

SEMI C33-0301

SPECIFICATIONS FOR n-METHYL 2-PYRROLIDONE

These specifications 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 C1.25, C7.16, and C8.11 in their entirety. Originally published in 1986, 1992, and 1998 respectively; previously published June 1999.

1 Purpose

1.1 The purpose of this document is to standardize requirements for n-methyl 2-pyrrolidone 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 n-methyl 2-pyrrolidone 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 n-methyl 2-pyrrolidone used in the semiconductor industry.

NOTICE: 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 or other limitations prior to use.

3 Limitations

3.1 None.

4 Referenced Standards and Documents

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	1.03 g/mL
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7 Requirements

7.1 The requirements for n-methyl 2-pyrrolidone for Grades 1, 2, and 3 are listed in Table 1.

8 Grade 1 Procedures

NOTE 2: Due to the uncertainty of acid concentration in the liquid residue, the final concentration can be estimated to be approximately 2% (v/v).

NOTE 3: Each laboratory is responsible for verifying the validity of the method within its own operation.

8.1 **Assay** — Analyze the sample by gas chromatography (see SEMI C1, Section 3.1, Guidelines for Assay by Wide Bore Column Gas Chromatography). The parameters cited have given satisfactory results.

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; <http://www.astm.org>

Column: 30 × 530 micron I.D. fused silica capillary, coated with 5 micron film of DB-1 or equivalent (100% methyl silicone which has been surface bonded and cross linked).

Column Temperature:	100°C isothermal
Injector Temperature:	250°C
Detector Temperature:	300°C
Sample Size:	0.2 µL splitless
Carrier Gas:	Helium at 5 mL/min
Detector:	Thermal Conductivity
Approximate Retention Times (min):	
Butyrolactone	15.2
1-Methyl 2-Pyrrolidone	20.2
Methyl Homologue	21.2
Methyl Homologue	23.0

8.2 *Color* — Dilute 10.0 mL of platinum-cobalt stock solution (APHA No. 500) with water. Compare this standard (APHA No. 50) 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 *Water* — Add 25 mL of methanol to a dry titration flask and add Karl Fischer (KF) reagent to a visually or electrometrically determined endpoint that persists for 30 seconds. Add 98 mL (100 g) of sample, taking care to protect the sample and contents of the flask from moisture. Stir vigorously and titrate with Karl Fischer reagent to the same endpoint.

$$\% \text{ Water (H}_2\text{O)} = \frac{\text{mL KF reagent} \times \text{KF factor (g H}_2\text{O/mL)} \times 100}{\text{Weight of sample (g)}}$$

8.4 *Free Amines* — Weigh 63 mL (65 g) of sample into a 500 mL beaker. Add 100 mL of 2-propanol and mix thoroughly. Into the solution, insert a pH and reference electrodes connected to a pH meter set to the direct voltage mode. Titrate potentiometrically with 0.05 N hydrochloric acid in 2-propanol. Express the result in terms of methylamine:

$$\% \text{ Free Amines as (CH}_3\text{NH}_2) = \frac{\text{mL} \times \text{N of HCl} \times 3.10}{\text{Weight of sample (g)}}$$

8.5 *Chloride* — In a 50 mL glass-stoppered graduated cylinder, dilute 24.5 mL (25 g) of sample with water to volume. Place a 10 mL aliquot of this solution into a 50 mL Nessler tube and a 30 mL aliquot into a second tube. To the first tube add 0.01 mg of chloride standard and mix. Dilute the contents of each tube to about 45 mL with water, mix, add 1 mL of nitric acid and 1 mL of silver nitrate reagent solution, mix thoroughly, and allow to stand for 10 minutes. Any turbidity produced by the sample should be no greater than that of the 0.01 mg standard.

8.6 *Phosphate* — Add 20 mL (20) of sample to 100 mL of dilute ammonium hydroxide (1 + 4). Prepare a standard containing 0.1 mg of phosphate ion (PO₄) in 100 mL of dilute ammonium hydroxide. Proceed as follows with each of the two solutions.

8.6.1 Add, while stirring vigorously, 3.5 mL of a 10% solution of ferric nitrate 9-hydrate. Allow to stand for 15 minutes. If the precipitate has not coagulated by this time, warm gently (avoid boiling). Filter and wash the precipitate on the filter with several portions of quite dilute ammonium hydroxide (1 + 9). Discard the filtrate and washings. Dissolve the precipitate on the filter with 50 mL nitric acid (1 + 3) added in small portions. Catch the filtrate in a 250 mL glass-stoppered conical flask. Add 13 mL of ammonium hydroxide (28%–32% NH₃) to the flask while swirling and continue agitation until any precipitate redissolves. Warm the solution to 40°C and add 50 mL of ammonium molybdate-nitric acid reagent solution. Shake vigorously for 5 minutes and allow to stand at 40°C for 2 hours. The precipitate, if any, for the sample should be no greater than that for the standard.

8.6.2 *Ammonium Molybdate-Nitric Acid Reagent Solution* — Mix thoroughly 100 g of molybdate acid, 85%, with 240 mL of water and 140 mL of ammonium hydroxide (28%–32% NH_3). Filter and add 60 mL of nitric acid. Cool and while stirring continually, pour into a cooled mixture of 400 mL of nitric acid and 960 mL of water. Add 0.1 g of ammonium phosphate, monobasic, $\text{NH}_4\text{H}_2\text{PO}_4$, allow to stand 24 hours and filter through glass wool.

8.7 *Arsenic and Antimony (as As)* — Evaporate 20 mL (20 g) of sample in a 150 mL beaker to a small volume on a hot plate. Cool, add carefully 15 mL of nitric acid and 5 mL of sulfuric acid, and evaporate to dense fumes of sulfur trioxide. Add 10 mL of nitric acid and again evaporate to dense fumes. If carbon is still present, cool, add 1 mL of 30% hydrogen peroxide, and evaporate to dense fumes of sulfur trioxide. Repeat this step with hydrogen peroxide addition until carbon has been removed completely. Cool, and cautiously wash the colorless residue 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).

8.8 *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), 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.

8.8.1 *Special Reagents*

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

8.8.1.2 *Mannitol Powder* — Use mannitol specified for reagent grade (A.C.S.) and determined, via the reagent blank, to be ultra metal ion content.

8.8.1.3 *5% Mannitol Solution* — Dissolve and dilute 5 g of mannitol to 100 mL using water meeting the criteria for Type E1.1 in ASTM D5127.

8.8.1.4 *2% (v/v) Hydrochloric Acid Solution* — Dilute 20 mL of ultra pure, 12 M hydrochloric acid to 1 L using water meeting the criteria for Type E1.1 in ASTM D5127.

8.8.2 *Sample Preparation*

8.8.2.1 In a clean environment, place 250 g of solvent 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. Take up liquid and all visible residue (from walls of dish) with 1 mL ultra pure, 12 M hydrochloric acid and continue heating until approximately 0.5 mL of liquid remains. No undissolved particulate matter should be observed. Otherwise, repeat the addition of hydrochloric acid until all particulate matter is dissolved. Transfer quantitatively to a 50 mL volumetric flask using 2% (v/v) hydrochloric acid and adjust liquid level to mark. Prepare a reagent blank using the same reagents and in the same manner as for the sample concentration.

8.8.3 *Analysis*

8.8.3.1 Using the prepared sample and reagent blank, analyze group 1 elements potassium (K) and sodium (Na) by atomic absorption spectroscopy and all other elements by plasma emission spectrometry. Apply, if necessary, a reagent blank correction to the final determined value of the sample.

9 **Grade 2 Procedures**

9.1 *Non-Metal Impurities* — See Section 8, which contains procedures for the following tests:

- Assay
- Color (APHA)
- Water (H_2O)

9.2 *Methyl Amines*