

SEMI C33-0213

SPECIFICATION FOR n-METHYL 2-PYRROLIDONE

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NOTICE: The section symbol (§) is used to reference a numbered section, paragraph, or header and all subordinate paragraphs, headers, and embedded material (i.e., EXCEPTIONs, lists) therein. The paragraph symbol (§) is used to reference a particular numbered paragraph and embedded material therein. When duplicated (i.e., §§ and §§) the symbols are used to reference more than one section or paragraph, respectively.

NOTICE: Paragraphs entitled 'NOTE:' are not an official part of this Standard or Safety Guideline and are not intended to modify or supersede the official Standard or Safety Guideline. These have been supplied by the global technical committee to enhance the usage of the Standard or Safety Guideline.

NOTICE: This Standard or Safety Guideline has an Inactive Status because the conditions to maintain Current Status have not been met. Inactive Standards or Safety Guidelines are available from SEMI and continue to be valid for use.

1 Purpose

1.1 The purpose of this Specification is to standardize requirements for n-methyl 2-pyrrolidone used in the semiconductor industry and testing procedures to support those specifications. 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 Specification is grades of n-methyl 2-pyrrolidone 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[®] Standards*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.

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>. ASTM trademark is owned by ASTM International.

6 Properties

Table 1 Properties of n-Methyl 2-Pyrrolidone

Chemical Formula	CH ₃ N(CH ₂) ₃ CO
CAS Number	872-50-4
Density at 25°C	1.03 g/mL

7 Requirements

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

8 Grade 1 Procedures

NOTE 1: Alternative methods may be used as long as they comply with SEMI C1 requirements for method validation.

8.1 *Assay* — Analyze the sample by gas chromatography (refer to SEMI C1, ‘Assay by Wide Bore Column Gas Chromatography’). The parameters cited have given satisfactory results.

8.1.1 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).

Table 2 Chromatography Conditions

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.

$$\% \text{ Water (H}_2\text{O)} = \frac{\text{mL KF reagent} \times \text{KF factor} \left(\frac{\text{gH}_2\text{O}}{\text{mL}} \right) \times 100}{\text{Mass of Sample (g)}} \quad (1)$$

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:

$$\% \text{ Free Amines as } (\text{CH}_3\text{NH}_2) = \frac{\text{Volume of HCl (mL)} \times \text{Normality of HCl} \times 3.10}{\text{Mass of Sample (g)}} \quad (2)$$

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 (refer to SEMI C1), mix thoroughly, and allow to stand for 10 minutes. Any turbidity produced by the sample shall be no greater than that of the 0.01 mg standard.

8.6 *Phosphate* — Add 20 mL (20 g) of sample to 100 mL of dilute ammonium hydroxide (1 + 4). Prepare a standard containing 0.1 mg of phosphate ion (PO_4) 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% to 32% NH_3) 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 (§ 8.6.2). Shake vigorously for 5 minutes and allow to stand at 40°C for 2 hours. The precipitate, if any, for the sample shall 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% to 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, carefully add 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 SEMI C1 under section, Trace Arsenic (and Antimony) Determination, starting with the sentence that begins “Swirl the flask....” Any red color in the silver diethyldithiocarbamate solution of the sample shall 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), 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). Alternate methods may be used as long as they comply with SEMI C1 requirements for method validation.

8.8.1 *Special Reagents*

8.8.1.1 *Hydrochloric Acid, Ultrapure* — Use hydrochloric acid with metal ion content less than 10 ppb for each element specified.

8.8.1.2 *Mannitol Powder* — Use mannitol specified for reagent grade (A.C.S.) and determined, via the reagent blank, to be ultra-low 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 in regard to metallic impurities.

8.8.1.4 *2% (v/v) Hydrochloric Acid Solution* — Dilute 20 mL of ultrapure hydrochloric acid (§ 8.8.1.1) to 1 L using water meeting the criteria for Type E1.1 in ASTM D5127 in regard to metallic impurities.

8.8.2 *Sample Preparation*

8.8.2.1 In a clean environment, place 250 g of sample 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 ultrapure, hydrochloric