



SEMI C31-0699

SPECIFICATION FOR METHANOL

This specification was technically approved by the Global Process Chemicals Committee and is 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 C1.10 in its entirety. Originally published in 1978.

1 Purpose

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

3 Limitations

3.1 None.

4 Referenced Documents

SEMI C1 — Specifications for Reagents

SEMI Suggested Guidelines for Pure Water for Semiconductor Processing

5 Terminology

5.1 None.

6 Physical Property (for information only)

Density at 25°C	0.79 g/mL
Boiling Point	64.5°C

7 Requirements

7.1 The requirements for methanol for Grade 1 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.

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.

Column: 30 meter × 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: 40°C isothermal for 5 minutes, then programmed to 200°C at 10°C/min.

Injector Temperature:	150°C
Detector Temperature:	250°C
Sample Size:	0.2 µL splitless
Carrier Gas:	Helium at 3 mL/min
Detector:	Thermal Conductivity
Approximate Retention Times (min):	
Methanol	3.0
Ethanol	4.0
Acetone	4.8

8.2 *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.

8.3 *Acidity* — To 25 mL of water in a glass-stoppered flask, add 10 mL of sample and 0.1 mL of phenolphthalein indicator solution. Add 0.01 N sodium hydroxide until a slight pink color persists after shaking for one-half minute. Add 42 mL (33 g) of the sample, mix well, and titrate with 0.01 N sodium hydroxide until the pink color is reproduced. Not more than 1.0 mL of the sodium hydroxide solution should be required.

8.4 *Alkalinity* — Add 126 mL (100 g) of sample to 25 mL of water and mix well. Add 0.05 mL of methyl red indicator solution. Titrate with 0.01 N hydrochloric acid until a slight pink color is produced. Not more than 1.0 mL of the hydrochloric acid should be required.

8.5 *Residue after Evaporation* — Evaporate 253 mL (200 g) of sample to dryness. Dry at 105°C for 30 minutes, cool in a desiccator, and weigh (see SEMI C1, Section 3.3, Determination of Residue After Evaporation).



8.6 Water — Add 50 mL of sample to a dry titration flask and add Karl Fischer (KF) reagent to a visually or electrometrically determined endpoint that persists for 30 seconds. Add 50 mL (40 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.

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

8.7 Solubility in Water — Mix 15 mL of sample with 45 mL of water. Allow to stand for 30 minutes. The solution should be as clear as an equal volume of water.

8.8 Boron — To 127 mL (100 g) of sample, add 0.10 mL of 10% sodium hydroxide solution, and evaporate to dryness in a nitrogen atmosphere using a covered chamber such as a Thiers assembly (or equivalent). Dissolve the residue with 2 mL of water and 0.10 mL of hydrochloric acid. Transfer to a test tube, cool in an ice bath, and add 10 mL of sulfuric acid. Then add 10 mL of carminic acid solution and remove from the ice bath. Allow to stand for 45 minutes. Prepare a standard containing 0.001 mg of boron treated exactly as the sample. Run a complete blank determination on 2 mL of water. Measure the absorbances of the sample and standard against the blank at 585 nm using 5.00 cm cells. The absorbance of the sample solution should be no greater than that of the standard.

8.9 Chloride — To 63 mL (50 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 and dilute to 20 mL with water. 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.

8.10 Phosphate — To 25 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 25 mL of 0.5 N sulfuric acid. Add 1 mL of ammonium molybdate reagent solution and 1 mL of p-(methylamino)phenol sulfate reagent solution. Allow to stand at room temperature for 2 hours. Any blue color produced should be no greater than that produced when 0.01 mg of phosphate ion (PO₄) is treated as the sample.

8.11 Arsenic and Antimony (as As) — Evaporate 253 mL (200 g) of sample in a 400 mL beaker to a small volume in a hood. Add 50 mL of water and again evaporate to a small volume. Repeat the evaporation with water addition. Do not allow to go to dryness. Add 5 mL of nitric acid and 5 mL of sulfuric acid and evaporate to dense fumes of sulfur trioxide. Cool, cautiously add 10 mL of water, and again evaporate to dense fumes of sulfur trioxide. Cool, and cautiously

wash 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 which begins: "Swirl the flask...." Any red color in the silver diethyldithiocarbamate solution from the sample should be no greater than that of the standard containing 0.002 mg of arsenic (As).

8.12 Trace Metal Analysis

8.12.1 Gold (Au) — Analyze by graphite atomic absorption using the manufacturer's recommended procedure. This technique has been shown to give satisfactory results using a 1:4 dilution and Zeeman background correction. Each laboratory must determine the appropriate dilution and background correction for its instrument to meet the specification limit.

8.12.2 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), 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 appropriate studies demonstrate recovery between 75 - 125% of a known sample spike for half of the value of each specified item.

8.12.3 Special Reagents

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

8.12.3.2 2% (v/v) Hydrochloric Acid Solution — Dilute 20 mL of ultra pure 12 M hydrochloric acid to 1 L using water meeting the SEMI Suggested Guidelines for Pure Water for Semiconductor Processing for "acceptable" or better.

8.12.4 Sample Preparation

8.12.4.1 In a clean environment, place 250 g of solvent in a PTFE dish. 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.