

SEMI C44-0708

SPECIFICATIONS AND GUIDELINES FOR SULFURIC ACID

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1 Purpose

1.1 The purpose of this document is to standardize requirements for sulfuric 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 sulfuric 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 sulfuric 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 Standard

SEMI C1 — Guide for the Analysis of Liquid Chemicals

4.2 ASTM Standard¹

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

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

5 Terminology

5.1 None.

6 Physical Property (for information only)

Chemical Formula	H ₂ SO ₄
CAS No.	7664-93-9
Density at 25°C	1.83 g/mL

7 Requirements

7.1 The requirements for sulfuric acid for Grades 1 and 2 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.

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8.1 *Assay* — Accurately weigh 1 mL of sample in a small glass-stoppered conical flask. Cautiously add 30 mL of water, cool, add 0.1 mL of methyl orange indicator solution, and titrate with standardized 1.0 N sodium hydroxide to a red to yellow color change.

$$\% \text{Assay} = \frac{\text{mL} \times \text{N of NaOH} \times 4.904}{\text{Weight of sample (g)}}$$

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* — Place 40 mL of water in each of two beakers. To one, add carefully 27 mL (50 g) of sample and to the other, 27 mL (50 g) of chloride-free sulfuric acid and 0.005 mg of chloride ion (Cl). Cool to room temperature and add 1 mL of nitric acid and 1 mL of silver nitrate reagent solution [SEMI C1]. Mix well; if necessary, make the volume of each solution identical by adding water. After 10 minutes, measure the turbidity of each solution using a suitable nephelometer. The turbidity in the sample should be no greater than the standard.

NOTE 2: Prepare chloride-free sulfuric acid in a hood by gently fuming sulfuric acid in a crucible or dish for at least 30 minutes. Cool and transfer to a tightly-capped glass bottle for storage.

8.4 *Nitrate* — Prepare the following solutions:

Sample Solution A:	Cautiously add 27 mL (50 g) of sample to 1.0 mL of water, dilute to 50 mL with brucine sulfate reagent solution and mix.
Control Solution B:	Cautiously add 27 mL (50 g) of sample to 1.0 mL of the standard nitrate solution containing 0.01 mg of nitrate ion (NO ₃) per mL, dilute to 50 mL with brucine sulfate reagent solution and mix.
Blank Solution C:	Use 50 mL of brucine sulfate reagent solution.

8.4.1 Heat the three solutions in a preheated (boiling) water bath for 10 minutes. Cool rapidly in an ice bath to room temperature. Set a photometer 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 be no greater than that Control Solution B.

8.5 *Phosphate* — Evaporate 11 mL (20 g) of sample to dryness in a platinum dish 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 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 (PO₄) is treated as the sample.

8.6 *Arsenic and Antimony (as As)* — To 109 mL (200 g) of sample in a beaker, add 5 mL of nitric acid and evaporate to about 10 mL in a hood. Cool. Cautiously add 10 mL of water, and again evaporate to about 5 mL. 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) in SEMI C1, 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).

8.7 *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), 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.