



SEMI C26-0699

SPECIFICATION AND GUIDELINE FOR HEXAMETHYLDISILAZANE (HMDS)

This specification and this guideline 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 April 23, 1999. Initially available on SEMI OnLine May 1999; to be published June 1999. This document replaces SEMI C1.23 and C7.10 in their entirety. Originally published in 1983 and 1991 respectively.

1 Purpose

1.1 The purpose of this document is to standardize requirements for hexamethyldisilazane 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 hexamethyldisilazane 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 hexamethyldisilazane 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 Properties (for information only)

Density at 25°C	0.77 g/mL
Boiling Point	126°C

7 Requirements

7.1 The requirements for hexamethyldisilazane for Grade 1 and Tier A are listed in Table 1.

8 Grade 1 Procedures

8.1 *Assay* — Analyze the sample by gas chromatography (see SEMI C1, Section 3.1, Guidelines for Assay by Wide Bore Columns 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% methylsilicone which has been bonded and cross linked).

Column Temperature: 40°C isothermal for 2 minutes, then programmed to 220°C at 10°C/min, and isothermal for 10 minutes.

Injector Temperature:	200°C
Detector Temperature:	300°C
Sample Size:	0.4 µL
Carrier Gas:	Helium at 8 mL/min
Detector:	Thermal Conductivity
Approximate Retention Times (min):	
Hexamethyldisilazane	14.3

8.2 *Trailing Impurities* — Use the chromatogram developed in the assay (see Section 8.1). With the relative retention time for hexamethyldisilazane taken as 1.0, establish the integrated area percents for trailing impurities with relative retention times from 1.3 to 4.0. The total of such trailing impurities should not exceed 0.1%.

8.3 *Appearance* — Place 15 mL of the sample in a 20 × 150 mm test tube and compare with water in a similar tube. Viewed across the column by means of transmitted light, the two liquids should be equal in clarity and free from suspended matter.

8.4 *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 should be no darker than the standard.

8.5 *Residue After Evaporation* — Evaporate 130 mL (100 g) of sample to dryness in a hood. Dry at 105°C for one hour, cool in a desiccator, and weigh (see SEMI C1, Section 3.3, Determination of Residue After Evaporation).

8.6 *UV Absorbance* — A UV scan is obtained on all HMDS electronic grade material to determine if any UV absorbing impurities are present: specifically toluene.



8.6.1 *Equipment* — Bausch and Lomb Spectronic 2000 Spectrophotometer or other double beam instrument capable of measurements at 270 nm. Cells - 1 cm path length.

8.6.2 *Reagents* — FC-113 and methanol for UV cell cleaning.

8.6.3 *Procedure* — Using water as the reference and sample cells, establish the baseline between 300 and 270 nm. Remove the water sample from the sample path and replace it with the HMDS sample. Read the absorbance between 300 and 270 nm. The absorbance at 270 nm should read 0.07 to 0.25.

NOTE 1: Oxygen will contribute to the UV absorbance.

NOTE 2: The sample must be at ambient temperature.

NOTE 3: The UV absorbance will increase or decrease with time.

NOTE 4: HMDS is flammable and corrosive.

8.7 *Chloride* — To a 500 mL separatory funnel, add 260 mL (200 g) of sample, 20 mL of water, and 1 mL of sodium hydroxide reagent solution. Shake well for 30 seconds and allow the two layers to separate. Carefully draw off the aqueous (lower) layer into a 250 mL beaker. Repeat the extraction five times and combine the six aqueous extracts. Add 2 mL of nitric acid to acidify the solution and arrange the beaker for magnetic stirring.

8.7.1 Using a pH meter fitted with a silver billet electrode (Beckman #89261, Corning #476065, or equivalent) and a silver/silver chloride reference electrode, determine the apparent pH versus mL readings while titrating the continuously stirred sample solution with 0.01 M methanolic silver nitrate solution. Add the silver nitrate solution in 0.1-0.2 mL increments from a 10 mL buret. Run a total blank. Plot the titration data on linear graph paper or use the second-derivative method to establish the endpoint.

ppm Chloride (Cl) =

$$\frac{(\text{mL sample} - \text{mL blank}) \times M \text{ of } \text{AgNO}_3 \times 35,460}{\text{Weight of sample (g)}}$$

8.7.2 *Standard Silver Nitrate in Methanol Solution* — Dissolve 1.700 grams of silver nitrate in absolute methanol and dilute to 1000 mL. Store this solution in an amber bottle and standardize immediately before use against a standard sodium chloride (NaCl) solution using the above second-derivative method.

8.8 *Heavy Metals (as Pb)* — Evaporate 130 mL (100 g) of sample to dryness in a hood. Dissolve the residue in 3 mL of dilute hydrochloric acid (1 + 1) and dilute with water to 15 mL. If necessary, filter through a small

filter, washing the evaporating dish and filter with 10 mL of water. Dilute to 25 mL with water. For the standard, dilute a solution containing 0.01 mg of lead ion (Pb) and 3 mL of dilute hydrochloric acid (1 + 1) to 25 mL with water. Adjust the pH of both solutions to between 3 and 4 (using a pH meter) with dilute ammonium hydroxide (10% NH₃) or with 1 N 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)* — To a 500 mL separatory funnel, add 260 mL (200 g) of sample, 20 mL of water, and 1 mL of sodium hydroxide reagent solution. Shake well for 30 seconds and allow the two layers to separate. Carefully draw off the aqueous (lower) layer into a 150 mL beaker. Repeat the extraction twice more, combining the three aqueous extracts.

8.9.1 Add 15 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 re-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 not exceed that for the standard containing 0.002 mg of arsenic (As).

8.10 *Trace Elements* — By a suitable emission spectrographic procedure, determine for each of the specified trace elements that its content is not greater than the stated specification limit (see SEMI C1, Section 3.5, Guidelines for Determination of Trace Elements by Emission Spectrography).

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.

12 Grade 5 Procedures

12.1 This section does not apply to this chemical.

13 VLSI Grade Procedures

13.1 This section does not apply to this chemical.