



SEMI C21-0600

SPECIFICATIONS AND GUIDELINES FOR AMMONIUM HYDROXIDE

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 10, 2000. Initially available on SEMI OnLine May 2000; to be published June 2000. This document replaces SEMI C1.4, C7.1, C8.1, C11.1, and C17.1 in their entirety. Originally published in 1978, 1990, 1992, 1994, and 1997 respectively.

1 Purpose

1.1 The purpose of this document is to standardize requirements for ammonium hydroxide 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 ammonium hydroxide 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 ammonium hydroxide 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 guideline for VLSI grade ammonium hydroxide is only applicable for materials that remain below 25°C during transport and storage.

4 Referenced Documents

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	0.90 g/mL
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7 Requirements

7.1 The requirements for ammonium hydroxide for Grades 1, 2, 3, and 4, and VLSI Grade 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 small glass-stoppered flask containing about 15 mL of water. Deliver from a pipet about 2 mL of the sample near the water surface, stopper immediately, and reweigh. Add 0.1 mL of methyl red indicator solution and titrate with standardized 1 N hydrochloric acid to a yellow-to-red color change.

$$\% \text{Assay} = \frac{\text{mL} \times \text{N of HCl} \times 1.703}{\text{Weight of sample (g)}}$$

8.2 *Appearance* — Place 15 mL of the sample in a 20 × 150 mm test tube and compare with water in a similar tube. Viewed across the column by means of transmitted light, the two liquids should be equal in clarity and free from suspended matter.

8.3 *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.

8.4 *Carbon Dioxide* — Dilute 11 mL (10 g) of sample with 10 mL of carbon dioxide-free water and add 5 mL of a clear, saturated solution of barium hydroxide. Any turbidity should be no greater than that produced when the same volume of the barium hydroxide solution is added to 21 mL of the carbon dioxide-free water containing 0.5 mg of anhydrous sodium carbonate.

8.5 *Substances Reducing Permanganate* — Dilute 3 mL (2.7 g) of sample with 5 mL of water. Add 50 mL of 10% sulfuric acid and 0.05 mL of 0.1 N (0.02 M) potassium permanganate. Boil for 5 minutes. The pink color should not be entirely discharged.



8.6 *Chloride* — To 22 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 10 mL of water. Add 1 mL of nitric acid. Filter, if necessary, through a chloride-free filter. Dilute to 20 mL with water and 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.

8.7 *Phosphate* — Evaporate 22 mL (20 g) of sample to dryness on a steam bath in a hood. Take up the residue with 25 mL of approximately 0.5 N sulfuric acid. Add 1 mL of ammonium molybdate reagent solution and 1 mL of p-(methylamino)phenol sulfate reagent solution, and 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_4) is treated as the sample.

8.8 *Total Sulfur (as SO_4)* — To 56 mL (50 g) of sample, add 1 mL of sodium carbonate reagent solution and evaporate on a steam bath in a hood to a volume of about 5 mL. Add 2 mL of bromine water and evaporate to dryness. Dissolve the residue with 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.

8.9 *Arsenic and Antimony (as As)* — Evaporate 44 mL (40 g) of sample in a 150 mL beaker to a small volume in a hood. Cool, cautiously add 10 mL of water and 5 mL of sulfuric acid, and 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 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).

8.10 *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 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.

8.10.1 *Special Reagents*

8.10.1.1 *5% Mannitol Solution* — Weigh out 5 g of Mannitol Powder (ACS Reagents Grade), and dilute to 100 mL using water meeting the SEMI Suggested Guidelines for Pure Water for Semiconductor Processing for "acceptable" or better. Mannitol solution is subject to attack by microorganisms and should be carefully monitored for such contamination.

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

8.10.1.3 *2% (v/v) Hydrochloric Acid Solution* — Dilute 20 mL of ultra pure hydrochloric acid to 1 L using water meeting the SEMI Suggested Guidelines for Pure Water for Semiconductor Processing for "acceptable" or better.

8.10.2 *Sample Preparation*

8.10.2.1 In a clean environment, place 250 mL of aqueous ammonium hydroxide 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. Cool. Add 1 mL of ultra pure, 12 M hydrochloric acid. Continue heating until approximately 0.5 mL of liquid remains. Cool. Transfer quantitatively to 50 mL volumetric flask using 2% (v/v) hydrochloric acid for rinsing and dilution to volume. Run reagent blank.

8.10.3 *Analysis*

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

NOTE 2: Due to the uncertainty of the acid concentration in the liquid residue, the final concentration can be estimated at approximately 1-2% (v/v). Standard calibration solutions are to use this same acid concentration.

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*

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

Assay

Color (APHA)

Carbon Dioxide

Substances Reducing Permanganate



9.2 Anions

9.2.1 The following method has given satisfactory results in determining anion impurities at the values specified for each of the following anions: chloride (Cl), phosphate (PO₄), nitrate (NO₃), and sulfate (SO₄). 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.

9.2.2 Special Reagents

9.2.2.1 *Eluent* — Prepare an eluent solution that is 2.2 mM sodium carbonate (Na₂CO₃) and 0.75 mM sodium bicarbonate (NaHCO₃) in deionized water meeting the SEMI Suggested Guidelines for Pure Water for Semiconductor Processing for "attainable" or better. Store eluent under a helium gas blanket.

9.2.2.2 *Regenerant* — Prepare a 0.025 N sulfuric acid (H₂SO₄) in deionized water meeting the SEMI Suggested Guidelines for Pure Water for Semiconductor Processing for "attainable" or better.

9.2.2.3 *Potassium Carbonate Solution* — Prepare a solution containing 500 mg of reagent grade potassium carbonate (K₂CO₃) into 100 mL of water meeting the SEMI Suggested Guidelines for Pure Water for Semiconductor Processing for "attainable" or better.

9.2.3 Sample Preparation

9.2.3.1 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 SEMI Suggested Guidelines for Pure Water for Semiconductor Processing for "attainable" water to a final volume of 20 mL.

9.2.4 Analysis

9.2.4.1 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.

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

9.3 Trace Metals Analysis

9.3.1 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), 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.

9.3.2 Special Reagents

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

9.3.2.2 *4% Nitric Acid Solution* — Dilute 40 mL of ultra pure nitric acid to 1 L using water meeting the SEMI Suggested Guidelines for Pure Water for Semiconductor Processing for "attainable."

9.3.2.3 *"Attainable" Water* — The water used for all the dilution, calibration, and standards should meet at a minimum the SEMI Suggested Guidelines for Pure Water for Semiconductor Processing for "attainable" in regard to cation analysis.

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

9.3.3 Sample Preparation

9.3.3.1 In a clean environment, evaporate a 50.0 g sample at low heat until approximately 20 g of the sample remains. Carefully add 1 mL of the ultra pure nitric acid and gently warm for several minutes. Cool to room temperature, add 25 µL of the indium internal standard, and dilute with "attainable" water to a final weight of 25.0 g.

9.3.4 Analysis

9.3.4.1 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 in 4% nitric acid solution with final concentration of 20 ng/g of the indium internal standard. Run a reagent blank.

10 Grade 3 Procedures

NOTE 4: 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 5: 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: