

SEMI C25-0699^E

SPECIFICATION FOR DICHLOROMETHANE (METHYLENE CHLORIDE)

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 C1.6 in its entirety. Originally published in 1978.

^E This document was editorially modified in March 2000. Changes were made to the note following Table 1.

1 Purpose

1.1 The purpose of this document is to standardize requirements for dichloromethane (methylene chloride) 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 dichloromethane 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 dichloromethane used in the semiconductor industry.

3 Limitations

3.1 None.

4 Referenced Documents

SEMI C1 — Specifications for Reagents

5 Terminology

5.1 None.

6 Physical Property (for information only)

Density at 25°C	1.32 g/mL
Boiling Point	39.8°C

7 Requirements

7.1 The requirements for dichloromethane 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):	
Dichloromethane	6.0
Chloroform	11.0
Carbon Tetrachloride	14.0

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 38 mL (50 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 *Residue After Evaporation* — Evaporate 76 mL (100 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).

8.5 *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 76 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.

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

8.6 Chloride — To a 100 mL separatory funnel, add 30 mL (40 g) of sample and 40 mL of water. Shake well for 30 seconds and allow the two layers to separate. Discard the sample (lower) layer. To a 20 mL portion of the water layer add 1 mL of nitric acid and 1 mL of silver nitrate reagent solution. Any turbidity produced should be no greater than that of a standard containing 0.01 mg of chloride ion (Cl) in an equal volume of solution containing the amounts of reagents used.

8.7 Phosphate — To 7.5 mL (10 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.

8.8 Heavy Metals (as Pb) — Evaporate 75 mL (100 g) of sample to dryness on a steam bath in a hood. Dissolve the residue in 3 mL of diluted hydrochloric acid (1 + 1) and dilute with water to 15 mL. If necessary, filter through a small filter and wash the evaporating dish and the filter with 10 mL of water. Dilute to 25 mL with water. For the standard, dilute a solution containing 0.02 mg of lead ion (Pb) and 3 mL of diluted hydrochloric acid (1 + 1) to 25 mL with water. Adjust the pH of both solutions to between 3 and 4 with diluted ammonium hydroxide (10% NH₃) or with acetic acid, and dilute with water to 40 mL. To each solution, add 10 mL of freshly prepared hydrogen sulfide water and compare. The sample solution should be no darker than the standard.

8.9 Arsenic and Antimony (as As) — Evaporate 152 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 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 of the sample should be no greater than that of the standard containing 0.002 mg of arsenic (As).

8.10 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.

8.10.1 Special Reagents

8.10.1.1 Mixed Acid — Mix one volume of ultra pure 70% nitric acid with four volumes of ultra pure 37% hydrochloric acid.

8.10.1.2 Standards — Composite standards containing 0.5 ppm of each element in 10% v/v mixed acid solution are stable for at least 60 days.

8.10.2 Sample Preparation — Place 2.5 mL of mixed acid into a clean 400 mL PTFE beaker. Weigh in 200 g of sample. Put a PTFE-coated stir bar in the solution and put the beaker in a hood. Evaporate the sample under a current of air, meeting class 100 cleanroom specifications, with stirring to ensure continuous contact of the acid and sample. Do not heat the sample to minimize the loss of volatile organo-metallics. Continue to evaporate until near dryness. Add 2.5 mL of mixed acid, mix carefully, and transfer the solution to a 25 mL volumetric flask. Rinse the beaker and dilute to volume with water.

8.10.3 Analysis

8.10.3.1 Analyze the sample by plasma emission spectrometry except sodium and potassium by atomic absorption or flame emission within 24 hours of dilution using matrix matched standards. Run a reagent blank and correct the data as necessary.

NOTE 2: The trace metal analysis procedure is provisional, pending second source verification of recovery data. To be completed.

9 Grade 2 Procedures

9.1 This section does not apply to this chemical.

10 Grade 3 Procedures

10.1 This section does not apply to this chemical.

11 Grade 4 Procedures

11.1 This section does not apply to this chemical.