SEMI C36-1213
SPECIFICATIONS FOR PHOSPHORIC ACID

This Standard was technically approved by the Liquid Chemicals Global Technical Committee. This edition was approved for publication by the global Audits and Reviews Subcommittee on August 22, 2013. Available at www.semiviews.org and www.semi.org in December 2013; originally published in 1981; previously published November 2007.

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. Alternative methods may be used as long as they comply with SEMI C1 requirements for method validation.

2 Scope

2.1 The scope of this Document is for grades of phosphoric acid 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

SEMI C35 — Specifications and Guides for Nitric Acid

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 Properties

Table 1 Properties of Phosphoric Acid

Molecular Formula	H_3PO_4
Molecular Weight	98.00
CAS Number	7664-38-2
Density at 25°C	1.63 g/mL (80%)
	1.69 g/mL (85%)

7 Requirements

7.1 The requirements for phosphoric acid for Grades 1, 2, and 3 are listed in Table 2.

[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 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 (see SEMI C1), and titrate with standardized 1 N sodium hydroxide to the first appearance of a blue color against a white background.

$$\%\ Assay = \frac{Volume\ NaOH\ (mL) \times Normality\ NaOH \times 4.900}{Mass\ of\ Sample\ (g)} \quad (1)$$

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 (see SEMI C1). Any turbidity produced shall 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 (see SEMI C1) 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 shall 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 (SO_4) 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 *Water* — The water used for all dilution, calibration and standards shall meet at a minimum, the criteria for Type E1.1 in ASTM D5127 with regards to sulfate content.

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 shall 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 ($SO_4 = 3 \times S$).

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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), chromium (Cr), nickel (Ni), lead (Pb), and antimony (Sb). Alternate methods may be used as long as they comply with SEMI C1 requirements for method validation.

8.5.2 *Special Reagents*

8.5.2.1 *Nitric Acid, Ultra Pure* — SEMI C35, Grade 2.

8.5.2.2 *Sample Preparation* — In a clean environment, weigh 1 g (5 g for arsenic) of sample into each of two 30 mL polypropylene cups. Add 0.2 mL nitric acid to each cup. Make standard addition to one cup. Dilute both cups to 10 g using water meeting the criteria for Type E1.1 in ASTM D5127 with regards to metal content. 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), titanium (Ti), and zinc (Zn). Alternate methods may be used as long as they comply with SEMI C1 requirements for method validation.

8.5.3.1 *Sample Preparation* — In a clean environment, weigh 5 g of sample into each of two 30 mL polypropylene cups. To one of the cups make standard addition. Add 5 g of water meeting the criteria for Type E1.1 in ASTM D5127 (with regards to metal content) to each cup. Mix.

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

8.6 *Trace Anion Analysis*

8.6.1 Ion chromatography has given satisfactory results for determining anion impurities at the values specified for each of the following: chloride (Cl), nitrate (NO_3) and sulfate (SO_4).

8.6.2 Ion chromatography columns[2]: ASRS-ULTRA Suppressor (2 mm), IonPac AS6-ICE Pre-separator (9 mm), IonPac AG11-HC Concentrator (4 mm), IonPac AG11-HC Guard (2 mm), IonPac AS11-HC Analytical (2 mm), IonPac ATC-1 Anion Trap Column (2 mm). Configure the ion chromatography system as described in references.[3,4] Eluent may be NaOH or generated KOH using EG40 Eluent Generator.[2]

8.6.3 Ion chromatography conditions:

Eluent	20 mM KOH or NaOH isocratic for 30 minutes, stepped to 100 mM for 10 minutes, return to 20 mM for 5 minutes
Eluent Flow Rate	0.38 mL/min
Pre-separation Flow Rate	0.5 mL/min
Pre-separation time	8 minutes
Concentrator collection time	4 minutes
Sample Volume	200 µL
Detection	Suppressed Conductivity
Suppressor	ASRS, Auto-suppression Recycle Mode
Current Setting	50 mA
Sample dilution	1:1 (w/w) with water meeting the criteria for Type E1.1 in ASTM D5127 (with regards to anion content)
Standard	High purity phosphoric acid spiked with 1 ppm Cl, 12 ppm SO_4 and 5 ppm NO_3

[2] Available from Dionex, Sunnyvale, CA; http://www.dionex.com

[3] Stover, F. S. "Automated trace anion determinations in concentrated electronic grade phosphoric acid by ion chromatography." *J. Chromatogr. A*, 956 (2002): pp. 121–28.

[4] Dionex Technical Note 44 "The determination of trace anions in concentrated phosphoric acid." Dionex, Sunnyvale, CA, 1998.

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