



SEMI C36-0699

SPECIFICATIONS AND GUIDELINE FOR PHOSPHORIC 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 April 23, 1999. Initially available on SEMI OnLine May 1999; to be published June 1999. This document replaces SEMI C1.13, C1.27, C7.24, and C8.10 in their entirety. Originally published in 1981, 1993, 1997, and 1999 respectively.

1 Purpose

1.1 The purpose of this document is to standardize requirements for phosphoric 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 phosphoric 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 phosphoric acid used in the semiconductor industry.

3 Limitations

3.1 None.

4 Referenced Documents

SEMI Suggested Guidelines for Pure Water for Semiconductor Processing

5 Terminology

5.1 None.

6 Physical Property (for information only)

Density at 25°C	80%	1.64 g/mL
	86%	1.70 g/mL

7 Requirements

7.1 The requirements for phosphoric acid for Grades 1 and 2 and Tier B are listed in Table 1.

8 Grade 1 Procedures

8.1 *Assay* — Weigh to the nearest 1 mg about 1 mL of sample in a 250 mL glass-stoppered flask, dilute with 120 mL of water, add 0.5 mL of thymolphthalein indicator solution, and titrate with standardized 1 N sodium hydroxide to the first appearance of a blue color against a white background.

$$\% \text{ Assay} = \frac{\text{mL} \times \text{N of NaOH} \times 4.900}{\text{Weight of sample (g)}}$$

8.2 *Chloride* — Dilute 9 mL (15 g) of sample with 25 mL of water, and add 0.5 mL of nitric acid and 1 mL of silver nitrate reagent solution. Any turbidity produced should be no greater than that produced when 0.015 mg of chloride ion (Cl) is treated as the sample.

8.3 *Nitrate* — Prepare the following solutions:

Sample Solution A:	Add 3 mL (5 g) of sample to 2 mL of water, dilute to 50 mL with brucine sulfate reagent solution and mix.
Control Solution B:	Add 3 mL (5 g) of sample to 0.025 mg of nitrate ion (NO ₃). Dilute to 50 mL with brucine sulfate reagent solution, and mix.
Blank Solution C:	Use 50 mL of the brucine sulfate reagent solution.

8.3.1 Heat the three solutions in a preheated (boiling water) bath for 10 minutes. Cool rapidly in an ice bath to room temperature. Set a spectrophotometer 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 not exceed that of Control Solution B.

8.4 Sulfate

8.4.1 The following inductively coupled plasma (ICP) method has given satisfactory results for the determination of sulfate (SO₄) by the analysis of sulfur (S) and subsequent calculation to determine the stoichiometric equivalent of sulfate.

NOTE 1: While this method has been shown to accurately determine sulfate concentration in phosphoric acid, the ICP methodology actually evaluates sulfur. Therefore, other sulfur species (organic, etc.) will also be determined by this method, and the "calculated" sulfate value may be higher than the actual sulfate concentration in a given sample.

8.4.2 Special Reagents

8.4.2.1 *"Attainable" Water* — The water used for all dilution, calibration and standards should meet at a minimum, the SEMI Suggested Guidelines for Pure



Water for Semiconductor Processing for "attainable" quality.

8.4.2.2 Scandium Internal Standard — A scandium standard solution is utilized such that final diluted samples will have a scandium concentration of 40 ppm.

8.4.3 Sample Preparation

8.4.3.1 Dilute 20 g of phosphoric acid to 100 mL with water. (An aliquot of the concentrated scandium standard solution should also be added during the dilution process such that the final diluted sample will have a scandium concentration of 40 ppm.)

8.4.4 Analysis

8.4.4.1 Using the prepared sample, analyze the sulfur content using inductively coupled plasma (ICP) spectroscopy that has been standardized using appropriate sulfur standard solutions. A wavelength of 180.731 nm has been shown to give satisfactory results.

8.4.5 Calculation

8.4.5.1 The associated sulfate (SO_4) concentration is determined using the stoichiometric conversion ($\text{SO}_4 = 3 \times \text{S}$).

8.5 Trace Metal Analysis

8.5.1 The following method has given satisfactory results in determining trace metal impurities at the value specified for each of the following trace metals: arsenic (As), gold (Au), cobalt (Co), chromium (Cr), nickel (Ni), lead (Pb), and antimony (Sb). 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 item specified.

8.5.2 Special Reagents

8.5.2.1 Nitric Acid, Ultra Pure — Use nitric specified for ultra low metal ion content.

8.5.2.2 Sample Preparation — In a clean environment, weigh 1.00 g (5.00 g for arsenic) of sample into each of two 30 mL polypropylene cups. Add 0.2 mL ultra pure nitric acid to each cup. Make standard addition to one cup. Dilute both cups to 10.0 g using water meeting the SEMI Suggested Guidelines for Pure Water for Semiconductor Processing for "acceptable" or better. Mix. Prepare reagent blank.

8.5.2.3 Analysis — Using the solutions from 8.5.2.2 and reagent blank, analyze elements specified by graphite furnace atomic absorption spectroscopy using manufacturer's recommended procedure.

8.5.3 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), calcium (Ca), copper (Cu), iron (Fe), lithium (Li), magnesium (Mg), manganese (Mn), potassium (K), sodium (Na), strontium (Sr), 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 item specified.

8.5.3.1 Sample Preparation — In a clean environment, weigh 5.00 g of sample into each of two 30 mL polypropylene cups. To one of the cups make standard addition. Add 5.00 g of water meeting the SEMI Suggested Guidelines for Pure Water for Semiconductor Processing for "acceptable" or better to each cup. Mix.

8.5.3.2 Analysis — Using the solutions from Section 8.5.3.1 and reagent blank, analyze elements specified by plasma emission spectroscopy using manufacturer's recommended procedure.

9 Grade 2 Procedures

9.1 Assay — Weigh to the nearest 1 mg about 1 mL of sample in a 250 mL glass-stoppered flask, dilute with 120 mL of water, add 0.5 mL of thymolphthalein indicator solution, and titrate with standardized 1 N sodium hydroxide to the first appearance of a blue color against a white background.

$$\% \text{ Assay} = \frac{\text{mL} \times \text{N of NaOH} \times 4.900}{\text{Weight of sample(g)}}$$

9.2 Chloride — Dilute 9 mL (15 g) of sample with 25 mL of water, and add 0.5 mL of nitric acid and 1 mL of silver nitrate reagent solution. Any turbidity produced should be no greater than that produced when 0.015 mg of chloride ion (Cl) is treated as the sample.

9.3 Nitrate — Prepare the following solutions:

Sample Solution A:	Add 3 mL (5 g) of sample to 2mL of water. Dilute to 50 mL with brucine sulfate reagent solution, and mix.
Control Solution B:	Add 3 mL (5 g) of sample to 0.025 mg of nitrate ion (NO_3). Dilute to 50 mL with brucine sulfate reagent solution, and mix.
Blank Solution C:	Use 50 mL of the brucine sulfate reagent solution.

9.3.1 Heat the three solutions in a preheated (boiling water) bath for 10 minutes. Cool rapidly in an ice bath to room temperature. Set a spectrophotometer 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