



SEMI C27-0699

SPECIFICATIONS AND GUIDELINES FOR HYDROCHLORIC ACID

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 by letter ballot dated April 23, 1999. Initially available on SEMI OnLine May 1999; to be published June 1999. This document replaces SEMI C1.7, C7.2, C8.2, C11.6, and C12.2 in their entirety. Originally published in 1978, 1990, 1992, 1996, and 1995 respectively.

1 Purpose

1.1 The purpose of this document is to standardize requirements for hydrochloric 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 hydrochloric 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 hydrochloric acid 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.

3 Limitations

3.1 None.

4 Referenced Standards

SEMI C1 — Specifications for Reagents

SEMI Suggested Guidelines for Pure Water for Semiconductor Processing

5 Terminology

5.1 None.

6 Physical Property (for information only)

Density at 25°C	1.19 g/mL
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7 Requirements

7.1 The requirements for hydrochloric acid for Grades 1 and 2, VLSI Grade, and Tiers B and C 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.

8.1 Assay — Accurately weigh a glass-stoppered conical flask containing about 30 mL of water. Deliver from a pipet about 3 mL of sample near the water surface, stopper immediately, and reweigh. Dilute to about 50 mL with water, add methyl orange indicator solution, and titrate with standardized 1 N sodium hydroxide to a red-to-yellow color change.

$$\% \text{Assay} = \frac{\text{mL} \times \text{N of NaOH} \times 3.646}{\text{Weight of sample (g)}}$$

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 Extractable Organic Substances — Cool 110 mL of sample in an ice bath. Add 5 mL of 2,2,4-trimethylpentane and 100 mL of water to each of two 250 mL separatory funnels. To a third funnel add 100 mL of water and 5 mL of the standard (see below). To the first funnel add 100 mL of the cooled sample, and 100 mL of water to each of the remaining two. Stopper, shake well, and allow the layers to separate. Inject 1.0 µL of each of the 2,2,4-trimethylpentane extracts into a gas chromatograph with a flame ionization detector. The following conditions have been found to be satisfactory: Column — 20% Carbowax® 20 M on 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_2) — 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_4) 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_4) 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 SEMI Suggested Guidelines for Pure Water for Semiconductor Processing for "acceptable" or better.

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