

SEMI C25-0306

SPECIFICATION FOR DICHLOROMETHANE (METHYLENE CHLORIDE)

This standard was technically approved by the global Liquid Chemicals Committee. This edition was approved for publication by the global Audits and Reviews Subcommittee on November 29, 2005. It was available at www.semi.org in February 2006 and on CD-ROM in March 2006. Originally published 1978; previously published June 1999.

NOTICE: This document was completely rewritten in 2006.

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.

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

SEMI C1 — Guide for the Analysis of Liquid Chemicals

NOTICE: Unless otherwise indicated, all documents cited shall be the latest published versions.

5 Terminology

5.1 None.

6 Physical Property (for information only)

6.1 Density at 25°C 1.32 g/ml

6.2 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, Guidelines for Assay by Wide Bore Column Gas Chromatography). The parameters cited have given satisfactory results.

Injector Temperature: 150°C, Detector: Thermal Conductivity, Detector Temperature: 250°C, Sample Size: 0.2 µL, splitless, Carrier Gas: Helium at 3 mL/min, Approximate Retention Times: Dichloromethane –6min., Chloroform: –11min., Carbon Tetrachloride –14min.

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.

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, 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, 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), arsenic and antimony (As and Sb) as As, barium (Ba), boron (B), cadmium (Cd), calcium (Ca), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), lithium (Li), magnesium (Mg), manganese (Mn), nickel (Ni), potassium (K), sodium (Na), tin (Sn), and zinc (Zn). Alternate methods may be used as long as appropriate studies demonstrate recovery between 75–125% of a known sample plus 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.