until approximately 0.5 mL of liquid remains. No undissolved particulate matter should be observed. Otherwise, repeat the addition of hydrochloric acid until all particulate matter is dissolved. Transfer quantitatively to a 50 mL volumetric flask using 2% (v/v) hydrochloric acid and adjust liquid level to mark. Prepare a reagent blank using the same reagents and in the same manner as for the sample concentration.

### 8.8.3 Analysis

8.8.3.1 Using the prepared sample and reagent blank, analyze group 1 elements potassium (K) and sodium (Na) by atomic absorption spectroscopy and all other elements by plasma emission spectrometry. Apply, if necessary, a reagent blank correction to the final determined value of the sample.

## 9 Grade 2 Procedures

9.1 Non-Metal Impurities — See Section 8, which contains procedures for the following tests:

Assay

Color (APHA)

Water ( $H_2O$ )

### 9.2 Methyl Amines

9.2.1 The following method has given satisfactory results in determining methyl amine impurities at the values specified for each of the following methyl amines: mono-methylamine (MMA), di-methylamine (DMA), and tri-methylamine (TMA). Alternative methods may be used as long as appropriate studies demonstrate a recovery between 75 - 125% of a known sample spike for half of the value of each specified element.

### 9.2.2 Special Reagents

9.2.2.1 *Eluent* — Prepare 0.025 N hydrochloric (HCl) solution in deionized water meeting the criteria for Type E1.1 in ASTM D5127.

9.2.2.2 *Regenerant* — Prepare a 0.1 M tetrabutylammonium hydroxide (TBAOH) solution in deionized water meeting the criteria for Type E1.1 in ASTM D5127.

9.2.3 *Sample Preparation* — Sample is injected neat.

### 9.2.4 Analysis

9.2.4.1 Using the prepared solutions and blanks, analyze mono-methylamine, di-methylamine, and tri-methylamine by ion chromatography. Run a reagent blank. Samples and reagent blanks should be prepared and analyzed in triplicate.

9.2.4.2 *Columns* — Precolumn should be CG2 (Dionex) or equivalent and separation column should be a CS2 (Dionex) or equivalent.

### 9.3 Anions

9.3.1 The following method has given satisfactory results in determining various anions at the values specified for each of the following anions: chloride (Cl), nitrate ( $NO_3$ ), phosphate ( $PO_4$ ), and sulfate ( $SO_4$ ). Alternate methods may be used as long as appropriate studies demonstrate a recovery between 75–125% of a known sample spike for half of the value of each specified anion.

### 9.3.2 Special Reagents

9.3.2.1 *Eluent* — Prepare a solution containing 0.38 g of sodium carbonate ( $Na_2CO_3$ ) and 0.29 g of sodium bicarbonate ( $NaHCO_3$ ) in 2 liters of deionized water meeting the criteria for Type E1.1 in ASTM D5127.

9.3.2.2 *Regenerant* — Deionized water meeting the criteria for Type E1.1 in ASTM D5127.

### 9.3.3 Sample Preparation

9.3.3.1 20 mL of NMP is added to a 100 mL plastic volumetric flask and is filled to the mark using deionized water meeting the criteria for Type E1.1 in ASTM D5127.

### 9.4 Analysis

9.4.1 Using the prepared solutions and blanks, analyze chloride, nitrate, phosphate, and sulfate by ion chromatography. Run a reagent blank. Samples and blanks should be prepared in triplicate.

9.4.2 *Columns* — Precolumn should be AG3 (Dionex) or equivalent and the separation column should be AS3 (Dionex) or equivalent.

### 9.5 Trace Metals Analysis

9.5.1 The following method has given satisfactory results in determining metal ion impurities at the values specified for each of the following metals: aluminum (Al), antimony (Sb), arsenic (As), boron (B), cadmium (Cd), calcium (Ca), chromium (Cr), cobalt (Co), copper (Cu), gold (Au), iron (Fe), lead (Pb), lithium (Li), magnesium (Mg), manganese (Mn), nickel (Ni), potassium (K), silver (Ag), sodium (Na), strontium (Sr),

tin (Sn), titanium (Ti), vanadium (V), and zinc (Zn). Alternate methods may be used as long as appropriate studies demonstrate a recovery between 75 - 125% of a known sample spike for half of the value of each specified element.

#### 9.5.2 Special Reagents

9.5.2.1 *Nitric Acid, Ultra Pure* — Use nitric acid specified for low metal ion content.

9.5.2.2 *Water* — The water used for all the dilution, calibration, and standards should meet, at a minimum, the criteria for Type E1.1 in ASTM D5127 in regard to cation analysis.

9.5.2.3 *Indium Internal Standard* — Make up the indium internal standard solution to a concentration of 20 µg/mL (ppm) from the appropriate concentrated indium standard solution.

#### 9.5.3 Sample Preparation

9.5.3.1 Place sample (1 gram) in a quartz dish. Slowly evaporate to dryness (45 min. at 70–80°C). Add 2 grams of concentrated nitric acid and heat for 15 minutes until approximately 1 gram remains. Remove the hotplate and add DI water to a final weight of 10 grams.

#### 9.5.4 Analysis

9.5.4.1 Using the prepared solution and blanks, analyze the elements by inductively coupled plasma mass spectrometry (ICP/MS). For calibration, the standards are made up with 1% nitric acid solution and the indium internal standard such that the final indium concentration is 20 ng/g.

### 10 Grade 3 Procedures

10.1 *Non-Metal Impurities* — See Section 8, which contains procedures for the following tests:

Assay

Color (APHA)

Water ( $H_2O$ )

#### 10.2 Methyl Amines

10.2.1 The following method has given satisfactory results in determining methyl amine impurities at the values specified for each of the following methyl amines: mono-methylamine (MMA), dimethylamine (DMA), and trimethylamine (TMA). Alternative methods may be used as long as appropriate studies demonstrate a recovery between 75 - 125% of a known sample spike for half of the value of each specified element.

#### 10.2.2 Special Reagents

10.2.2.1 *Eluent* — Prepare 0.025 N hydrochloric acid (HCl) solution in deionized water meeting the criteria for Type E1.1 in ASTM D5127.

10.2.2.2 *Regenerant* — Prepare a 0.1 M tetrabutylammonium hydroxide (TBAOH) solution in deionized water meeting the criteria for Type E1.1 in ASTM D5127.

10.2.3 *Sample Preparation* — Sample is injected neat.

#### 10.2.4 Analysis

10.2.4.1 Using the prepared solutions and blanks, analyze mono-methylamine, di-methylamine, and tri-methylamine by ion chromatography. Run a reagent blank. Samples and reagent blanks should be prepared and analyzed in triplicate.

10.2.4.2 *Columns* — Pre-column should be CG2 (Dionex) or equivalent and separation column should be a CS2 (Dionex) or equivalent.

### 10.3 Anions

10.3.1 The following method has given satisfactory results in determining various anions at the values specified for each of the following anions: chloride (Cl), nitrate ( $NO_3^-$ ) phosphate ( $PO_4^{3-}$ ) and sulfate ( $SO_4^{2-}$ ). Alternate methods may be used as long as appropriate studies demonstrate a recovery between 75–125% of a known sample spike for half of the value of each specified anion.

#### 10.3.2 Special Reagents

10.3.2.1 *Eluent* — Prepare a solution containing 0.38 g of sodium carbonate ( $Na_2CO_3$ ) and 0.29 g of sodium bicarbonate ( $NaHCO_3$ ) in 2 liters of deionized water meeting the criteria for Type E1.1 in ASTM D5127.

10.3.2.2 *Regenerant* — Deionized water meeting the criteria for Type E1.1 in ASTM D5127.

#### 10.3.3 Sample Preparation

10.3.3.1 20 mL of NMP is added to a 100 mL plastic volumetric flask and is filled to the mark using deionized water meeting the criteria for Type E1.1 in ASTM D5127.

#### 10.3.4 Analysis

10.3.4.1 Using the prepared solutions and blanks, analyze chloride, nitrate, phosphate, and sulfate by ion chromatography. Run a reagent blank. Samples and blanks should be prepared in triplicate.

10.3.4.2 *Columns* — Pre-column should be AG3 (Dionex) or equivalent and the separation column should be AS3 (Dionex) or equivalent.

## 10.4 Trace Metal Analysis

10.4.1 The following method has given satisfactory results in determining metal ion impurities at the values specified for each of the following metals: aluminum (Al), antimony (Sb), arsenic (As), boron (B), calcium (Ca), chromium (Cr), copper (Cu), gold (Au), iron (Fe), lead (Pb), magnesium (Mg), manganese (Mn), nickel (Ni), potassium (K), sodium (Na), tin (Sn), titanium (Ti), and zinc (Zn). Alternate methods may be used as long as appropriate studies demonstrate a recovery between 75–125% of a known sample spike for half of the value of each specified element.

### 10.4.2 Special Reagents

10.4.2.1 *Nitric Acid, Ultra Pure* — Use nitric acid specified for low metal ion content.

10.4.2.2 *Water* — The water used for all the dilution, calibration, and standards should meet, at a minimum, the criteria for Type E1.1 in ASTM D5127 in regard to cation analysis.

### 10.4.3 Sample Preparation

10.4.3.1 In a 100 mL volumetric, add 20 mL of sample and fill to the mark such that the final solution contains 2% nitric acid.

### 10.4.4 Standard Preparation

10.4.4.1 Four standards are prepared such that the final solution contains 2% nitric acid (i.e., 2% of 70% nitric acid vol/vol) and 20% vol/vol sample. The four standards are 0.5, 1, 5, and 10 ppb.

### 10.4.5 Analysis

10.4.5.1 This is a method of standard addition procedure. Using the prepared solutions, analyze the

elements by inductively coupled plasma mass spectrometry (ICP/MS).

10.4.5.2 Hot plasma conditions with shield are used for the following elements: Ti, Mn, Ni, Cu, As, Sb, Sn, Au, and Pb.

10.4.5.3 Cold plasma conditions with shield are used for the follow elements, B, Na, Mg, Al, K, Ca, Cr, Fe, and Zn.

## 11 Grade 4 Procedures

11.1 This section does not apply to this chemical.

## 12 Grade 5 Procedures

12.1 This section does not apply to this chemical.

## 13 VLSI Grade Procedures

13.1 This section does not apply to this chemical.

## 14 Tier A Procedures

14.1 This section does not apply to this chemical.

## 15 Tier B Procedures

15.1 This section does not apply to this chemical.

## 16 Tier C Procedures

16.1 This section does not apply to this chemical.

## 17 Tier D Procedures

17.1 This section does not apply to this chemical.

**Table 1 Impurity Limits and Other Requirements for n-Methyl 2-Pyrrolidone**

Previous SEMI Reference #	C1.25-95	C7.16-95	C8.11-0698
	Grade 1	Grade 2	Grade 3
(Specification)	(Specification)	(Specification)	(Specification)
Assay (see NOTE 1) ( $\text{CH}_3\text{N}(\text{CH}_2)_3\text{CO}$ )	99.5% min	99.8% min	99.8%
Color (APHA)	50 max	50 max	30 max
Water ( $\text{H}_2\text{O}$ )	0.05% max	0.05% max	0.03% max
Free Amines (as $\text{CH}_3\text{NH}_2$ )	50 ppm max	5,000 ppb max	5 ppm max
Chloride (Cl)	1 ppm max	500 ppb max	300 ppb max
Nitrate ( $\text{NO}_3$ )	--	500 ppb max	400 ppb max
Phosphate ( $\text{PO}_4$ )	5 ppm max	500 ppb max	250 ppb max
Sulfate ( $\text{SO}_4$ )	--	500 ppb max	250 ppb max
Aluminum (Al)	0.1 ppm max	20 ppb max	5 ppb max
Antimony (Sb)	--	20 ppb max	10 ppb max
Arsenic (As)	--	20 ppb max	10 ppb max
Arsenic and Antimony (as As)	0.1 ppm max	--	--



Previous SEMI Reference #	C1.25-95	C7.16-95	C8.11-0698
	Grade 1 (Specification)	Grade 2 (Specification)	Grade 3 (Specification)
Boron (B)	0.1 ppm max	20 ppb max	10 ppb max
Cadmium (Cd)	--	20 ppb max	--
Calcium (Ca)	--	20 ppb max	5 ppb max
Chromium (Cr)	0.1 ppm max	100 ppb max	10 ppb max
Cobalt (Co)	--	20 ppb max	--
Copper (Cu)	0.1 ppm max	20 ppb max	5 ppb max
Gold (Au)	0.1 ppm max	20 ppb max	5 ppb max
Iron (Fe)	0.1 ppm max	20 ppb max	10 ppb max
Lead (Pb)	0.1 ppm max	20 ppb max	5 ppb max
Lithium (Li)	--	20 ppb max	--
Magnesium (Mg)	0.1 ppm max	20 ppb max	5 ppb max
Manganese (Mn)	0.1 ppm max	100 ppb max	5 ppb max
Nickel (Ni)	0.1 ppm max	20 ppb max	5 ppb max
Potassium (K)	0.1 ppm max	20 ppb max	5 ppb max
Silver (Ag)	--	20 ppb max	--
Sodium (Na)	0.3 ppm max	20 ppb max	10 ppb max
Strontium (Sr)	--	20 ppb max	--
Tin (Sn)	0.1 ppm max	20 ppb max	5 ppb max
Titanium (Ti)	0.1 ppm max	20 ppb max	5 ppb max
Vanadium (V)	--	20 ppb max	--
Zinc (Zn)	0.1 ppm max	100 ppb max	10 ppb max
Particles in bottles: size, #/mL	≥ 1.0 µm, 10 max	≥ 0.5 µm, 200 max	≥ 0.5 µm, 15 max

NOTE 1: Assay by gas chromatography includes 3- and 4-methyl homologs.

**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.

The user's attention is called to the possibility that compliance with this standard may require use of copyrighted material or of an invention covered by patent rights. By publication of this standard, SEMI takes no position respecting the validity of any patent rights or copyrights asserted in connection with any item mentioned in this standard. Users of this standard 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 C34-0699

# SPECIFICATION AND GUIDELINE FOR MIXED ACID ETCHANTS

This specification and this guideline were technically approved by the Global Process Chemicals Committee and are the direct responsibility of the North American Process Chemicals Committee. Current edition approved by the North American Regional Standards Committee on April 23, 1999. Initially available on SEMI OnLine May 1999; to be published June 1999. This document replaces SEMI C2.1 and C7.19 in their entirety. Originally published in 1981 and 1995 respectively.

## 1 Purpose

1.1 The purpose of this document is to standardize requirements for mixed acid etchants used in the semiconductor industry and testing procedures to support those standards. Test methods have been shown to give statistically valid results. This document also provides guidelines for grades of mixed acid etchants for which a need has been identified. In the case of the guidelines, the test methods may not have been statistically validated yet.

## 2 Scope

2.1 The scope of this document is all grades of mixed acid etchants used in the semiconductor industry.

## 3 Limitations

3.1 None.

## 4 Referenced Documents

SEMI C1 — Specifications for Reagents

SEMI C2 — Specifications for Etchants

## 5 Terminology

*mixed acid etchant* — any combination of nitric, hydrofluoric, and acetic acids with the relative composition expressed in terms of volumes of 70% nitric acid, 49% hydrofluoric acid, and glacial acetic acid, respectively. In the expression, all the relative volumes shall be reduced to a ratio of the smallest whole numbers. For example, a 3:1:2 mixed acid etchant would imply a mixture of 3 volumes of 70% nitric acid, 1 volume of 49% hydrofluoric acid, and 2 volumes of glacial acetic acid. If a component is absent, its relative volume shall be taken as zero. For example, a 3:1:0 mixed acid etchant would imply that no acetic acid is present.

## 6 Composition

6.1 The content of each of the components of a mixed acid etchant shall be expressed on a weight/weight basis of the 100% acids in the total mixture. For the volume-to-weight conversion, the densities shall be taken as 1.415, 1.153 g/mL, and 1.050 g/mL for 70% nitric acid,

49% hydrofluoric acid, and glacial acetic acid, respectively.

## 7 Tolerances

Nitric Acid:	± 1.0% ( $\pm 0.16 \text{ meq/g}$ )
Hydrofluoric Acid:	± 0.5% ( $\pm 0.25 \text{ meq/g}$ )
Acetic Acid:	± 1.0% ( $\pm 0.17 \text{ meq/g}$ )

## 8 Requirements

8.1 The requirements for mixed acid etchants for Grade 1 and Tier A are listed in Table 1.

## 9 Grade 1 Procedures

9.1 *Total Acidity* — Accurately weigh a sample containing 30 to 40 milliequivalents of acidity in a polyethylene weighing bottle. Transfer with water to a 250 mL polyethylene beaker and dilute to approximately 100 mL. Add 10 drops of phenolphthalein indicator solution and titrate with 1 N standardized sodium hydroxide to a faint pink end point. Calculate the total acidity (A):

$$\text{Total Acidity} (\text{meq/g}) = \frac{\text{mL} \times \text{N of NaOH}}{\text{Weight of sample (g)}} = A$$

9.2 *Hydrofluoric Acid* — Accurately weigh a sample containing 0.3 to 0.5 g of hydrofluoric acid in a polyethylene weighing bottle. Transfer with water to a polyethylene beaker and dilute to approximately 100 mL. Add 10 drops of phenolphthalein indicator solution and titrate with 1 N or stronger sodium hydroxide solution to a faint pink endpoint. Add 25 mL of Acetate Buffer for Hydrofluoric Acid Determination and 1 g of Eriochrome Cyanine R indicator mixture. Mix continuously by magnetic stirring and titrate with standardized aluminum chloride solution to a pink-purple endpoint.

$$\% \text{ Hydrofluoric Acid} = \frac{\text{mL} \times \text{HF factor of AlCl}_3 \text{ soln.}}{\text{Weight of sample (g)}} = A$$

9.3 *Nitric Acid* — Accurately weigh a sample containing 0.9 to 1.1 g of nitric acid in a polyethylene weighing bottle. Quantitatively transfer into a 100 mL volumetric flask containing 50 mL of 2% boric acid solution, dilute to volume with water, and mix thoroughly. Following the manufacturer's direction,

ready a spectrophotometer and set the wavelength to 302 nm. Transfer the sample solution to a 1 cm fused silica cell and measure the absorbance of the sample solution versus water. Read from a previously established calibration curve the grams of nitric acid present in the sample solution (see SEMI C2, Section 3.2, Determination of Nitric Acid by Ultraviolet Absorption Spectrophotometry).

$$\% \text{ Nitric Acid} = \frac{\text{grams of HNO}_3 \text{ calibration curve} \times 100}{\text{Weight of sample (g)}}$$

**9.4 Acetic Acid** — The acetic acid content is calculated by deducting the acidity found for each of the other components from the value for the total acidity.

$$\% \text{ Acetic Acid} = \left[ A - \frac{\% \text{HF}}{2.001} - \frac{\% \text{HNO}_3}{6.302} \right] \times 6.005$$

**9.5 Arsenic and Antimony (as As)** — To 50 g of sample in a polyfluorocarbon dish, add 5 mL of hydrochloric acid and 5 mL of sulfuric acid. Mix gently and evaporate in a sandbath in a hood to dense fumes of sulfur trioxide. Cool, cautiously add 10 mL of water, and re-evaporate to dense fumes of sulfur trioxide. Cool, and cautiously wash into a generator flask with water to make a volume of 35 mL. Proceed as described in the General Method for Arsenic (and Antimony) under SEMI C1, Section 3.4.5, starting with the sentence which begins, "Swirl the flask..." Any red color in the silver diethyldithiocarbamate solution of the sample should not exceed that in the standard containing 0.0015 mg of arsenic (As).

**9.6 Trace Element Contents** — Determine the levels of specified trace elements and establish that they do not exceed the specification limits using a suitable emission spectrographic procedure (see SEMI C1, Section 3.5, for Guidelines for Determination of Trace Elements by Emission Spectrography).

## 10 Grade 2 Procedures

10.1 This section does not apply to this chemical.

## 11 Grade 3 Procedures

11.1 This section does not apply to this chemical.

## 12 Grade 4 Procedures

12.1 This section does not apply to this chemical.

## 13 Grade 5 Procedures

13.1 This section does not apply to this chemical.

## 14 VLSI Grade Procedures

14.1 This section does not apply to this chemical.

## 15 Tier A Procedures

15.1 Standardized test methods are being developed for all parameters at the purity levels indicated. Until standardized test methods are published, test methodology shall be determined by user and producer. The Process Chemicals Committee considers a test method to be valid only if there is a documented recovery study showing a recovery of 75 - 125%. Recovery is for a known sample spike at 50% of the specified level.

## 16 Tier B Procedures

16.1 This section does not apply to this chemical.

## 17 Tier C Procedures

17.1 This section does not apply to this chemical.

## 18 Tier D Procedures

18.1 This section does not apply to this chemical.

**Table 1 Impurity Limits and Other Requirements for Mixed Acid Etchants**

Previous SEMI Reference #	C2.1-95	C7.19-95
Grade 1 (Specification)	Tier A (Guideline)	
Aluminum (Al)	0.3 ppm max	10 ppb max
Antimony (Sb)	--	10 ppb max
Arsenic (As)	--	10 ppb max
Arsenic and Antimony (as As)	0.03 ppm max	--
Barium (Ba)	--	10 ppb max
Boron (B)	0.2 ppm max	10 ppb max

Previous SEMI Reference #	C2.1-95	C7.19-95
	Grade 1	Tier A
	(Specification)	(Guideline)
Cadmium (Cd)	0.3 ppm max	10 ppb max
Calcium (Ca)	--	10 ppb max
Chromium (Cr)	0.2 ppm max	10 ppb max
Cobalt (Co)	--	10 ppb max
Copper (Cu)	0.1 ppm max	10 ppb max
Gallium (Ga)	--	10 ppb max
Germanium (Ge)	--	10 ppb max
Gold (Au)	0.3 ppm max	--
Iron (Fe)	0.3 ppm max	10 ppb max
Lead (Pb)	0.3 ppm max	10 ppb max
Magnesium (Mg)	0.3 ppm max	10 ppb max
Manganese (Mn)	--	10 ppb max
Molybdenum (Mo)	--	10 ppb max
Nickel (Ni)	0.1 ppm max	10 ppb max
Potassium (K)	0.3 ppm max	10 ppb max
Sodium (Na)	0.3 ppm max	10 ppb max
Strontium (Sr)	0.3 ppm max	--
Tin (Sn)	0.3 ppm max	10 ppb max
Titanium (Ti)	0.3 ppm max	10 ppb max
Zinc (Zn)	0.3 ppm max	10 ppb max
Particles in bottles: size, #/mL	≥1.0 µm	≥1.0 µm, 25 max

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.

The user's attention is called to the possibility that compliance with this standard may require use of copyrighted material or of an invention covered by patent rights. By publication of this standard, SEMI takes no position respecting the validity of any patent rights or copyrights asserted in connection with any item mentioned in this standard. Users of this standard 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 C35-0301

## SPECIFICATIONS AND GUIDELINE FOR NITRIC ACID

These specifications and this guideline were technically approved by the Global Process Chemicals Committee and are the direct responsibility of the North American Process Chemicals Committee. Current edition approved by the North American Regional Standards Committee on October 17, 1999. Initially available at [www.semi.org](http://www.semi.org) February 2001; to be published March 2001. This document replaces SEMI C1.12, C7.6, and C8.6 in their entirety. Originally published in 1979, 1990, and 1992 respectively; previously published June 1999.

### 1 Purpose

1.1 The purpose of this document is to standardize requirements for nitric acid used in the semiconductor industry and testing procedures to support those standards. Test methods have been shown to give statistically valid results. This document also provides guidelines for grades of nitric acid for which a need has been identified. In the case of the guidelines, the test methods may not have been statistically validated yet.

### 2 Scope

2.1 The scope of this document is all grades of nitric acid used in the semiconductor industry.

2.2 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.

### 3 Limitations

3.1 None.

### 4 Referenced Standards

#### 4.1 SEMI Standards

SEMI C1 — Specifications for Reagents

#### 4.2 ASTM Standards<sup>1</sup>

ASTM D5127 — Standard Guide for Ultra Pure Water Used in the Electronics and Semiconductor Industry

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

### 5 Terminology

5.1 None.

### 6 Physical Property (for information only)

Density at 25°C	1.42 g/mL
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<sup>1</sup> American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, Pennsylvania 19428-2959, USA. Telephone: 610.832.9585, Fax: 610.832.9555. Website: [www.astm.org](http://www.astm.org)

### 7 Requirements

7.1 The requirements for nitric acid for Grades 1 and 2 and Tier B are listed in Table 1.

### 8 Grade 1 Procedures

NOTE 2: Each laboratory is responsible for verifying the validity of the method within its own operation.

8.1 *Assay* — Accurately weigh a small glass-stoppered conical flask containing about 15 mL of water. Deliver from a pipet about 2 mL of the sample near the water surface, stopper immediately, cool, and reweigh. Dilute to about 50 mL with water, add 0.10 mL of methyl orange indicator solution, and titrate with standardized 1 N sodium hydroxide to a red to yellow color change.

$$\% \text{ Assay} = \frac{\text{mL} \times \text{N of NaOH} \times 6.301}{\text{Weight of sample (g)}}$$

8.2 *Color* — Dilute 2.0 mL of platinum-cobalt stock solution (APHA No. 500) to 100 mL with water. Compare this standard (APHA No. 10) with 100 mL of sample in Nessler tubes. View vertically over a white background. The sample must be no darker than the standard.

8.3 *Chloride* — Dilute 84 mL (120 g) of sample with 10 mL of water, add 1 mL of silver nitrate reagent solution, and evaporate to dryness on a steam bath in a hood. Dissolve the residue in 0.5 mL of ammonium hydroxide, dilute with 20 mL of water, and add 1.5 mL of nitric acid. Any turbidity produced should be no greater than that produced when 0.01 mg of chloride ion (Cl) is treated as the sample.

8.4 *Phosphate* — To 35 mL (50 g) of sample add 10 mL of sodium carbonate reagent solution and evaporate to dryness on a steam bath in a hood. Dissolve the residue in 25 mL of 0.5 N sulfuric acid. Add 1 mL of ammonium molybdate reagent solution and 1 mL of p-(methylamino)phenol sulfate reagent solution. Allow to stand at room temperature for 2 hours. Any blue color produced should be no greater than that produced when 0.01 mg of phosphate ion (PO<sub>4</sub>) is treated as the sample.

8.5 *Sulfate* — To 70 mL (100 g) of sample add 10 mL of sodium carbonate reagent solution and evaporate to

dryness in a hood. Dissolve the residue in 10 mL of water and 1 mL of dilute hydrochloric acid (1 + 19); filter if necessary. Add 1 mL of barium chloride reagent solution, mix, and allow to stand for 10 minutes. Any turbidity developed should be no greater than that produced when 0.05 mg of sulfate ion ( $\text{SO}_4^-$ ) is treated as the sample.

**8.6 Arsenic and Antimony (as As)** — To 141 mL (200 g) of sample in a 400 mL beaker add 5 mL of sulfuric acid, and evaporate to dense fumes of sulfur trioxide in a hood. Cool, cautiously add 10 mL of water, and again evaporate to dense fumes of sulfur trioxide. Cool, and cautiously wash into a generator flask with water to make a volume of 35 mL. Proceed as described in the General Method for Arsenic (and Antimony) under SEMI C1, Section 3.4.5, starting with the sentence which begins, "Swirl the flask...." Any red color in the silver diethyldithiocarbamate solution of the sample should be no greater than that of the standard containing 0.001 mg of arsenic (As).

### 8.7 Trace Metal Analysis

**8.7.1 Gold (Au)** — Analyze by graphite atomic absorption using the manufacturer's recommended procedure. This technique has been shown to give satisfactory results using a 1:4 dilution and Zeeman background correction. Each laboratory must determine the appropriate dilution and background correction for its instrument to meet the specification limit.

**8.7.2** The following method has given satisfactory results in determining trace metal impurities at the value specified for each of the following trace metals: aluminum (Al), boron (B), calcium (Ca), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), magnesium (Mg), manganese (Mn), nickel (Ni), potassium (K), sodium (Na), tin (Sn), titanium (Ti), and zinc (Zn). Alternate methods may be used as long as appropriate studies demonstrate recovery between 75–125% of a known sample spike for half of the value of each specified item.

### 8.7.3 Special Reagents

**8.7.3.1 Nitric Acid, Ultra Pure** — Use nitric acid specified for ultra low metal ion content.

**8.7.3.2 2% Nitric Acid Solution** — Dilute 20 mL of ultra pure nitric acid to 1 L using water meeting the criteria for Type E1.1 in ASTM D5127.

### 8.7.4 Sample Preparation

**8.7.4.1** In a clean environment, place 250 g of sample in a PTFE evaporating dish. Slowly evaporate on a hot plate, avoiding loss of sample by effervescence or spattering until approximately 2 mL of liquid remains. Cool, and transfer quantitatively to a 50 mL volumetric

flask using 2% nitric acid for rinsing and dilution to volume. Run a reagent blank.

### 8.7.5 Analysis

**8.7.5.1** Using the acid sample and reagent blank, analyze group 1 elements by flame atomic absorption spectroscopy and all other elements by plasma emission spectroscopy.

## 9 Grade 2 Procedures

NOTE 3: Each laboratory is responsible for verifying the validity of the method within its own operation.

**9.1 Non-Metal Impurities** — See Section 8, which contains procedures for the following tests:

Assay

Color (APHA)

Chloride

Phosphate

Sulfate

### 9.2 Trace Metals Analysis

**9.2.1** The following method has given satisfactory results in determining metal ion impurities at the values specified for each of the following metals: aluminum (Al), antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), bismuth (Bi), boron (B), calcium (Ca), chromium (Cr), cobalt (Co), copper (Cu), gallium (Ga), germanium (Ge), gold (Au), iron (Fe), lead (Pb), lithium (Li), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), niobium (Nb), potassium (K), silver (Ag), sodium (Na), strontium (Sr), tantalum (Ta), tin (Sn), titanium (Ti), vanadium (V), zinc (Zn), and zirconium (Zr). Alternate methods may be used as long as appropriate studies demonstrate a recovery between 75 - 125% of a known sample spike for half of the value of each specified element.

### 9.2.2 Special Reagents

**9.2.2.1 Nitric Acid, Ultra Pure** — Use nitric acid specified for low metal ion content.

**9.2.2.2 7.0% Nitric Acid Solution** — Dilute 20 g of ultrapure nitric acid to 200 g using water meeting the criteria for Type E1.1 in ASTM D5127.

**9.2.2.3 Water** — The water used for all the dilution, calibration and standards should meet at a minimum the criteria for Type E1.1 in ASTM D5127 in regard to cation analysis.

**9.2.2.4 Indium Internal Standard** — Make up a indium internal standard solution to a concentration of 20  $\mu\text{g}/\text{mL}$  (ppm) from a appropriate concentrated indium standard solution.

### 9.2.3 Sample Preparation

9.2.3.1 In a clean environment, place 2.00 g of sample into a tared FEP bottle (30 mL), dilute with Type E1.1 water to a final weight of 20.0 g. Add 20  $\mu$ L of the indium internal standard solution. Run a reagent blank.

### 9.2.4 Analysis

9.2.4.1 Using the prepared solutions and blanks, analyze sodium, potassium, calcium and iron by graphite furnace atomic absorption (GFAA) and the remaining elements by inductively coupled plasma mass spectrometry (ICP/MS). For calibration, the standards are made up with the 7.0% nitric acid solution and the indium internal standard such that the final concentration is 20 ng/g of indium.

## 10 Grade 3 Procedures

10.1 This section does not apply to this chemical.

## 11 Grade 4 Procedures

11.1 This section does not apply to this chemical.

## 12 Grade 5 Procedures

12.1 This section does not apply to this chemical.

## 13 VLSI Grade Procedures

13.1 This section does not apply to this chemical.

## 14 Tier A Procedures

14.1 This section does not apply to this chemical.

## 15 Tier B Procedures

15.1 Standardized test methods are being developed for all parameters at the purity levels indicated. Until standardized test methods are published, test methodology shall be determined by user and producer. The Process Chemical Committee considers a test method to be valid only if there is a documented recovery study showing a recovery of 75–125%. Recovery is for a known sample spike at 50% of the specified level.

## 16 Tier C Procedures

16.1 This section does not apply to this chemical.

## 17 Tier D Procedures

17.1 This section does not apply to this chemical.

**Table 1 Impurity Limits and Other Requirements for Nitric Acid**

Previous SEMI Reference #	C1.12-96	C7.6-95	C8.6-95
Grade 1	Grade 2	Tier B	
(Specification)	(Specification)	(Guideline)	
Assay ( $\text{HNO}_3$ )	69.0–70.0%	69.0–70.0%	69.0–70.0%
Color (APHA)	10 max (see NOTE 1)	10 max	10 max
Chloride (Cl)	0.08 ppm max	80 ppb max	50 ppb max
Phosphate ( $\text{PO}_4$ )	0.2 ppm max	200 ppb max	50 ppb max
Sulfate ( $\text{SO}_4$ )	0.5 ppm max	500 ppb max	50 ppb max
Aluminum (Al)	0.2 ppm max	5 ppb max	1 ppb max
Antimony (Sb)	--	5 ppb max	--
Arsenic (As)	--	10 ppb max	--
Arsenic and Antimony (as As)	0.005 ppm max	--	1 ppb max
Barium (Ba)	--	10 ppb max	1 ppb max
Beryllium (Be)	--	10 ppb max	1 ppb max
Bismuth (Bi)	--	10 ppb max	1 ppb max
Boron (B)	0.1 ppm max	10 ppb max	1 ppb max
Cadmium (Cd)	--	5 ppb max	1 ppb max
Calcium (Ca)	0.2 ppm max	10 ppb max	1 ppb max
Chromium (Cr)	0.1 ppm max	10 ppb max	1 ppb max
Cobalt (Co)	--	10 ppb max	1 ppb max
Copper (Cu)	0.05 ppm max	10 ppb max	1 ppb max
Gallium (Ga)	--	10 ppb max	1 ppb max
Germanium (Ge)	--	5 ppb max	1 ppb max



Previous SEMI Reference #	C1.12-96	C7.6-95	C8.6-95
	Grade 1 (Specification)	Grade 2 (Specification)	Tier B (Guideline)
Gold (Au)	0.3 ppm max	5 ppb max	1 ppb max
Iron (Fe)	0.2 ppm max	5 ppb max	1 ppb max
Lead (Pb)	0.1 ppm max	10 ppb max	1 ppb max
Lithium (Li)	--	5 ppb max	1 ppb max
Magnesium (Mg)	0.3 ppm max	10 ppb max	1 ppb max
Manganese (Mn)	0.2 ppm max	10 ppb max	1 ppb max
Molybdenum (Mo)	--	10 ppb max	1 ppb max
Nickel (Ni)	0.05 ppm max	10 ppb max	1 ppb max
Niobium (Nb)	--	10 ppb max	1 ppb max
Potassium (K)	0.3 ppm max	5 ppb max	1 ppb max
Silicon (Si)	--	--	1 ppb max
Silver (Ag)	--	10 ppb max	1 ppb max
Sodium (Na)	0.3 ppm max	5 ppb max	1 ppb max
Strontium (Sr)	--	10 ppb max	1 ppb max
Tantalum (Ta)	--	10 ppb max	1 ppb max
Thallium (Tl)	--	10 ppb max	1 ppb max
Tin (Sn)	0.3 ppm max	10 ppb max	1 ppb max
Titanium (Ti)	0.3 ppm max	10 ppb max	1 ppb max
Vanadium (V)	--	10 ppb max	1 ppb max
Zinc (Zn)	0.3 ppm max	10 ppb max	1 ppb max
Zirconium (Zr)	--	10 ppb max	1 ppb max
Particles in bottles: size, #/mL	≥ 1.0 µm, 25 max	≥ 0.5 µm, 25 max	≥ 0.5 µm, 5 max ≥ 0.2 µm, TBD

NOTE 1: This material may darken during storage due to a photochemical reaction.

**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.

The user's attention is called to the possibility that compliance with this standard may require use of copyrighted material or of an invention covered by patent rights. By publication of this standard, SEMI takes no position respecting the validity of any patent rights or copyrights asserted in connection with any item mentioned in this standard. Users of this standard 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 C36-0705

## SPECIFICATIONS FOR PHOSPHORIC ACID

This specification was technically approved by the global Liquid Chemicals Committee. This edition was approved for publication by the global Audits and Reviews Subcommittee on April 7, 2005. It was available at [www.semi.org](http://www.semi.org) in June 2005 and on CD-ROM in July 2005. Originally published in 1981; previously published March 2001.

### 1 Purpose

1.1 The purpose of this document is to standardize requirements for phosphoric acid used in the semiconductor industry and testing procedures to support those standards. Test methods have been shown to give statistically valid results.

### 2 Scope

- 2.1 The scope of this document is all grades of phosphoric acid used in the semiconductor industry.
- 2.2 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 limitations prior to use.

### 3 Limitations

- 3.1 None.

### 4 Referenced Standards and Documents

#### 4.1 ASTM Standards<sup>1</sup>

ASTM D5127 — Standard Guide for Ultra Pure Water Used in the Electronics and Semiconductor Industry

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

### 5 Terminology

- 5.1 None.

### 6 Physical Property (for information only)

Density at 25°C	80%	1.64 g/mL
	86%	1.70 g/mL

### 7 Requirements

- 7.1 The requirements for phosphoric acid for Grades 1, 2, and 3 are listed in Table 1.

### 8 Grade 1 Procedures

8.1 *Assay* — Weigh to the nearest 1 mg about 1 mL of sample in a 250 mL glass-stoppered flask, dilute with 120 mL of water, add 0.5 mL of thymolphthalein indicator solution, and titrate with standardized 1 N sodium hydroxide to the first appearance of a blue color against a white background.

$$\% \text{ Assay} = \frac{\text{mL} \times \text{N of NaOH} \times 4.900}{\text{Weight of sample (g)}}$$

8.2 *Chloride* — Dilute 9 mL (15 g) of sample with 25 mL of water, and add 0.5 mL of nitric acid and 1 mL of silver nitrate reagent solution. Any turbidity produced should be no greater than that produced when 0.015 mg of chloride ion (Cl) is treated as the sample.

<sup>1</sup> American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, Pennsylvania 19428-2959, USA. Telephone: 610.832.9585, Fax: 610.832.9555, Website: [www.astm.org](http://www.astm.org)



### 8.3 Nitrate — Prepare the following solutions:

Sample Solution A:	Add 3 mL (5 g) of sample to 2 mL of water, dilute to 50 mL with brucine sulfate reagent solution and mix.
Control Solution B:	Add 3 mL (5 g) of sample to 0.025 mg of nitrate ion ( $\text{NO}_3^-$ ). Dilute to 50 mL with brucine sulfate reagent solution, and mix.
Blank Solution C:	Use 50 mL of the brucine sulfate reagent solution.

8.3.1 Heat the three solutions in a preheated (boiling water) bath for 10 minutes. Cool rapidly in an ice bath to room temperature. Set a spectrophotometer at 410 nm and, using 1 cm cells, adjust the instrument to read zero absorbance with Blank Solution C in the light path. Then determine the absorbance of Sample Solution A. Adjust the instrument to read zero absorbance with Sample Solution A in the light path and determine the absorbance of Control Solution B. The absorbance of Sample Solution A should not exceed that of Control Solution B.

### 8.4 Sulfate

8.4.1 The following inductively coupled plasma (ICP) method has given satisfactory results for the determination of sulfate ( $\text{SO}_4^{2-}$ ) by the analysis of sulfur (S) and subsequent calculation to determine the stoichiometric equivalent of sulfate.

NOTE 2: While this method has been shown to accurately determine sulfate concentration in phosphoric acid, the ICP methodology actually evaluates sulfur. Therefore, other sulfur species (organic, etc.) will also be determined by this method, and the "calculated" sulfate value may be higher than the actual sulfate concentration in a given sample.

#### 8.4.2 Special Reagents

8.4.2.1 *Water* — The water used for all dilution, calibration and standards should meet at a minimum, the criteria for Type E1.1 in ASTM D5127.

8.4.2.2 *Scandium Internal Standard* — A scandium standard solution is utilized such that final diluted samples will have a scandium concentration of 40 ppm.

#### 8.4.3 Sample Preparation

8.4.3.1 Dilute 20 g of phosphoric acid to 100 mL with water. (An aliquot of the concentrated scandium standard solution should also be added during the dilution process such that the final diluted sample will have a scandium concentration of 40 ppm.)

#### 8.4.4 Analysis

8.4.4.1 Using the prepared sample, analyze the sulfur content using inductively coupled plasma (ICP) spectroscopy that has been standardized using appropriate sulfur standard solutions. A wavelength of 180.731 nm has been shown to give satisfactory results.

#### 8.4.5 Calculation

8.4.5.1 The associated sulfate ( $\text{SO}_4^{2-}$ ) concentration is determined using the stoichiometric conversion ( $\text{SO}_4 = 3 \times \text{S}$ ).

### 8.5 Trace Metal Analysis

8.5.1 The following method has given satisfactory results in determining trace metal impurities at the value specified for each of the following trace metals: arsenic (As), gold (Au), cobalt (Co), chromium (Cr), nickel (Ni), lead (Pb), and antimony (Sb). Alternate methods may be used as long as they are validated for each trace metal according to SEMI C1, 'Method Validation'.

#### 8.5.2 Special Reagents

8.5.2.1 *Nitric Acid, Ultra Pure* — Use nitric specified for ultra low metal ion content.

8.5.2.2 *Sample Preparation* — In a clean environment, weigh 1.00 g (5.00 g for arsenic) of sample into each of two 30 mL polypropylene cups. Add 0.2 mL ultra pure nitric acid to each cup. Make standard addition to one cup.



Dilute both cups to 10.0 g using water meeting the criteria for Type E1.1 in ASTM D5127. Mix. Prepare reagent blank.

8.5.2.3 *Analysis* — Using the solutions from ¶8.5.2.2 and reagent blank, analyze elements specified by graphite furnace atomic absorption spectroscopy using manufacturer's recommended procedure.

8.5.3 The following method has given satisfactory results in determining trace metal impurities at the value specified for each of the following trace metals: aluminum (Al), calcium (Ca), copper (Cu), iron (Fe), lithium (Li), magnesium (Mg), manganese (Mn), potassium (K), sodium (Na), strontium (Sr), titanium (Ti), and zinc (Zn). Alternate methods may be used as long as they are validated for each trace metal according to SEMI C1, 'Method Validation'.

8.5.3.1 *Sample Preparation* — In a clean environment, weigh 5.00 g of sample into each of two 30 mL polypropylene cups. To one of the cups make standard addition. Add 5.00 g of water meeting the criteria for Type E1.1 in ASTM D5127 to each cup. Mix.

8.5.3.2 *Analysis* — Using the solutions from ¶8.5.3.1 and reagent blank, analyze elements specified by plasma emission spectroscopy using manufacturer's recommended procedure.

## 8.6 *Trace Anion Analysis*

8.6.1 Ion chromatography has been used successfully for the determination of anion impurities at the values specified for each of the following: chloride (Cl), nitrate (NO<sub>3</sub>) and sulfate (SO<sub>4</sub>). Alternative methods may be used as long as they are validated for each anion according to SEMI C1, 'Method Validation'.

8.6.2 The ion chromatography columns<sup>2</sup> used were as follows: ASRS-ULTRA Suppressor (2 mm), IonPac AS6-ICE Pre-separator (9 mm), IonPac AG11-HC Concentrator (4 mm), IonPac AG11-HC Guard (2 mm), IonPac AS11-HC Analytical (2 mm), IonPac ATC-1 Anion Trap Column (2 mm). Configure the ion chromatography system as described in references<sup>3,4</sup>. Eluent may be NaOH or generated KOH using EG40 Eluent Generator<sup>2</sup>.

8.6.3 The following ion chromatography conditions were used:

Eluent	20 mM KOH or NaOH isocratic for 30 min, stepped to 100 mM for 10 min, return to 20 mM for 5 min
Eluent Flow Rate	0.38 mL/min
Pre-separation Flow Rate	0.5 mL/min
Pre-separation time	8 min
Concentrator collection time	4 min
Sample Volume	200 µL
Detection	Suppressed Conductivity
Suppressor	ASRS, Auto-suppression Recycle Mode
Current Setting	50 mA
Sample dilution	1:1 with de-ionized water (high purity)
Standard	High purity phosphoric acid spiked with 1 ppm Cl, 12 ppm SO <sub>4</sub> and 5 ppm NO <sub>3</sub>

## 8.6.4 *Calculation of Results*

Ion Concentration =

(Area S<sub>1</sub> – Area B<sub>1</sub>) (Conc. Of Std<sub>1</sub>) (Dilution Factor)

$$\text{Area Std}_1 - \text{Area B}_2$$

Area S<sub>1</sub> = Peak Area of Sample Ion

2 Available from Dionex, Sunnyvale, CA, ([www.dionex.com](http://www.dionex.com))

3 "Automated trace anion determinations in concentrated electronic grade phosphoric acid by ion chromatography", F. S. Stover, *J. Chromatogr. A*, 956 (2002) 121-128.

4 "The determination of trace anions in concentrated phosphoric acid", Dionex Technical Note 44, Dionex, Sunnyvale, CA, 1998.



Area B<sub>1</sub> = Peak Area of Ion from Instrument (H<sub>2</sub>O) Blank

Area Std<sub>1</sub> = Peak Area of Ion from Spiked Standard

Area B<sub>2</sub> = Peak Area of Ion from Standard Blank

Conc. Of Std<sub>1</sub> = Concentration of Ion in Spiked Standard

## 9 Grade 2 Procedures

9.1 *Assay* — Weigh to the nearest 1 mg about 1 mL of sample in a 250 mL glass-stoppered flask, dilute with 120 mL of water, add 0.5 mL of thymolphthalein indicator solution, and titrate with standardized 1 N sodium hydroxide to the first appearance of a blue color against a white background.

$$\% \text{ Assay} = \frac{\text{mL} \times \text{N of NaOH} \times 4.900}{\text{Weight of sample(g)}}$$

9.2 *Chloride* — Dilute 9 mL (15 g) of sample with 25 mL of water, and add 0.5 mL of nitric acid and 1 mL of silver nitrate reagent solution. Any turbidity produced should be no greater than that produced when 0.015 mg of chloride ion (Cl<sup>-</sup>) is treated as the sample.

9.3 *Nitrate* — Prepare the following solutions:

Sample Solution A:	Add 3 mL (5 g) of sample to 2mL of water. Dilute to 50 mL with brucine sulfate reagent solution, and mix.
Control Solution B:	Add 3 mL (5 g) of sample to 0.025 mg of nitrate ion (NO <sub>3</sub> <sup>-</sup> ). Dilute to 50 mL with brucine sulfate reagent solution, and mix.
Blank Solution C:	Use 50 mL of the brucine sulfate reagent solution.

9.3.1 Heat the three solutions in a preheated (boiling water) bath for 10 minutes. Cool rapidly in an ice bath to room temperature. Set a spectrophotometer at 410 nm and, using 1 cm cells, adjust the instrument to read zero absorbance with Blank Solution C in the light path. Then determine the absorbance of Sample Solution A. Adjust the instrument to read zero absorbance with Sample Solution A in the light path and determine the absorbance of Control Solution B. The absorbance of Sample Solution A should not exceed that of Control Solution B.

### 9.4 *Sulfate*

9.4.1 The following inductively coupled plasma (ICP) method has given satisfactory results for the determination of sulfate (SO<sub>4</sub><sup>2-</sup>) by the analysis of sulfur (S) and subsequent calculation to determine the stoichiometric equivalent of sulfate.

NOTE 3: While this method has been shown to accurately determine sulfate concentration in phosphoric acid, the ICP methodology actually evaluates sulfur. Therefore, other sulfur species (organic, etc.) will also be determined by this method, and the "calculated" sulfate value may be higher than the actual sulfate concentration in a given sample.

#### 9.4.2 *Special Reagents*

9.4.2.1 *Water* — The water used for all dilution, calibration, and standards should meet, at a minimum, the criteria for Type E1.1 in ASTM D5127.

9.4.2.2 *Scandium Internal Standard* — A scandium standard solution is utilized such that final diluted samples will have a scandium concentration of 40 ppm.

#### 9.4.3 *Sample Preparation*

9.4.3.1 Dilute 20 g of phosphoric acid to 100 mL with water. (An aliquot of the concentrated scandium standard solution should also be added during the dilution process such that the final diluted sample will have a scandium concentration of 40 ppm.)



#### 9.4.4 Analysis

9.4.4.1 Using the prepared sample, analyze the sulfur content using inductively coupled plasma (ICP) spectroscopy that has been standardized using appropriate sulfur standard solutions. A wavelength of 180.731 nm has been shown to give satisfactory results.

#### 9.4.5 Calculation

9.4.5.1 The associated sulfate ( $\text{SO}_4$ ) concentration is determined using the stoichiometric conversion ( $\text{SO}_4 = 3 \times \text{S}$ ).

### 9.5 Trace Metal Analysis

9.5.1 The following method has given satisfactory results in determining trace metal impurities at the value specified for each of the following trace metals: aluminum (Al), antimony (Sb), arsenic (As), cadmium (Cd), calcium (Ca), chromium (Cr), cobalt (Co), copper (Cu), gold (Au), iron (Fe), lead (Pb), lithium (Li), magnesium (Mg), manganese (Mn), nickel (Ni), potassium (K), sodium (Na), strontium (Sr), titanium (Ti), and zinc (Zn). Alternate methods may be used as long as they are validated for each trace metal according to SEMI C1, ‘Method Validation’.

#### 9.5.1.1 Special Reagents

9.5.1.1.1 *Phosphoric Acid, Ultra Pure* — Use phosphoric acid specified for ultra low metal ion content.

9.5.1.1.2 *Nitric Acid, Ultra Pure* — Use nitric acid specified for ultra low metal ion content.

9.5.1.1.3 *Water* — The water used for all dilution, calibration, and standards should meet, at a minimum, the criteria for Type E1.1 in ASTM D5127.

9.5.1.1.4 *Internal Standard Stock Solution* — An internal standard stock solution containing beryllium (Be), germanium (Ge), indium (In), lutetium (Lu), and scandium (Sc) is utilized such that final measured solutions will have a concentration of 100 ppb of each internal standard element.

9.5.1.1.5 *External Standard Stock Solution* — An external standard stock solution containing the elements in ¶9.5.1 and the internal standard elements in ¶9.5.1.4 is utilized such that final diluted external calibration standards will have appropriate concentrations for sample elements and will contain 100 ppb of internal standard elements.

9.5.2 *Sample Preparation* — In a clean environment, weigh 4.00 g of sample into a 100 mL polypropylene flask. Add an aliquot of the internal standard stock solution such that the final diluted sample will have a concentration of 100 ppb of each internal standard element. Add 2 mL of nitric acid, ultra pure, and dilute to 100 mL with Type E1.1 water.

9.5.2.1 *Analysis* — Analyze elements utilizing inductively coupled plasma mass spectrometry (ICP - MS). Calibrate the sample elements with matrix matched blank and external standards.

9.6 *Trace Anion Analysis* — see ¶8.6, which contains procedures for trace anions.

## 10 Grade 3 Procedures

10.1 *Assay* — Weigh to the nearest 1 mg about 1 mL of sample in a 250 mL glass-stoppered flask, dilute with 120 mL of water, add 0.5 mL of thymolphthalein indicator solution, and titrate with standardized 1 N sodium hydroxide to the first appearance of a blue color against a white background.

10.2 *Chloride* — Dilute 9 mL (15 g) of sample with 25 mL of water, and add 0.5 mL of nitric acid and 1 mL of silver nitrate reagent solution. Any turbidity produced should be no greater than that produced when 0.015 mg of chloride ion ( $\text{Cl}^-$ ) is treated as the sample.



### 10.3 Nitrate — Prepare the following solutions:

Sample Solution A:	Add 3 mL (5 g) of sample to 2 mL of water. Dilute to 50 mL with brucine sulfate reagent solution, and mix.
Control Solution B:	Add 3 mL (5 g) of sample to 0.025 mg of nitrate ion ( $\text{NO}_3^-$ ) Dilute to 50 mL with brucine sulfate reagent solution, and mix.
Blank Solution C:	Use 50 mL of the brucine sulfate reagent solution.

10.3.1 Heat the three solutions in a preheated (boiling water) bath for 10 minutes. Cool rapidly in an ice bath to room temperature. Set a spectrophotometer at 410 nm and, using 1 cm cells, adjust the instrument to read zero absorbance with Blank Solution C in the light path. Then determine the absorbance of Sample Solution A. Adjust the instrument to read zero absorbance with Sample Solution A in the light path and determine the absorbance of Control Solution B. The absorbance of Sample Solution A should not exceed that of Control Solution B.

### 10.4 Sulfate

10.4.1 The following inductively coupled plasma (ICP) method has given satisfactory results for the determination of sulfate ( $\text{SO}_4^{2-}$ ) by the analysis of sulfur (S) and subsequent calculation to determine the stoichiometric equivalent of sulfate.

NOTE 3: While this method has been shown to accurately determine sulfate concentration in phosphoric acid, the ICP method actually evaluates sulfur. Therefore, other sulfur species (organic, etc.) will also be determined by this method, and the “calculated” sulfate value may be higher than the actual sulfate concentration in a given sample.

#### 10.4.2 Special Reagents

10.4.2.1 *Water* — The water used for all dilution, calibration, and standards should meet, at a minimum, the criteria for Type E1.1 in ASTM D5127.

10.4.2.2 *Scandium Internal Standard* — A scandium standard solution is utilized such that final diluted samples will have a scandium concentration of 40 ppm.

#### 10.4.3 Sample Preparation

10.4.3.1 Dilute 20 g of phosphoric acid to 100 mL with water. (An aliquot of the concentrated scandium standard solution should also be added during the dilution process such that the final diluted sample will have a scandium concentration of 40 ppm.)

#### 10.4.4 Analysis

10.4.4.1 Using the prepared sample, analyze the sulfur content using inductively coupled plasma (ICP) spectroscopy that has been standardized using appropriate sulfur standard solutions. A wavelength of 180.731 nm has been shown to give satisfactory results.

#### 10.4.5 Calculation

10.4.5.1 The associated sulfate ( $\text{SO}_4^{2-}$ ) concentration is determined using the stoichiometric conversion ( $\text{SO}_4 = 3 \times \text{S}$ ).

### 10.5 Trace Metal Analysis

10.5.1 The following method has given satisfactory results in determining trace metal impurities at the value specified for each of the following trace metals: aluminum (Al), antimony (Sb), arsenic (As), barium (Ba), boron (B), cadmium (Cd), calcium (Ca), chromium (Cr), cobalt (Co), copper (Cu), gold (Au), iron (Fe), lead (Pb), lithium (Li), magnesium (Mg), manganese (Mn), nickel (Ni), potassium (K), silicon (Si), sodium (Na), strontium (Sr), titanium (Ti), and zinc (Zn). Alternate methods may be used as long as they are validated for each trace metal according to SEMI C1, ‘Method Validation’.



#### 10.5.1.1 Special Reagents

10.5.1.1.1 *Phosphoric Acid, Ultra Pure* — Use phosphoric acid specified for ultra low metal ion content for preparation of matrix matched calibration standards.

10.5.1.1.2 *Water* — The water used for all dilution, calibration, and standards should meet, at a minimum, the criteria for Type E1.1 in ASTM D5127.

10.5.1.1.3 *Internal Standard Stock Solution* — An internal standard stock solution containing beryllium (Be), germanium (Ge), indium (In), and lutetium (Lu) is utilized such that final measured solutions will have concentrations of Be - 10 ppb, Ge - 20 ppb, In - 5 ppb, and Lu - 5 ppb as internal standard elements.

10.5.1.1.4 *External Standard Stock Solution* — An external standard stock solution containing the elements in ¶10.5.1 is utilized such that final diluted external calibration standards will have appropriate concentrations for the measurement of the sample elements.

10.5.2 *Sample Preparation* — In a clean environment, weigh 5.00 g of sample into a 10 mL polypropylene sample tube. Add an aliquot of the internal standard stock solution such that the final diluted sample will have the concentration of internal standard elements in ¶10.5.1.1.3. Dilute contents to 10 mL with Type E1.1 water.

10.5.2.1 *Analysis* — Analyze elements using inductively coupled plasma mass spectrometry (ICP - MS). Calibrate the sample elements with matrix matched blank and external standards.

10.6 Trace Anion Analysis – see ¶8.6, which contains procedures for trace anions.

### 11 Grade 4 Procedures

11.1 This section does not apply to this chemical.

### 12 Grade 5 Procedures

12.1 This section does not apply to this chemical.

### 13 Tier A Procedures

13.1 This section does not apply to this chemical.

### 14 Tier B Procedures

14.1 This section does not apply to this chemical.

### 15 Tier C Procedures

15.1 This section does not apply to this chemical.

### 16 Tier D Procedures

16.1 This section does not apply to this chemical.

**Table 1 Impurity Limits and Other Requirements for Phosphoric Acid**

Previous SEMI Reference #	C1.13-96, C1.27-96	C7.24-0697	
	Grade 1	Grade 2	Grade 3
	(Specification)	(Specification)	(Specification)
Assay ( $\text{H}_3\text{PO}_4$ ) (80%)	79.0–81.0%	79.0–81.0%	79.0–81.0%
Assay ( $\text{H}_3\text{PO}_4$ ) (86%)	85.0–87.0%	85.0–87.0%	85.0–87.0%
Nitrate ( $\text{NO}_3$ )	5 ppm max	5 ppm max	5 ppm max
Sulfate ( $\text{SO}_4$ )	--	12 ppm max	12 ppm max
Total Sulfur (as $\text{SO}_4$ )	12 ppm max	--	--
Chloride (Cl)	1 ppm max	1 ppm max	1 ppm max
Aluminum (Al)	0.5 ppm max	300 ppb max	50 ppb max
Antimony (Sb)	10 ppm max	3500 ppb max	1,000 ppb max

Previous SEMI Reference #	C1.13-96, C1.27-96	C7.24-0697	
	Grade 1 (Specification)	Grade 2 (Specification)	Grade 3 (Specification)
Arsenic (As)	0.05 ppm max	50 ppb max	50 ppb max
Barium (Ba)	--	--	50 ppb max
Boron (B)	--	--	50 ppb max
Cadmium (Cd)	--	450 ppb max	50 ppb max
Calcium (Ca)	1.5 ppm max	1100 ppb max	150 ppb max
Chromium (Cr)	0.2 ppm max	200 ppb max	50 ppb max
Cobalt (Co)	0.05 ppm max	50 ppb max	50 ppb max
Copper (Cu)	0.05 ppm max	50 ppb max	50 ppb max
Gold (Au)	0.3 ppm max	150 ppb max	50 ppb max
Iron (Fe)	2.0 ppm max	700 ppb max	100 ppb max
Lead (Pb)	0.3 ppm max	300 ppb max	50 ppb max
Lithium (Li)	0.1 ppm max	100 ppb max	10 ppb max
Magnesium (Mg)	0.2 ppm max	200 ppb max	50 ppb max
Manganese (Mn)	0.1 ppm max	100 ppb max	50 ppb max
Nickel (Ni)	0.2 ppm max	200 ppb max	50 ppb max
Potassium (K)	1.5 ppm max	450 ppb max	150 ppb max
Silicon (Si)	--	--	50 ppb max
Sodium (Na)	2.5 ppm max	500 ppb max	250 ppb max
Strontium (Sr)	0.1 ppm max	100 ppb max	10 ppb max
Titanium (Ti)	0.3 ppm max	300 ppb max	50 ppb max
Zinc (Zn)	2.0 ppm max	400 ppb max	50 ppb max
Particles in bottles: size, #/mL	(See <sup>#1</sup> )	(See <sup>#1</sup> )	(See <sup>#1</sup> )

<sup>#1</sup> Due to the limitations of current particle counters, particle size and number are to be agreed upon between supplier and user. See SEMI C1, 'Calibration and Measurement Method for Particles in Liquids'.

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