

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 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 Standards¹

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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¹ 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

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 (PO₄) 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 (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 $\mu\text{g/mL}$ (ppm) from a appropriate concentrated indium standard solution.