

SEMI C27-0918

SPECIFICATION AND GUIDE FOR HYDROCHLORIC ACID

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1 Purpose

1.1 The purpose of this Document is to standardize requirements for grades of hydrochloric acid used in the semiconductor industry and testing procedures to support those specifications. Alternative methods may be used as long as they have been validated in accordance with the requirements of SEMI C1. This Document also provides a Guide for tiers of hydrochloric acid for which a need has been identified. In the case of the Guide, the test methods may not have been statistically validated.

2 Scope

2.1 The scope of this Document is grades and tiers of hydrochloric acid used in the semiconductor industry.

NOTICE: SEMI Standards and Safety Guidelines do not purport to address all safety issues associated with their use. It is the responsibility of the users of the Documents 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 and Safety Guidelines

SEMI C1 — Guide for the Analysis of Liquid Chemicals

SEMI C35 — Specification and Guide for Nitric Acid

SEMI C44 — Specification and Guide for Sulfuric Acid

4.2 ASTM Standard¹

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

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

5 Terminology

5.1 Abbreviations and Acronyms

5.1.1 DDT — dichlorodiphenyltrichloroethane

5.1.2 FEP — fluorinated ethylene-propylene

5.1.3 GFAA — graphite furnace atomic absorption

5.1.4 ICP-MS — inductively coupled plasma mass spectrometry

5.1.5 PTFE — polytetrafluoroethylene

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6 Properties

Table 1 Properties of Hydrochloric Acid

Chemical Formula	HCl
CAS Number	7647-01-0
Concentration	36.5–38.0 Wt.%
Density at 25°C	1.19 g/mL

7 Requirements

7.1 The requirements for hydrochloric acid for Grades 1 and 2, and the recommended values for Tiers B and C are listed in Table 2.

8 Grade 1 Procedures

NOTE 1: Alternative methods may be used as long as they have been validated in accordance with the requirements of SEMI C1.

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.

$$\% \text{ Assay} = \frac{\text{Volume of NaOH (mL)} \times \text{Normality of NaOH} \times 3.646}{\text{Mass of Sample (g)}}$$

8.2 *Color* — Dilute 2.0 mL of platinum-cobalt stock solution (APHA No. 500) to 100 mL with water. Compare this diluted standard (APHA No. 10) with 100 mL of sample in Nessler tubes. View vertically over a white background. The sample shall 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 μ L of each of the 2,2,4-trimethylpentane extracts into a gas chromatograph with a flame ionization detector. Use the following conditions: Column — 20% Carbowax® 20 M on Chromosorb P (80/100), 3 m $\times$ 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 dichlorodiphenyltrichloroethane (DDT): Column — 5% silicone gum SESE-30 on Chromosorb® W (60/80), 1.5 $\times$ 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 shall 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 3 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 shall be free from impurities that interfere with the chromatographic analysis.

8.4 *Free Halogen (as Cl₂)* — 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 shall not acquire a pink color in one-half minute.

8.5 Phosphate

8.5.1 Special Reagents

8.5.1.1 *Sulfuric Acid* — SEMI C44, Grade 2.

8.5.1.2 *0.5 N Sulfuric Acid* — Dilute 14 g of sulfuric acid (see ¶ 8.5.1.1) to 1 L.

8.5.2 To 170 mL (200 g) of sample, add 10 mL of sodium carbonate reagent solution (see SEMI C1) and evaporate to dryness on a steam bath in a hood. Dissolve the residue in 25 mL of 0.5 N sulfuric acid (see ¶ 8.5.1.1). Add 1 mL of ammonium molybdate reagent solution (see SEMI C1) and 1 mL of p-(methyamino)phenol solution (see SEMI C1). Allow to stand at room temperature for two hours. Any blue color produced shall be no greater than that produced when 0.01 mg of phosphate ion (PO_4) is treated like the sample.

8.6 Sulfate

8.6.1 Special Reagents

8.6.1.1 *Hydrochloric Acid* — Use hydrochloric acid; SEMI C27, Grade 2.

8.6.1.2 *Dilute Hydrochloric Acid (1 + 19)* — Dilute 1 part by volume hydrochloric acid (see ¶ 8.6.1.1) with 19 parts by volume deionized water.

8.6.2 To 85 mL (100 g) of sample, add 10 mL of sodium carbonate reagent solution (see SEMI C1) and evaporate to dryness in a hood. Dissolve the residue in 10 mL of water and 1 mL of dilute hydrochloric acid (see ¶ 8.6.1.2); filter, if necessary. Add 1 mL of barium chloride reagent solution (see SEMI C1), mix, and allow to stand 10 minutes. Any turbidity shall 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 (see SEMI C1), 5 mL of hydrochloric acid, and 2 mL of starch indicator solution (see SEMI C1) 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 shall be required.

8.8 Arsenic and Antimony (as As)

8.8.1 Special Reagents

8.8.1.1 *Sulfuric Acid* — SEMI C44, Grade 2.

8.8.1.2 *Nitric Acid* — SEMI C35, Grade 2.

8.8.2 To 168 mL (200 g) of sample in a 400 mL beaker, add 10 mL of nitric acid (see ¶ 8.8.1.2) and 5 mL of sulfuric acid (see ¶ 8.8.1.1), 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) in SEMI C1, starting with the sentence that begins: “Swirl the flask...” Any red color in the silver diethyldithiocarbamate solution from the sample shall be no greater than that of the standard containing 0.001 mg of arsenic (As) (see SEMI C1).

8.9 *Trace Metal Analysis* — Use the following method to determine 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). Alternative methods may be used as long as appropriate method validation as per SEMI C1 can be demonstrated.

8.9.1 Special Reagents

8.9.1.1 *Nitric Acid, Ultra Pure* — SEMI C35, Grade 2.

8.9.1.2 *2% Nitric Acid Solution* — Dilute 20 mL of nitric acid (see ¶ 8.9.1.1) 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 polytetrafluoroethylene (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 that evaporation typically requires 2 1/2 to 4 hours. Cool. Transfer quantitatively to a 50 mL volumetric flask using 2% nitric acid (see ¶ 8.9.1.2) for rinsing and dilution to the 50 mL volume. Run a reagent blank.