SEMI C21-0708
SPECIFICATIONS AND GUIDELINES FOR AMMONIUM HYDROXIDE

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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.

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

4.2 *ASTM Standard*[1]

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)

Molecular Formula	NH_4OH
CAS Number	7664-41-7
Density at 25°C	0.90 g/mL

7 Requirements

7.1 The requirements for ammonium hydroxide for Grades 1, 2, 3, 4 and Tier D 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.

[1] ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959, USA; Telephone: +1.610.832.9585, Fax: +1.610.832.9555, http://www.astm.org

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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 *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.

8.6 *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.

8.7 *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.

8.8 *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.

NOTE 2: See § 10.3.1 for Arsenic (As) and Antimony (Sb) analysis.

8.8.1 *Special Reagents*

8.8.1.1 *5% Mannitol Solution* — Weigh out 5 g of Mannitol Powder (ACS Reagents Grade), and dilute to 100 mL using water meeting the criteria for Type E1 in ASTM D5127. Mannitol solution is subject to attack by microorganisms and should be carefully monitored for such contamination.

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

8.8.1.3 *2% (v/v) Hydrochloric Acid Solution* — Dilute 20 mL of ultra pure hydrochloric acid to 1 L using water meeting the criteria for Type E1 in ASTM D5127.

8.8.2 *Sample Preparation*

8.8.2.1 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.

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8.8.3 *Analysis*

8.8.3.1 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 3: Due to the uncertainty of the acid concentration in the liquid residue, the final concentration can be estimated at approximately 1% to 2% (v/v). Standard calibration solutions are to use this same acid concentration.

9 Grade 2 Procedures

NOTE 4: Each laboratory is responsible for verifying the validity of the method within its own operation.

9.1 *Non-Metal Impurities*

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

- Assay
- Color (APHA)
- Carbon Dioxide

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 (PO_4), nitrate (NO_3), and sulfate (SO_4). Alternative methods may be used as long as appropriate method validation as per SEMI C1 can be demonstrated.

9.2.2 *Special Reagents*

9.2.2.1 *Eluent* — Prepare an eluent solution that is 2.2 mM sodium carbonate (Na_2CO_3) and 0.75 mM sodium bicarbonate ($NaHCO_3$) in deionized water meeting the criteria for Type E1.1 in ASTM D5127. Store eluent under a helium gas blanket.

9.2.2.2 *Regenerant* — Prepare a 0.025 N sulfuric acid (H_2SO_4) in deionized water meeting the criteria for Type E1.1 in ASTM D5127.

9.2.2.3 *Potassium Carbonate Solution* — Prepare a solution containing 500 mg of reagent grade potassium carbonate (K_2CO_3) into 100 mL of water meeting the criteria for Type E1.1 in ASTM D5127.

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 criteria for Type E1.1 in ASTM D5127 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), 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.

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 criteria for Type E1.1 in ASTM D5127.

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