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SEMI C2-95

SPECIFICATIONS FOR ETCHANTS

1 Preface

1.1 The SEMI Committee on Chemical Reagents began its efforts on etchants in 1979. With this publication, the Committee establishes definitions for three major types of etchant mixtures; mixed acid etchants, buffer oxide etchants, and phosphoric etchants. Specifications and analytical procedures are introduced for each type.

1.2 Etchants within all of the requirements can be described as "meeting SEMI specifications."

1.3 Where an analytical procedure different from that provided is substituted by a supplier or user, the burden of proof is on said supplier or user to confirm the equivalency.

2 Definitions

2.1 All definitions set forth in SEMI C1, Section 2 are adopted for SEMI C2.

2.2 *Etchant* — The exact definition of an etchant mixture shall be set forth as the initial paragraph of its Standard. The composition shall be expressed as a ratio of the relative volumes taken of the components in an assigned order. In the expression, all the relative volumes shall be reduced to a ratio of the smallest whole numbers. If a component is absent, its relative volume shall be taken as zero.

2.3 *Composition* — The content of each component of an etchant shall be expressed on a weight/weight basis of the 100% component (for example, 100% HF, not 49% HF). Any tolerance allowed for the content of a component shall be expressed on a weight/weight basis of that 100% component.

3 General Procedures and Guidelines to Certain Methods

3.1 The general procedures and guidelines for certain methods set forth in SEMI C1, Section 3 are adopted for SEMI C2.

3.2 *Determination of Nitric Acid by Ultraviolet Absorption Spectrophotometry*

3.2.1 *Introduction* — The photometric determination of nitric acid in various etchant mixtures is based on the strong absorption of the nitrate ion in the ultraviolet region. For this spectral region fused silica (quartz) cells are required.

3.2.2 *Preparation of Calibration Curve* — Secure a bottle of nitric acid (70%) and determine its assay in

duplicate. Accurately weigh 2.8 to 3.0 g dilute with 100 mL of water, add 10 drops of phenolphthalein indicator solution to each solution, and titrate with standardized 1 N sodium hydroxide solution to a pink end-point.

$$\% \text{ Nitric Acid} (\frac{w}{w}) = \frac{\text{mL} \times N \text{ of NaOH} \times 6.302}{\text{Weight of Sample(g)}}$$

If the results do not differ by more than 0.2%, average them. Otherwise, repeat the analysis.

3.2.3 In five previously tared weighing bottles, accurately weigh about 1.0, 1.2, 1.4, 1.6 and 1.8 g of the previously assayed 70% nitric acid. Calculate the weight, in grams, of 100% nitric acid present in each of these five standards. Quantitatively transfer each standard to a separate 100 mL volumetric flask, dilute to volume with water, and mix thoroughly.

3.2.4 Following the manufacturer's directions, ready a spectrophotometer and set the wavelength to 302 nm. Measure the absorbance of each standard versus water using a 1 cm fused silica cell. On (linear) coordinate graph paper plot the absorbance versus the weight, in grams, of 100% nitric acid for each standard. Draw the best-fitting straight line through the points.

3.2.5 *Application to Acid Etch Mixtures* — Proceed as given under the Standard for the relevant etchant.

4 Reagent and Standard Solutions

4.1 The reagent and standard solutions set forth in SEMI C1, Section 4 are adopted for SEMI C2.

4.2 *Acetate Buffer for Hydrofluoric Acid Determination* — Dissolve 106 g of sodium acetate trihydrate, $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$, and 137 g of ammonium acetate, $\text{CH}_3\text{COOHN}_4$, in about 700 mL of water. Add 5.1 mL of glacial acetic acid, adjust to pH 5.5-6.6 with dilute ammonium hydroxide (10% NH_3) or dilute acetic acid (20%), and dilute to 1000 mL with water.

4.3 *Aluminum Chloride Standard Solution Preparation* — Dissolve 40.0 g of aluminum chloride hexahydrate, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, in about 700 mL of water and 0.5 mL of hydrochloric acid contained in a 1000 mL volumetric flask; dilute to volume with water, and mix thoroughly.

4.3.1 *Standardization* — Transfer 1.5 mL of hydrofluoric acid to a 250 mL polyethylene beaker containing 50 mL of water. Add 10 drops of phenolphthalein indicator solution. With magnetic stirring, titrate with standardized 1N sodium hydroxide solution to a pink



endpoint. Record the volume of base delivered (A). Add 25 mL of Acetate Buffer for Hydrofluoric Acid Determination and 1 g of Eriochrome Cyanine R indicator mixture; mix thoroughly. With magnetic stirring, titrate with the aluminum chloride solution to a pink-purple endpoint. Record the volume of this solution delivered (B).

$$\text{HF Factor} = \frac{A \times N \text{ of NaOH} \times 2.001}{B \text{ of AlCl}_3 \text{ soln.}}$$

4.4 Eriochrome Cyanine A Indicator Mixture — Using a mortar and pestle, thoroughly grind and mix 0.1 g of Eriochrome Cyanine R (C.I. 43820) with 100 g of potassium nitrate.

5 Safety

Because of the continuing evolution of safety precautions, it is impossible in this publication to provide definite statements relating to the safe handling of individual etchants. The user is referred to product labels, product and safety data sheets, government regulations, and other relevant literature.

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The user's attention is called to the possibility that compliance with this standard may require use of copyrighted material or of an invention covered by patent rights. By publication of this standard, SEMI takes no position respecting the validity of any patent rights or copyrights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of any such patent rights or copyrights, and the risk of infringement of such rights, are entirely their own responsibility.



SEMI C10-0305

GUIDE FOR DETERMINATION OF METHOD DETECTION LIMITS

This guide was technically approved by the Global Liquid Chemicals Committee and is the direct responsibility of the North American Liquid Chemicals Committee. Current edition approved by the North American Regional Standards Committee on November 4, 2004. Initially available at www.semi.org January 2005; to be published March 2005. Originally published in 1998; previously published February 1999.

1 Purpose

1.1 To provide a minimal set of guidelines for the quantitative determination of a method detection limit (MDL) from data supporting a SEMI Process Chemicals or Gases specification.

2 Scope

2.1 This guide applies to trace contaminants specified in SEMI Process Chemicals or Gases standards and guidelines. All relevant trace contaminants should have an MDL determined from a regression analysis of a calibration curve that is equal to, or less than, their specifications. This guide is intended for use in both establishing new specifications within SEMI as well as verification of performance to SEMI specifications.

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 Referenced Standards

3.1 SEMI Standard

SEMI C16 — Guide for Precision Reporting/Data Traceability

3.2 Other Document¹

Applied Regression Analysis, 3rd Edition, Norman R. Draper and Harry Smith, John Wiley and Sons, © 1998

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

4 Terminology

None.

5 Boundary Conditions

NOTE 1: A series of boundary conditions is required of the data from which the MDL is to be determined from.

5.1 Data should be collected on at least two standards at different concentration levels, not including the blank.

5.2 The concentration levels investigated must either span the relevant specification or include it as a level. For this purpose, the calibration range can be adjusted for instrument sensitivity by pre-concentration or dilution, if applicable.

5.3 A minimum of three independent sample determinations should be taken on each concentration level of the standard investigated.

5.4 Matrix Effects

5.4.1 The blank and the standards should be matrix-matched with the sample when testing a specification and run under the same conditions, both during calibration and sample analysis.

5.4.2 If external standards in a different matrix are used for calibration, the user must compensate for matrix effects using suitable internal standards.

¹John Wiley & Sons, Inc., 605 Third Avenue New York, NY 10158-0012, 212.850.6000



5.5 Where applicable, this guide supersedes the earlier related SEMI Guide: SEMI C16.

5.6 The frequency of the MDL determination should be part of the quality assurance program for the laboratory.

6 Procedure

NOTE 2: The determination of the MDL should be performed under the same conditions that samples will normally be run. All appropriate precautions to avoid contamination should be followed.

6.1 *Reagents and Standards* — Reagents and standards used should be of the same high-purity as used in the analysis of samples. Accurate standard solutions of trace contaminants are needed for the preparation of the calibration standards. Commercially available standard solutions are suitable. These solutions should be traceable to NIST standards. Working standard solutions should be prepared on the day of use by dilution of the stock standard solution. Standards and blanks should be matrix-matched to the sample to be analyzed.

6.2 Operating Conditions

6.2.1 *Instrumental* — Principles of instrumental analysis are provided within many monographs. No general operating conditions are given here since these will vary with the instrument type and design; consequently, the manufacturers manual should be followed.

6.2.2 *Standard and Sample Preparation* — With certain methods, the achievable MDL can be improved by pre-concentration. Some methods require matrix dilution to run some analyses and may also affect the MDL.

6.2.3 *Calibration* — Calibrate the instrument for all specified trace contaminants using measurement and preparation protocols identical to those used in sample preparation and measurement, wherever appropriate. The calibration data structure used to determine the MDL should be as close to identical as possible to the data structure normally used for calibration in the laboratory. Minimum data requirements should be determinations at, at least, two concentration levels (standards), each independently sampled 3 times. The lowest concentration standard should be at, or below, the specification and give a measurable signal. The blank may be used in the calculation of the MDL if its variability is judged to be representative of that of a very low-level standard. All instrument response data used in the analysis should be measurable. The calibration range can be adjusted for instrument sensitivity by pre-concentration or dilution to match with how the samples are analyzed. Use the data collected to calculate the MDL using the formulas in the next section.

6.3 Quantification of the MDL

6.3.1 The MDL is calculated by using the results from a *regression analysis* of the calibration data to obtain a 3 sigma equivalent (in probability) upper confidence limit of individual measurements. Two alternative computational methods are provided for linear calibration models. One provides the MDL based on an ordinary least squares (OLS) regression analysis; the other on a weighted least squares (WLS) based regression analysis. These two computational alternatives **do not** provide the same MDL. The OLS algorithm is appropriate when signal uncertainty remains relatively constant over the window of calibration; otherwise, the WLS algorithm is more appropriate. A third alternative allows the use of similar regression-based approaches for MDL determination in the presence of a more complex calibration model (e.g., nonlinear, multivariate), or when distributional assumptions of the other alternatives are not appropriate. Many software packages perform regression analysis, and their use is recommended.

6.3.2 Statistical Definitions

6.3.2.1 *Method detection limit (MDL)* — The level at which the errors in the *measurement method* become large enough such that the preset maximum acceptable risk of seeing the quantified level, when none of the contaminant in question is present in the sample, is exceeded.

6.3.2.2 *risk* — This guide uses 0.13% as the maximum acceptable risk. This is the probability of observing a given result from a normal distribution that is 3 or more standard deviations above the average. Risk is set on a per-contaminant basis.

6.3.2.3 *calibration curve* — An estimate of the relationship between concentration and instrument response (signal intensity). A line, which has not been constrained to pass through the origin, is implicitly assumed in the subsequently provided formulae.

6.3.2.4 *regression analysis* — A curve-fitting technique from which the calibration curve can be estimated.

6.3.2.5 *Ordinary Least Squares (OLS)* — A curve-fitting criterion which, for a given calibration model, minimizes.

$$\sum_{i=1}^n (Y_i - \text{Predicted } Y_i)^2$$

Appropriate use of this criterion implicitly assumes that, on average, each determination is made with equal reliability.

6.3.2.6 *Weighted Least Squares (WLS)* — A curve-fitting criterion which, for a given calibration model, minimizes.

$$\sum_{i=1}^n w_i (Y_i - \text{Predicted } Y_i)^2$$

where, w_i is the weight assigned to the i^{th} data point.

Appropriate use of this criterion implicitly assumes that all w_i are strictly inversely proportional to each point's standard deviation (measure of variation).

6.3.2.7 *t-statistic* — Student's *t* is used instead of the Z-statistic (normal distribution) when the standard deviation is estimated from relatively small quantities of data. It is used herein to explicitly control the risk at 0.13%, regardless of sample size.

- X_s — The concentrations of the standards used in quantifying the MDL.
- Y_s — The instrument's response (signal intensity) to each of the X_s in question.

6.3.3 Calculations — OLS and Linear Calibration Model

6.3.3.1 A line, which is not constrained to pass through the origin, is used as the calibration model. OLS is used to estimate the model. The MDL is located by determining the 3 sigma equivalent Upper Confidence Limit at $X = 0$ and using a linear calibration model to convert this result into the corresponding concentration (MDL).

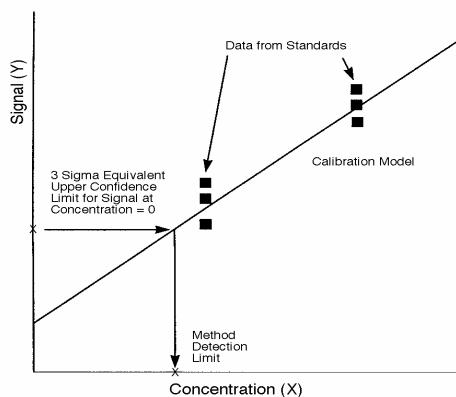


Figure 1
Graphical Visualization of MDL
Determination Process



$$MDL = \frac{(UCL - b)}{m}$$

(1) where,

- m = slope determined by OLS analysis
(equation 2)
- b = intercept determined by OLS analysis
(equation 3)
- $UCL = 3$ sigma equivalent Upper Confidence Limit at $X = 0$ (equation 4)

$$m = \frac{SS_{xy}}{SS_{xx}}$$

(2), where SS stands for Sum of Squares and

$$\begin{aligned} SS_{xy} &= \sum_i (X_i - \bar{X})(Y_i - \bar{Y}) \\ &= \sum_i X_i Y_i - \frac{(\sum_i X_i)(\sum_i Y_i)}{n} \end{aligned}$$

where n = total number of observations and i is an index which ranges from 1 to n by 1 in the summations and

$$SS_{xx} = \sum_i (X_i - \bar{X})^2 = \sum_i (X_i^2) - \frac{(\sum_i X_i)^2}{n}$$

$$b = \bar{Y} - m\bar{X}$$

(3), where

$$\bar{X} = \frac{\sum_i X_i}{n}$$

and

$$\bar{Y} = \frac{\sum_i Y_i}{n}$$

$$UCL = b + t_{n-2, 0.0013} \left(1 + \frac{1}{n} + \frac{(\bar{X})^2}{SS_{xx}} \right)^{1/2} s$$



(4), where

$t_{n-2, 0.0013}$ is a t - statistic (from Table 1)

with $n - 2$ degrees of freedom and 0.0013

as the desired risk of detecting a false positive

signal (one - sided, 3 sigma equivalent) and

s = standard deviation of regression model

$$= \sqrt{\frac{\sum_i (Y_i - Y_i^*)^2}{n-2}}$$

where, $Y_i^* = mX_i + b$

Table 1 3-Sigma Equivalent t-Table

$n-2$	t	$n-2$	t	$n-2$	t
4	6.62	10	3.96	16	3.54
5	5.51	11	3.85	17	3.51
6	4.90	12	3.76	18	3.48
7	4.53	13	3.69	19	3.45
8	4.28	14	3.64	20	3.42
9	4.09	15	3.59		

6.3.3.2 Such analyses should be performed by using a spreadsheet or computer program. It is not recommended to do them by hand. The previous equations neither require nor prevent use of data from blank quantification. In order to use blank data in the MDL quantification with OLS, the blank should be measurable, be likely to give a response which is consistent with the pattern in the other calibration data, and provide a similar level of variability to that obtained from the investigated standards.

6.3.4 Calculations — WLS and Linear Calibration Model

6.3.4.1 A line which is not constrained to pass through the origin is used as the calibration model. WLS is used to estimate the model in which the weights are determined as a function of the observed variability at each concentration level. The MDL is located by determining the 3 sigma equivalent Upper Confidence Limit at $X = 0$ and using a linear calibration model to convert this result into the corresponding concentration (MDL). While many of the WLS analysis quantity names are identical to those in the OLS analysis (e.g., \bar{X} , \bar{Y} , SS_{xx} , and SS_{xy}), the calculations are not.

$$MDL = \frac{(UCL - b)}{m}$$

(5), where

- m = slope determined by WLS analysis

(equation 6)

- b = intercept determined by WLS analysis

(equation 7)

- $UCL = 3$ sigma equivalent Upper Confidence Limit

at $X = 0$ using WLS (equation 8)



For each of the j levels of concentration, determine the variance of the k determinations (where k can differ for each concentration level, but must be at least 3) as :

$$S_j^2 = \frac{\sum_{l=1}^k (Y_{j,l} - \bar{Y}_j)^2}{(k-1)} \text{ where,}$$

$$\bar{Y}_j = \frac{\sum_{l=1}^k Y_{j,l}}{k} \text{ is used to determine}$$

the normalized weight w_j , for any

determination at the j^{th} level of concentration as :

$$w_j = \frac{n}{\sum_j \left(\frac{1}{S_j^2} \right)} \frac{1}{S_j^2}, \text{ then}$$

$$m = \frac{SS_{xy}}{SS_{xx}}$$

(6), where

SS stands for Sum of Squares and

$$SS_{xy} = \sum_i w_i (X_i - \bar{X})(Y_i - \bar{Y}), \text{ where } n = \text{total}$$

number of observations and i is an index which ranges from 1 to n by 1 in the summations and

$$\bar{X} = \frac{\sum_i w_i X_i}{n},$$

$$\bar{Y} = \frac{\sum_i w_i Y_i}{n}, \text{ and}$$

$$SS_{xx} = \sum_i w_i (X_i - \bar{X})^2$$

$$b = \bar{Y} - m\bar{X}$$

(7), where

$$UCL = b + t_{n-2, 0.0013} \left(\frac{1}{w_0} + \frac{1}{n} + \frac{(\bar{X})^2}{SS_{xx}} \right)^{1/2} s$$

(8), where

w_0 is the weight at the intercept (w_0 is either

the weight associated with the blank measurements

if they were included in the analysis or the weight

of the lowest concentration standard if the blank

measurements are not included in the analysis),

$t_{n-2, 0.0013}$ is a t -statistic (from Table 1) with $n - 2$

degrees of freedom and 0.0013 as the desired risk

of detecting a false positive signal (one-sided,

3 sigma equivalent) and

s = standard deviation of regression model

$$= \left(\frac{SS_{yy} - mSS_{xy}}{n - 2} \right)^{1/2} \text{ where,}$$

$$SS_{yy} = \sum_i w_i (Y_i - \bar{Y})^2$$

6.3.4.2 Since some calculations, for example that of s , may lead to computation of a relatively small difference between two relatively large numbers; it is critical that all previous calculations not be based on rounded numbers. In general, such analyses should be performed using a spreadsheet or computer program.

6.3.4.3 The previous equations neither require nor prevent use of data from blank quantification. In order to use blank data in the MDL quantification with WLS, the blank should be measurable, be likely to give a response which is consistent with the pattern in the other calibration data, and provide a level of variability consistent with the pattern seen in the investigated standards.

6.3.5 *Alternative Calculations* — Situations exist for which both prior alternatives (¶6.3.3 and ¶6.3.4) may be inappropriate. For example:

- (a) a calibration model may be nonlinear,
- (b) a calibration model may be multivariate in nature,
- (c) the implicit assumption of normality of residuals (errors in predictions about the calibration) may not be an appropriate distributional assumption,
- (d) the lowest level standard used in calibration may be too far above the true MDL.

6.3.5.1 In case (a), a nonlinear model can be used instead of the default linear model in performing a regression analysis which quantifies the Upper Confidence Limit for individuals at $X = 0$ at a *3 sigma equivalent probability level* (and back-projects this result through the nonlinear calibration model to estimate the MDL). How to accomplish this is the responsibility of those applying this alternative. In some situations, a transformation of scale (X and/or Y) may linearize the model such that the previously provided calculations are again applicable.



6.3.5.2 In case (b), a multivariate calibration model can be used instead of the default linear model in performing a regression analysis which quantifies the Upper Confidence Limit for individuals at $X = 0$ at a *3 sigma equivalent probability level* (and back-projects this result through the multivariate calibration model using the observed point of maximum interference in terms of the other concentrations in the range of calibration to estimate the MDL). How to accomplish this is the responsibility of those applying this alternative.

6.3.5.3 In case (c), other error distributions than the normal, can be used wherever appropriate. The same philosophical approach should be applied; a regression analysis which quantifies the Upper Confidence Limit for individuals at $X = 0$ at a *3 sigma equivalent probability level* (and back-projects this result through the calibration model to estimate the MDL). How to accomplish this is the responsibility of those applying this alternative.

6.3.5.4 In case (d), it is more likely that one will obtain a higher MDL than is truly the case. This phenomena is more likely to occur when the blank is not usable in the regression analysis for any reason. The only fix for this is to reapply the procedure with a set of standards which is not so distant from the MDL, but still otherwise meets the requirements provided herein.

6.3.5.5 In cases (a), (b), and (c), or any combination thereof, the use of appropriate computer/statistical tools is the responsibility of those applying these alternatives. Additional information on regression analysis methods can be found in *Applied Regression Analysis*, 3rd Edition, Norman R. Draper and Harry Smith, John Wiley and Sons, © 1998.

6.3.6 Example — Results of Applying (see ¶6.3.3 and ¶6.3.4)

6.3.6.1 Limited result summaries for obtaining the MDL by OLS and WLS are provided for the calibration data in Table 2. These results (Table 3) can be used to benchmark one's implementation of the computational methodology.

Table 2 Calibration Data

Ppb	signal	ppb	signal	ppb	signal
1	5.03	5	19.87	10	39.90
1	5.00	5	21.20	10	38.28
1	4.91	5	20.45	10	40.93

Table 3 Result Summaries

Statistic	OLS	WLS
MDL	1.097	0.108
UCL	5.390	1.531
m	3.857	3.869
b	1.157	1.112
s	0.800	0.00997

6.3.6.2 Note the relatively large difference in the estimated MDL (1.10 vs. 0.11) resulting from passing the same data through each of the OLS and WLS algorithms. This data has very different levels of variability, depending on the concentration level of the standard (Table 4). Such data should be analyzed with the WLS rather than the OLS algorithm.

Table 4 Signal Variation by Concentration Level

Concentration Level	Standard Deviation	Variance
1	0.062	0.0038
5	0.667	0.4449
10	1.336	1.7849



7 Quality Assurance

7.1 Each laboratory that uses this method should do so in accordance with the established quality assurance protocols in place. The MDL, of specified trace contaminants, should be determined whenever a major recalibration of the method and/or instrument is required. The new values should then be used whenever results are reported. A schedule of periodic verification of the MDL, for key trace contaminants, should be incorporated into the program.

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SEMI C16-0299 (Reapproved 0305) GUIDE FOR PRECISION AND DATA REPORTING PRACTICES

This guide was technically approved by the Global Liquid Chemicals Committee and is the direct responsibility of the North American Liquid Chemicals Committee. Current edition approved by the North American Regional Standards Committee on November 4, 2004. Initially available at www.semi.org January 2005; to be published March 2005. Originally published in 1997; previously published February 1999.

1 Purpose

1.1 To provide a minimal set of guidelines for precision and data reporting practices for data supporting a Process Chemicals or Gases SEMI specification.

2 Scope

2.1 This guide applies to data collected to support establishment of a SEMI Process Chemicals or Gases specification or verification of performance to such a SEMI specification.

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 Referenced Standards

3.1 *SEMI Standard*

SEMI C1 — Specifications for Reagents

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

4 Terminology

None.

5 Standards

5.1 For each standard used in the study, the following should be reported:

5.1.1 Preparation method before analysis (e.g., dilution, evaporation).

5.1.2 Sample matrix.

5.1.3 Concentration.

5.1.4 n = number of determinations made on the standard.

5.1.5 The average of the n determinations.

5.1.6 The standard deviation of the n measurements (if $n > 1$).

5.1.7 Range of values observed (if $n > 1$).

5.1.8 Traceability of the standard.

5.1.9 If standard was produced internally, how was it produced.

6 Samples

6.1 For all reported sample results, including recovery studies, use as many of the reporting requirements for standards as are applicable.



7 Detection Limits

7.1 If a detection limit is reported, the specific method or published variant by which the detection limit was obtained, should be named. The level of the lowest standard used in determination of a detection limit should be reported.

8 Internal Standards

8.1 For procedures calling for concentration of an analyte by cryogenic trapping, acid extraction, distillation, hydrolyzation, etc., a recovery study as per Method Validation (§3.14 of SEMI C1) is required. For a method to be viable, a recovery in the range of 75–125% is recommended.

9 Calibration Models

9.1 The span of the calibration data should include the relevant specification.

9.2 The form of the calibration model (line through origin, line, etc.) should be stated. The assumption of linearity, underlying reliance on two point (zero and span) calibrations for analytical instruments, should be justified by reporting the basis for such an assumption.

9.3 A list of which standards were used to develop the calibration model should be provided.

9.4 Information on which fitting technique was used (i.e., regression using ordinary least squares, weighted least squares, partial least squares) should be provided.

9.5 Identify which, if any, transformations were applied to the calibration data prior to the fitting of the calibration model.

9.6 Identify which response was modeled to establish calibration (i.e., peak area, peak height, response factor).

9.7 A list of the types of standards employed (i.e., internal standards, external standards, method of standard addition) should be provided.

9.8 Report how the calibration data is incorporated in producing the results of an analysis (i.e., zero and span correction, graph).

10 Method Precision

10.1 An estimate of method precision should be provided at the level of the specification. Any known interferants or factors which may affect method precision should be stated.

11 Summary

11.1 Since only a minimal set of guidelines is provided, those using this guide are encouraged to provide more detail or use more stringent guidelines than those suggested.

NOTICE: SEMI makes no warranties or representations as to the suitability of the standards set forth herein for any particular application. The determination of the suitability of the standard is solely the responsibility of the user. Users are cautioned to refer to manufacturer's instructions, product labels, product data sheets, and other relevant literature, respecting any materials or equipment mentioned herein. These standards are subject to change without notice.

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SEMI C18-0301

SPECIFICATION FOR ACETIC ACID

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 October 17, 1999. Initially available at www.semi.org February 2001; to be published March 2001. This document replaces SEMI C1.1 in its entirety. Originally published in 1978; previously published June 1999.

1 Purpose

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

2.2 These standards do not purport to address safety issues, if any, associated with their use. It is the responsibility of the user of these standards to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

3 Limitations

3.1 None.

4 Referenced Standards

4.1 SEMI Standards

SEMI C1 — Specifications for Reagents

4.2 ASTM Standards¹

ASTM D5127 — Standard Guide for Ultra Pure Water Used in the Electronics and Semiconductor Industry

NOTE 1: As listed or revised, all documents cited shall be the latest publications of adopted standards.

5 Terminology

5.1 None.

6 Physical Property (for information only)

Density at 25°C	1.05 g/mL
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NOTE 2: This material freezes at about 16°C.

¹ American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, Pennsylvania 19428-2959, USA. Telephone: 610.832.9585, Fax: 610.832.9555. Website: www.astm.org

7 Requirements

7.1 The requirements for acetic acid for Grade 1 are listed in Table 1.

8 Grade 1 Procedures

NOTE 3: Each laboratory is responsible for verifying the validity of the method within its own operation.

8.1 *Assay* — Place 15 mL (15.8 g) of sample in a 20 × 150 mm test tube in which is centered an accurate thermometer. The sample tube is centered by one or more stoppers in an outer tube about 38 × 20 mm. Cool the entire apparatus, without stirring, in a bath of shaved or crushed ice and sufficient water to immerse the outer tube above the level of the acetic acid. When the thermometer temperature is about 13°C stir to induce freezing and read the thermometer every half minute. The temperature that remains constant for 1 to 2 minutes is the freezing point and should not be below 16°C, indicating not less than 99.7% as CH₃COOH.

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 *Residue after Evaporation* — Evaporate 95 mL (100 g) of sample in a tared porcelain or silica dish to dryness on a steam bath in a hood. Dry at 105°C for 30 minutes, cool in a desiccator, and weigh (see SEMI C1, Section 3.3, Determination of Residue After Evaporation).

8.4 *Solubility in Water* — Mix 10 mL of sample with 30 mL of water. Allow to stand 1 hour. The solution should be as clear as an equal volume of water.

8.5 *Chloride* — Dilute 9.5 mL (10 g) of sample with 10 mL of water. Add 1 mL of silver nitrate reagent solution and evaporate to dryness on a steam bath in a hood. Dissolve the residue in 0.5 mL of ammonium hydroxide, dilute with 20 mL of water and add 1.5 mL of nitric acid. Any turbidity produced should be no greater than that produced when 0.01 mg of chloride ion (Cl⁻) is treated as the sample.

8.6 *Phosphate* — Evaporate 9.5 mL (10 g) of sample to dryness on a steam bath in a hood. Dissolve the residue, warming if necessary, 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 should be no greater than that produced when 0.01 mg of phosphate ion (PO_4^{2-}) is treated as the sample.

8.7 *Substances Reducing Dichromate* — To 10 mL (10.5 g) of sample, add 1.0 mL of 0.1 N (0.017 M) potassium dichromate solution and cautiously add 10 mL of sulfuric acid. Cool the solution to room temperature and allow to stand for 30 minutes. Add 50 mL of water slowly and cautiously with continual swirling, allow to cool, and then add 1 mL of freshly prepared potassium iodide reagent solution. Titrate the liberated iodine with 0.1 N (0.1 M) thiosulfate solution using starch as the indicator. Compare the volume of thiosulfate solution required with that for a 10 mL water blank prepared in parallel with the sample. The difference between the titrations for sample and blank should be no greater than 0.40 mL.

8.8 *Substances Reducing Permanganate* — Dilute 40 mL (42 g) of sample with 10 mL of water. Cool to 15°C, add 0.30 mL of 0.1 N (0.02 M) potassium permanganate, and allow to stand at 15°C for 10 minutes. The pink color should not be entirely discharged.

8.9 *Sulfate* — To 95 mL (100 g) of sample, add 10 mL of sodium carbonate reagent solution and evaporate to dryness in a hood. Dissolve the residue in 10 mL of water and 1 mL of dilute hydrochloric acid (1 + 19); filter if necessary. Add 1 mL of barium chloride reagent solution, mix and allow to stand for 10 minutes. Any turbidity developed should be no greater than that produced when 0.05 mg of sulfate ion (SO_4^{2-}) is treated as the sample.

8.10 *Arsenic and Antimony (as As)* — To 190 mL (200 g) of sample in a 400 mL beaker, add 5 mL of nitric acid and 5 mL of sulfuric acid and evaporate to dense fumes of sulfur trioxide in a hood. 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 0.001 mg of arsenic (As).

8.11 *Acetic Anhydride* — Place 52.2 g (50 mL) of sample in a 250 mL titration flask. In a second flask

place 50 mL of glacial acetic acid known to be free from acetic anhydride (see NOTE 3). Into each flask pipet 10 mL of 1.0% solution of 4, 4' -methylenedianiline (4, 4' -diaminodiphenylmethane) in glacial acetic acid (see NOTE 4) and add 0.10 mL of 1.0% solution of crystal violet in glacial acetic acid. Titrate each solution with a 0.1 N solution of perchloric acid in glacial acetic acid (see NOTE 5) to a green endpoint. Subtract the volume for the titration of the sample from the volume for the other titration. One mL of 0.1 N perchloric acid corresponds to 0.0194% ($\text{CH}_3\text{CO})_2\text{O}$ for a 50 mL sample.

NOTE 4: Glacial acetic acid suspected of containing anhydride may be purified by adding 0.50 mL of water per 100 mL and digesting overnight in a glass-stoppered flask on the steam bath. If this acid is used for comparison in the above test, 0.25 mL of water should be added to the flask containing the test sample just before the endpoint, because water affects the indicator change slightly.

NOTE 5: Dissolve 2.50 g of 4, 4' -methylenedianiline (colorless or only slightly colored) in glacial acetic acid to make 250 mL. Protect the solution from light.

NOTE 6: Slowly add 4.5 mL of 70% perchloric acid to about 400 mL of glacial acetic acid and dilute with glacial acetic acid to 500 mL. Standardize against potassium hydrogen phthalate in glacial acetic acid solution using crystal violet as indicator.

8.12 *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.

8.12.1 *Special Reagents*

8.12.1.1 *Solution A* — Glycerol (ACS Reagent Grade) 10 g, Adipic Acid (99+%) 1 g, EDTA Acid (ACS Reagent Grade) 0.1 g. Dilute to 1 L using water meeting the criteria for Type E1 in ASTM D5127.

8.12.1.2 *Nitric Acid, Ultra Pure* — Use nitric acid specified for ultra low metal ion content.

8.12.1.3 *2% Nitric Acid Solution* — Dilute 10 mL of ultra pure nitric acid to 1 L using water meeting the criteria for Type E1 in ASTM D5127.

8.12.2 *Sample Preparation*

8.12.2.1 In a clean environment, place 100 grams of sample in a PTFE dish. Add 50 mL of solution A. Slowly evaporate on a hot water bath avoiding loss of

sample by effervescence or spattering until there is no further loss of liquid. Cool. Add 1 mL of ultra pure, 70% nitric acid. While maintaining volume, carefully warm several minutes to dissolve any residue. Cool. Transfer quantitatively to a 50 mL volumetric flask using 2% nitric acid for rinsing and dilution to volume. Run a reagent blank.

8.12.3 Analysis

8.12.3.1 Using the acidic sample standards and a reagent blank, analyze group I elements by flame atomic absorption spectroscopy and all other elements by plasma emission spectroscopy.

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.

14 Tier A Procedures

14.1 This section does not apply to this chemical.

15 Tier B Procedures

15.1 This section does not apply to this chemical.

16 Tier C Procedures

16.1 This section does not apply to this chemical.

17 Tier D Procedures

17.1 This section does not apply to this chemical.

Table 1 Impurity Limits and Other Requirements for Acetic Acid

Previous SEMI Reference #	C1.1-96
	Grade 1
	(Specification)
Assay (CH_3COOH)	99.7% min
Color (APHA)	10 max
Residue after Evaporation	10 ppm max
Solubility in Water	To pass test
Substances Reducing Dichromate	To pass test
Substances Reducing Permanganate	To pass test
Chloride (Cl)	1 ppm max
Phosphate (PO_4)	1 ppm max
Sulfate (SO_4)	0.5 ppm max
Acetic Anhydride [$(\text{CH}_3\text{CO})_2\text{O}$]	0.1% max
Aluminum (Al)	0.3 ppm max
Arsenic and Antimony (as As)	0.005 ppm max
Boron (B)	0.2 ppm max
Calcium (Ca)	0.3 ppm max
Chromium (Cr)	0.2 ppm max
Copper (Cu)	0.1 ppm max
Gold (Au)	0.3 ppm max
Iron (Fe)	0.2 ppm max
Lead (Pb)	0.3 ppm max
Magnesium (Mg)	0.3 ppm max
Manganese (Mn)	0.3 ppm max
Nickel (Ni)	0.1 ppm max
Potassium (K)	0.3 ppm max



Previous SEMI Reference #	C1.1-96
	Grade 1
	(Specification)
Sodium (Na)	0.3 ppm max
Tin (Sn)	0.3 ppm max
Titanium (Ti)	0.3 ppm max
Zinc (Zn)	0.3 ppm max
Particles in bottles: size, #/mL	≥1.0 µm, 25 max

NOTICE: SEMI makes no warranties or representations as to the suitability of the standards set forth herein for any particular application. The determination of the suitability of the standard is solely the responsibility of the user. Users are cautioned to refer to manufacturer's instructions, product labels, product data sheets, and other relevant literature respecting any materials mentioned herein. These standards are subject to change without notice.

The user's attention is called to the possibility that compliance with this standard may require use of copyrighted material or of an invention covered by patent rights. By publication of this standard, SEMI takes no position respecting the validity of any patent rights or copyrights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of any such patent rights or copyrights, and the risk of infringement of such rights, are entirely their own responsibility.



SEMI C19-0301

SPECIFICATION FOR ACETONE

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 October 17, 1999. Initially available at www.semi.org February 2001; to be published March 2001. This document replaces SEMI C1.2 in its entirety. Originally published in 1978; previously published June 1999.

1 Purpose

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

2.2 These standards do not purport to address safety issues, if any, associated with their use. It is the responsibility of the user of these standards to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

3 Limitations

3.1 None.

4 Referenced Documents

4.1 SEMI Standards

SEMI C1 — Specifications for Reagents

4.2 ASTM Standards¹

ASTM D5127 — Standard Guide for Ultra Pure Water Used in the Electronics and Semiconductor Industry

NOTE 1: As listed or revised, all documents cited shall be the latest publications of adopted standards.

5 Terminology

5.1 None.

6 Physical Property (for information only)

Density at 25°C	0.79 g/mL
Boiling Point	56.3°C

¹ American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, Pennsylvania 19428-2959, USA. Telephone: 610.832.9585, Fax: 610.832.9555. Website: www.astm.org

7 Requirements

7.1 The requirements for acetone for Grade 1 are listed in Table 1.

8 Grade 1 Procedures

NOTE 2: 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 1 mm film of DB-1701 or equivalent (14% cyanopropylphenyl which has been surface bonded and crosslinked).

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:	1 μL split
Carrier Gas:	Helium at 3 mL/min
Detector:	Flame Ionization
Approximate Retention Times (min):	
Methanol	1.1
Acetaldehyde	2.3
Acetone	2.9
Isopropanol	3.3
Cumene	10.0
Mesityl Oxide	11.8
Diacetone Alcohol	12.0

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 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 25 mL (20 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 25 mL of pyridine to a dry titration flask and add Karl Fischer (KF) reagent to a visually or electrometrically determined endpoint that persists for 30 seconds. Add 25 mL (20 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.

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

8.7 Solubility in Water — Mix 40 mL of sample with 40 mL of water. Allow to stand for 30 minutes. The solution should be as clear as an equal volume of water.

8.8 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, dilute to 20 mL with water, and 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.

8.9 Phosphate — To 125 mL (100 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.

8.10 Arsenic and Antimony (as As) — Evaporate 250 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, 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 of the sample should be no greater than that of the standard containing 0.002 mg of arsenic (As).

8.11 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.

8.11.1 Special Reagents

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

8.11.1.2 Mannitol Powder — Use mannitol specified for reagent grade (A.C.S.) and determined, via the reagent blank, to be ultra low metal ion content.

8.11.1.3 5% Mannitol Solution — Dissolve and dilute 5 g of mannitol to 100 mL using water meeting the criteria for Type E1 in ASTM D5127.

8.11.1.4 2% (v/v) Hydrochloric Acid Solution — Dilute 20 mL of ultra pure, 12 M hydrochloric acid to 1 L using water meeting the criteria for Type E1 in ASTM D5127.

8.11.2 Sample Preparation

8.11.2.1 In a clean environment, place 250 g of solvent 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 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.

8.11.3 Analysis

8.11.3.1 Using the prepared sample and reagent blank, analyze group I elements potassium (K) and sodium (Na) by atomic absorption spectroscopy and all other elements by plasma emission spectrometry. Apply, if necessary, a reagent blank correction to the final determined value of the sample.

NOTE 3: Due to the uncertainty of acid concentration in the liquid residue the final concentration can be estimated to be approximately 2% (v/v).

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.

14 Tier A Procedures

14.1 This section does not apply to this chemical.

15 Tier B Procedures

15.1 This section does not apply to this chemical.

16 Tier C Procedures

16.1 This section does not apply to this chemical.

17 Tier D Procedures

17.1 This section does not apply to this chemical.

Table 1 Impurity Limits and Other Requirements for Acetone

Previous SEMI Reference #	C1.2-96
	Grade 1
	(Specification)
Assay ($[\text{CH}_3]_2\text{CO}$)	99.5% min
Color (APHA)	10 max
Acidity	0.3 $\mu\text{eq/g}$ max
Alkalinity	0.5 $\mu\text{eq/g}$ max
Residue after Evaporation	5 ppm max
Water (H_2O)	0.5% max
Solubility in Water	To pass test
Chloride (Cl)	0.2 ppm max
Phosphate (PO_4)	0.1 ppm max
Aluminum (Al)	0.1 ppm max
Arsenic and Antimony (as As)	0.01 ppm max
Boron (B)	0.1 ppm max
Calcium (Ca)	0.1 ppm max
Chromium (Cr)	0.1 ppm max
Copper (Cu)	0.1 ppm max
Gold (Au)	0.1 ppm max
Iron (Fe)	0.1 ppm max
Lead (Pb)	0.1 ppm max
Magnesium (Mg)	0.1 ppm max
Manganese (Mn)	0.1 ppm max
Nickel (Ni)	0.1 ppm max
Potassium (K)	0.1 ppm max
Sodium (Na)	0.1 ppm max
Tin (Sn)	0.1 ppm max
Titanium (Ti)	0.1 ppm max



Previous SEMI Reference #	C1.2-96
	Grade 1
	(Specification)
Zinc (Zn)	0.1 ppm max
Particles in bottles: size, #/mL	$\geq 1.0 \mu\text{m}$, 10 max

NOTICE: SEMI makes no warranties or representations as to the suitability of the standards set forth herein for any particular application. The determination of the suitability of the standard is solely the responsibility of the user. Users are cautioned to refer to manufacturer's instructions, product labels, product data sheets, and other relevant literature respecting any materials mentioned herein. These standards are subject to change without notice.

The user's attention is called to the possibility that compliance with this standard may require use of copyrighted material or of an invention covered by patent rights. By publication of this standard, SEMI takes no position respecting the validity of any patent rights or copyrights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of any such patent rights or copyrights, and the risk of infringement of such rights, are entirely their own responsibility.



SEMI C20-1101

SPECIFICATION AND GUIDELINES FOR AMMONIUM FLUORIDE 40%

This specification and these guidelines 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 August 27, 2001. Initially available at www.semi.org September 2001; to be published November 2001. This document replaces SEMI C1.3, C7.18, and C11.2 in their entirety. Originally published in 1978, 1995, and 1994 respectively. Previously published March 2001.

1 Purpose

1.1 The purpose of this document is to standardize requirements for ammonium fluoride 40% 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 ammonium fluoride 40% 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 ammonium fluoride 40% used in the semiconductor industry.

2.2 The VLSI grade purity level is typically required by semiconductor devices with geometries of 0.8–1.2 microns.

2.3 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 limitations prior to use.

3 Limitations

3.1 None.

4 Referenced Standards

SEMI C1 — Specifications for Reagents

NOTE 1: Unless otherwise indicated, all documents cited shall be the latest published versions.

5 Terminology

5.1 None.

6 Physical Property (for information only)

Density at 25°C	1.11 g/mL
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7 Requirements

7.1 The requirements for ammonium fluoride 40% for Grade 1, VLSI Grade, and Tiers A and B are listed in Table 1.

8 Grade 1 Procedures

8.1 *Assay* — Accurately weigh 3 g of sample in a polyethylene weighing bottle. Transfer with water to a polyethylene beaker and dilute to 100 mL. Add 40 mL of neutralized formaldehyde solution and stir magnetically for 15 minutes or allow to stand for 1/2 hour. Titrate with standardized 1 N sodium hydroxide to a slight pink color.

$$\% \text{ Assay} = \frac{\text{mL} \times \text{N of NaOH} \times 3.704}{\text{Weight of sample (g)}}$$

NOTE 2: *Neutralized formaldehyde solution*: Dilute 20 mL of 37% formaldehyde solution with 20 mL of water, add 0.1 mL of phenolphthalein indicator solution, and titrate with 0.1 N sodium hydroxide to a slight pink color.

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 *pH of a 1% solution* — Dilute 2.5 mL (2.8 g) of sample to 100 mL with carbon dioxide- and ammonia-free water. Using a pH meter determine the pH at 25°C 1 to 2 minutes after immersion of electrodes. The pH range 6.0–7.5 corresponds to 0.2% free hydrogen fluoride (HF) to 0.2% ammonium hydroxide (NH_4OH) in the original solution.

8.4 *Chloride* — Mix 2.2 mL (2.5 g) of sample with 20 mL of water containing 0.5 g of boric acid. Add 1 mL of nitric acid and 1 mL of silver nitrate reagent solution, and allow to stand for 5 minutes. Any turbidity produced should be no greater than that produced when 0.01 mg of chloride ion (Cl^-) is treated as the sample.

8.5 *Nitrate* — To 2 mL of water in a white plastic beaker, add 0.9 mL (1 g) of sample, 1 mL of sulfuric acid, 0.05 mL of 0.01 N (0.002 M) potassium permanganate, mix, and decolorize with sodium

arsenite reagent solution. Dilute to 50 mL with brucine sulfate reagent solution and mix. Heat the solution in a preheated (boiling water) bath for 10 minutes. Cool rapidly in an ice bath to room temperature. The yellow color of the sample should be no greater than that produced when 0.01 mg of nitrate ion (NO_3^-) is treated as the sample.

8.6 Phosphate — To a 9 mL (10 g) sample in a platinum dish, add 1 mL of sodium carbonate reagent solution and 40 mL of nitric acid. Evaporate carefully, to prevent spattering, to near dryness. Cool, wash down the sides of the dish with 5 mL of nitric acid, and evaporate to dryness. Repeat the evaporation with nitric acid two more times to ensure complete removal of all the fluoride. To the cooled dish, add 25 mL of 0.5 N sulfuric acid to dissolve the residue, warming if necessary. Cool, transfer to a color comparison tube, and add 1 mL of ammonium molybdate reagent solution, 1 mL of p-(methylamino)phenol sulfate reagent solution, and allow to stand at room temperature for 2 hours. Any blue color should be no greater than that produced when 0.01 mg of phosphate ion (PO_4^{3-}) is treated as the sample.

8.7 Sulfate — To 23 mL (25 g) of sample, add 10 mL of sodium carbonate reagent solution and heat gently until sample has been volatilized. To the residue add 5 mL of hydrochloric acid and evaporate to dryness in a hood. Dissolve the residue in 10 mL of water and 1 mL of dilute hydrochloric acid (1 + 19); filter if necessary. Add 1 mL of barium chloride reagent solution, mix, and allow to stand for 10 minutes. Any turbidity developed should be no greater than that produced when 0.05 mg of sulfate ion (SO_4^{2-}) solution is treated as the sample.

8.8 Arsenic and Antimony (as As) — To 30 mL (33 g) in a fluoroplastic beaker, add 20 mL of nitric acid and 5 mL of hydrochloric acid, and evaporate to dryness in a sand bath in a hood. Completely volatilize the ammonium fluoride, but do not bake. Add 10 mL of water 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 that 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 0.001 mg of arsenic (As).

8.9 Trace Element Contents — 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 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 Specific procedures for this grade do not exist. Refer to Section 8 for available procedures.

14 Tier A Procedures

14.1 Standardized test methods are being developed for all parameters at the purity levels indicated. The Process Chemicals Committee considers a test method to be valid only if there is a documented recovery study showing a recovery of 75–125%. Recovery is for a known sample spike at 50% of the specified level.

15 Tier B Procedures

15.1 Standardized test methods are being developed for all parameters at the purity levels indicated. The Process Chemicals Committee considers a test method to be valid if there is a documented recovery study showing a recovery of 75–125%. Recovery is for a known sample spike at 50% of the specified level.

16 Tier C Procedures

16.1 This section does not apply to this chemical.

17 Tier D Procedures

17.1 This section does not apply to this chemical.

Table 1 Impurity Limits and Other Requirements for Ammonium Fluoride 40%

Previous SEMI Reference #	C1.3-95	C11.2-94	C7.18-95	--
	Grade 1	VLSI Grade	Tier A	Tier B
	(Specification)	(Guideline)	(Guideline)	(Guideline)
Assay (NH_4F)	39.0–41.0% min	39–41% min	39.0–41.0%	39.0–41.0%
Color (APHA)	10 max	10 max	10 max	10 max
Residue after Ignition	--	10 ppm max	--	--
pH (1% solution at 25°C)	6.0–7.5	6.2–7.0	6.0–7.5	6.0–7.5
Ammonium Hydrogen Fluoride (NH_4HF_2)	--	200 ppm max	--	--
Chloride (Cl)	4 ppm max	2 ppm max	2 ppm max	2 ppm max
Nitrate (NO_3)	10 ppm max	10 ppm max	3 ppm max	3 ppm max
Phosphate (PO_4)	1 ppm max	0.2 ppm max	0.5 ppm max	0.5 ppm max
Sulfate (SO_4)	2 ppm max	2 ppm max	2 ppm max	2 ppm max
Aluminum (Al)	0.2 ppm max	0.05 ppm max	10 ppb max	1 ppb max
Antimony (Sb)	--	--	10 ppb max	1 ppb max
Arsenic (As)	--	--	10 ppb max	1 ppb max
Arsenic and Antimony (as As)	0.03 ppm max	0.03 ppm max	--	--
Barium (Ba)	--	0.01 ppm max	10 ppb max	1 ppb max
Beryllium (Be)	--	0.01 ppm max	--	--
Bismuth (Bi)	--	0.02 ppm max	--	--
Boron (B)	0.2 ppm max	0.05 ppm max	10 ppb max	1 ppb max
Cadmium (Cd)	--	0.01 ppm max	10 ppb max	1 ppb max
Calcium (Ca)	0.2 ppm max	0.1 ppm max	10 ppb max	1 ppb max
Chromium (Cr)	0.1 ppm max	0.01 ppm max	10 ppb max	1 ppb max
Cobalt (Co)	--	0.01 ppm max	--	--
Copper (Cu)	0.1 ppm max	0.01 ppm max	10 ppb max	1 ppb max
Gallium (Ga)	--	0.01 ppm max	--	--
Germanium (Ge)	--	0.05 ppm max	--	--
Gold (Au)	0.3 ppm max	0.02 ppm max	--	--
Indium (In)	--	0.01 ppm max	--	--
Iron (Fe)	0.2 ppm max	0.05 ppm max	10 ppb max	1 ppb max
Lead (Pb)	0.3 ppm max	0.01 ppm max	10 ppb max	1 ppb max
Lithium (Li)	--	0.01 ppm max	10 ppb max	1 ppb max
Magnesium (Mg)	0.2 ppm max	0.05 ppm max	10 ppb max	1 ppb max
Manganese (Mn)	0.2 ppm max	0.01 ppm max	10 ppb max	1 ppb max
Molybdenum (Mo)	--	0.01 ppm max	--	--
Nickel (Ni)	0.3 ppm max	0.01 ppm max	10 ppb max	1 ppb max
Platinum (Pt)	--	0.05 ppm max	--	--
Potassium (K)	0.3 ppm max	0.05 ppm max	10 ppb max	1 ppb max
Silicon (Si)	--	200 ppm max	3000 ppb max (See NOTE 1.)	--
Silver (Ag)	--	0.05 ppm max	--	--
Sodium (Na)	0.3 ppm max	0.1 ppm max	10 ppb max	1 ppb max
Strontium (Sr)	--	0.01 ppm max	--	--
Thallium (Tl)	--	0.02 ppm max	--	--
Tin (Sn)	0.2 ppm max	0.02 ppm max	10 ppb max	1 ppb max
Titanium (Ti)	0.3 ppm max	0.01 ppm max	10 ppb max	1 ppb max
Vanadium (V)	--	0.01 ppm max	10 ppb max	1 ppb max
Zinc (Zn)	0.2 ppm max	0.05 ppm max	10 ppb max	1 ppb max
Zirconium (Zr)	--	0.01 ppm max	--	--



Previous SEMI Reference #	C1.3-95	C11.2-94	C7.18-95	--
	Grade 1 (Specification)	VLSI Grade (Guideline)	Tier A (Guideline)	Tier B (Guideline)
Particles in bottles: size, #/mL	$\geq 1.0 \mu\text{m}$, 25 max	$\geq 0.5 \mu\text{m}$, 250 max	See NOTE 2.	See NOTE 2.

NOTE 1: For III-V compound users only.

NOTE 2: Due to the limitations of current particle counters, particle size and number are to be agreed upon between supplier and user. See SEMI C1, Section 3.9 for particle counting methodology.

NOTICE: SEMI makes no warranties or representations as to the suitability of the standard set forth herein for any particular application. The determination of the suitability of the standard is solely the responsibility of the user. Users are cautioned to refer to manufacturer's instructions, product labels, product data sheets, and other relevant literature respecting any materials or equipment mentioned herein. These standards are subject to change without notice.

The user's attention is called to the possibility that compliance with this standard may require use of copyrighted material or of an invention covered by patent rights. By publication of this standard, SEMI takes no position respecting the validity of any patent rights or copyrights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of any such patent rights or copyrights, and the risk of infringement of such rights, are entirely their own responsibility.



SEMI C21-0301

SPECIFICATIONS AND GUIDELINES FOR AMMONIUM HYDROXIDE

These specifications and guidelines 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 October 17, 1999. Initially available on SEMI OnLine February 2001; to be published March 2001. This document replaces SEMI C1.4, C7.1, C8.1, C11.1, and C17.1 in their entirety. Originally published in 1978, 1990, 1992, 1994, and 1997 respectively; previously published June 2000.

1 Purpose

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

2.2 The VLSI grade purity level is typically required by semiconductor devices with geometries of 0.8–1.2 microns.

2.3 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 limitations prior to use.

3 Limitations

3.1 The guideline for VLSI grade ammonium hydroxide is only applicable for materials that remain below 25°C during transport and storage.

4 Referenced Standards

4.1 SEMI Standards

SEMI C1 — Specifications for Reagents

4.2 ASTM Standards¹

ASTM D5127 — Standard Guide for Ultra Pure Water Used in the Electronics and Semiconductor Industry

NOTE 1: As listed or revised, all documents cited shall be the latest publications of adopted standards.

5 Terminology

5.1 None.

6 Physical Property (for information only)

Density at 25°C	0.90 g/mL
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7 Requirements

7.1 The requirements for ammonium hydroxide for Grades 1, 2, 3, and 4, and VLSI Grade are listed in Table 1.

8 Grade 1 Procedures

NOTE 2: Each laboratory is responsible for verifying the validity of the method within its own operation.

8.1 *Assay* — Accurately weigh a small glass-stoppered flask containing about 15 mL of water. Deliver from a pipet about 2 mL of the sample near the water surface, stopper immediately, and reweigh. Add 0.1 mL of methyl red indicator solution and titrate with standardized 1 N hydrochloric acid to a yellow-to-red color change.

$$\% \text{ Assay} = \frac{\text{mL} \times \text{N of HCl} \times 1.703}{\text{Weight of sample (g)}}$$

8.2 *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.

8.3 *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.

8.4 *Carbon Dioxide* — Dilute 11 mL (10 g) of sample with 10 mL of carbon dioxide-free water and add 5 mL of a clear, saturated solution of barium hydroxide. Any turbidity should be no greater than that produced when

¹ American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, Pennsylvania 19428-2959, USA. Telephone: 610.832.9585, Fax: 610.832.9555. Website: www.astm.org

the same volume of the barium hydroxide solution is added to 21 mL of the carbon dioxide-free water containing 0.5 mg of anhydrous sodium carbonate.

8.5 Substances Reducing Permanganate — Dilute 3 mL (2.7 g) of sample with 5 mL of water. Add 50 mL of 10% sulfuric acid and 0.05 mL of 0.1 N (0.02 M) potassium permanganate. Boil for 5 minutes. The pink color should not be entirely discharged.

8.6 Chloride — To 22 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 10 mL of water. Add 1 mL of nitric acid. Filter, if necessary, through a chloride-free filter. Dilute to 20 mL with water and 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.

8.7 Phosphate — Evaporate 22 mL (20 g) of sample to dryness on a steam bath in a hood. Take up the residue with 25 mL of approximately 0.5 N sulfuric acid. Add 1 mL of ammonium molybdate reagent solution and 1 mL of p-(methylamino)phenol sulfate reagent solution, and allow to stand for 2 hours at room temperature. Any blue color should be no greater than that produced when 0.01 mg of phosphate ion (PO₄³⁻) is treated as the sample.

8.8 Total Sulfur (as SO₄) — To 56 mL (50 g) of sample, add 1 mL of sodium carbonate reagent solution and evaporate on a steam bath in a hood to a volume of about 5 mL. Add 2 mL of bromine water and evaporate to dryness. Dissolve the residue with 10 mL of water and 1 mL of dilute hydrochloric acid (1 + 19); filter, if necessary. Add 1 mL of barium chloride reagent solution, mix, and allow to stand for 10 minutes. Any turbidity developed should be no greater than that produced when 0.05 mg of sulfate ion (SO₄²⁻) is treated as the sample.

8.9 Arsenic and Antimony (as As) — Evaporate 44 mL (40 g) of sample in a 150 mL beaker to a small volume in a hood. Cool, cautiously add 10 mL of water and 5 mL of sulfuric acid, and 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 that 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 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 5% Mannitol Solution — Weigh out 5 g of Mannitol Powder (ACS Reagents Grade), and dilute to 100 mL using water meeting the criteria for Type E1 in ASTM D5127. Mannitol solution is subject to attack by microorganisms and should be carefully monitored for such contamination.

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

8.10.1.3 2% (v/v) Hydrochloric Acid Solution — Dilute 20 mL of ultra pure hydrochloric acid to 1 L using water meeting the criteria for Type E1 in ASTM D5127.

8.10.2 Sample Preparation

8.10.2.1 In a clean environment, place 250 mL of aqueous ammonium hydroxide 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. Cool. Add 1 mL of ultra pure, 12 M hydrochloric acid. Continue heating until approximately 0.5 mL of liquid remains. Cool. Transfer quantitatively to 50 mL volumetric flask using 2% (v/v) hydrochloric acid for rinsing and dilution to volume. Run reagent blank.

8.10.3 Analysis

8.10.3.1 Using the acid sample and reagent blank, analyze group 1 elements by flame atomic absorption spectroscopy and all other elements by plasma emission spectroscopy.

NOTE 3: Due to the uncertainty of the acid concentration in the liquid residue, the final concentration can be estimated at approximately 1-2% (v/v). Standard calibration solutions are to use this same acid concentration.

9 Grade 2 Procedures

NOTE 4: Each laboratory is responsible for verifying the validity of the method within its own operation.

9.1 Non-Metal Impurities

9.1.1 See Section 8, which contains procedures for the following tests:

Assay
Color (APHA)
Carbon Dioxide
Substances Reducing Permanganate

9.2 Anions

9.2.1 The following method has given satisfactory results in determining anion impurities at the values specified for each of the following anions: chloride (Cl), phosphate (PO_4), nitrate (NO_3), and sulfate (SO_4). Alternate methods may be used as long as appropriate studies demonstrate a recovery between 75–125% of a known sample spike for half of the value of each specified anion.

9.2.2 Special Reagents

9.2.2.1 *Eluent* — Prepare an eluent solution that is 2.2 mM sodium carbonate (Na_2CO_3) and 0.75 mM sodium bicarbonate (NaHCO_3) in deionized water meeting the criteria for Type E1.1 in ASTM D5127. Store eluent under a helium gas blanket.

9.2.2.2 *Regenerant* — Prepare a 0.025 N sulfuric acid (H_2SO_4) in deionized water meeting the criteria for Type E1.1 in ASTM D5127.

9.2.2.3 *Potassium Carbonate Solution* — Prepare a solution containing 500 mg of reagent grade potassium carbonate (K_2CO_3) into 100 mL of water meeting the criteria for Type E1.1 in ASTM D5127.

9.2.3 Sample Preparation

9.2.3.1 In a clean environment, place 40 g of sample into a clean beaker. Add 1 mL of a 5 mg/mL potassium carbonate solution and evaporate carefully (at 100°C) to a volume of 0.5 mL. Dilute with water meeting the criteria for Type E1.1 in ASTM D5127 to a final volume of 20 mL.

9.2.4 Analysis

9.2.4.1 Using the prepared solutions and blanks, analyze chloride, nitrate, phosphate, and sulfate by ion chromatography. Run a reagent blank. Samples and reagent blanks should be prepared and analyzed in triplicate.

9.2.4.2 *Columns* — Precolumn should be AG4-A (Dionex) or equivalent and Separation column should be AS4-A (Dionex) or equivalent.

9.3 Trace Metals Analysis

9.3.1 The following method has given satisfactory results in determining metal ion impurities at the values specified for each of the following metals: aluminum (Al), antimony (Sb), arsenic (As), boron (B), calcium

(Ca), chromium (Cr), copper (Cu), gold (Au), iron (Fe), lead (Pb), magnesium (Mg), manganese (Mn), nickel (Ni), potassium (K), sodium (Na), titanium (Ti), and zinc (Zn). Alternate methods may be used as long as appropriate studies demonstrate a recovery between 75–125% of a known sample spike for half of the value of each specified element.

9.3.2 Special Reagents

9.3.2.1 *Nitric Acid, Ultra Pure* — Use nitric acid specified for low metal ion content.

9.3.2.2 *4% Nitric Acid Solution* — Dilute 40 mL of ultra pure nitric acid to 1 L using water meeting the criteria for Type E1.1 in ASTM D5127.

9.3.2.3 *Water* — The water used for all the dilution, calibration, and standards should meet at a minimum the criteria for Type E1.1 in ASTM D5127 in regard to cation analysis.

9.3.2.4 *Indium Internal Standard* — Make up an indium internal standard solution to a concentration of 20 $\mu\text{g}/\text{mL}$ (ppm) from an appropriate concentrated indium standard solution.

9.3.3 Sample Preparation

9.3.3.1 In a clean environment, evaporate a 50.0 g sample at low heat until approximately 20 g of the sample remains. Carefully add 1 mL of the ultra pure nitric acid and gently warm for several minutes. Cool to room temperature, add 25 μL of the indium internal standard, and dilute with Type E1.1 water to a final weight of 25.0 g.

9.3.4 Analysis

9.3.4.1 Using the prepared solutions and blanks, analyze sodium, potassium, calcium, and iron by graphite furnace atomic absorption (GFAA) and the remaining elements by inductively coupled plasma mass spectrometry (ICP/MS). For calibration, the standards are made up in 4% nitric acid solution with final concentration of 20 ng/g of the indium internal standard. Run a reagent blank.

10 Grade 3 Procedures

NOTE 5: The analytical procedures associated with this standard are not intended to be the only acceptable procedure or the best procedure available. The published procedures have been found to meet the required criteria for acceptance of an analytical procedure. Alternate procedures may be used if they meet the same criteria as the published procedures.

NOTE 6: Each laboratory is responsible for verifying the validity of each method within its own operation.

10.1 Non-Metal Impurities

10.1.1 See Section 8, which contains procedures for the following tests:

- Assay
- Color (APHA)
- Carbon Dioxide
- Substances Reducing Permanganate

10.2 Anions

10.2.1 The following method has given satisfactory results in determining anion impurities at the values specified for each of the following anions: chloride (Cl), phosphate (PO_4), and sulfate (SO_4). Alternate methods may be used as long as appropriate studies demonstrate a recovery between 75–125% of a known sample spike for half of the value of each specified element.

10.2.2 Special Reagents

10.2.2.1 *Eluent* — Prepare an eluent solution that is 2.2 mM sodium carbonate (Na_2CO_3) and 0.75 mM sodium bicarbonate (NaHCO_3) in deionized water meeting the criteria for Type E1.1 in ASTM D5127. Store eluent under a helium gas blanket.

10.2.2.2 *Regenerant* — Prepare a 0.025 N sulfuric acid (H_2SO_4) in deionized water meeting the criteria for Type E1.1 in ASTM D5127.

10.2.2.3 *Potassium Carbonate Solution* — Prepare a solution containing 500 mg of reagent grade potassium carbonate (K_2CO_3) in 100 mL of water meeting the criteria for Type E1.1 in ASTM D5127.

10.2.3 Sample Preparation

10.2.3.1 In a clean environment, place 40 g of sample into a clean beaker. Add 1 mL of a 5 mg/mL potassium carbonate solution and evaporate carefully (at 100°C) to a volume of 0.5 mL. Dilute with water meeting the criteria for Type E1.1 in ASTM D5127 to a final volume of 20 mL.

10.2.4 Analysis

10.2.4.1 Using the prepared solutions and blanks, analyze chloride, nitrate, phosphate, and sulfate by ion chromatography. Run a reagent blank. Samples and reagent blanks should be prepared and analyzed in triplicate.

10.2.4.2 *Columns* — Precolumn should be AG4-A (Dionex) or equivalent, and separation column should be AS4-A (Dionex) or equivalent.

10.3 Trace Metals Analysis

10.3.1 The following method has given satisfactory results in determining metal ion impurities at the values specified for each of the following metals: aluminum (Al), antimony (Sb), arsenic (As), 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 a recovery between 75–125% of a known sample spike for half of the value of each specified element.

10.3.2 Special Reagents

10.3.2.1 *Nitric Acid, Ultra Pure* — Use nitric acid specified for low metal ion content.

10.3.2.2 *4% Nitric Acid Solution* — Dilute 40 mL of ultra pure nitric acid to 1 L using water meeting the criteria for Type E1.1 in ASTM D5127.

10.3.2.3 *Water* — The water used for all the dilution, calibration, and standards should meet, at a minimum, the criteria for Type E1.1 in ASTM D5127 in regard to cation analysis.

10.3.2.4 *Indium Internal Standard* — Make up an indium internal standard solution to a concentration of 20 $\mu\text{g}/\text{mL}$ (ppm) from an appropriate concentrated indium standard solution.

10.3.3 Sample Preparation

10.3.3.1 In a clean environment, evaporate a 50.0 g sample at low heat until approximately 20 g of the sample remains. Carefully add 1 mL of the ultra pure nitric acid and gently warm for several minutes. Cool to room temperature, add 25 μL of the indium internal standard, and dilute with Type E1.1 water to a final weight of 25.0 g.

10.3.4 Analysis

10.3.4.1 Using the prepared solutions and blanks, analyze sodium, potassium, calcium, and iron by graphite furnace atomic absorption (GFAA) and the remaining elements by inductively coupled plasma mass spectrometry (ICP/MS). For calibration, the standards are made up in 4% nitric acid solution with final concentration of 20 ng/g of the indium internal standard. Run a reagent blank.

11 Grade 4 Procedures

NOTE 7: The analytical procedures associated with this standard are not intended to be the only acceptable procedure or the best procedure available. The published procedures have been found to meet the required criteria for acceptance of an analytical procedure. Alternate procedures may be used if they meet the same criteria as the published procedures.

NOTE 8: Each laboratory is responsible for verifying the validity of each method within its own operation.

11.1 Non-Metal Impurities

11.1.1 See Section 8, which contains procedures for the following tests:

- Assay
- Color (APHA)
- Carbon Dioxide
- Substances Reducing Permanganate

11.2 Anions

11.2.1 The following method has given satisfactory results in determining anion impurities at the values specified for each of the following anions: chloride (Cl), phosphate (PO_4), nitrate (NO_3), and sulfate (SO_4). Alternate methods may be used as long as appropriate studies demonstrate a recovery between 75–125% of a known sample spike for half of the value of each specified anion.

11.2.2 Reagents

11.2.2.1 *Eluent* — Prepare an eluent solution that is 2.2 mM sodium carbonate (Na_2CO_3) and 0.75 mM sodium bicarbonate (NaHCO_3) in deionized water meeting the criteria for Type E1.1 in ASTM D5127. Store eluent under a helium gas blanket.

11.2.2.2 *Regenerant* — Prepare a 0.025 N sulfuric acid (H_2SO_4) in deionized water meeting the criteria for Type E1.1 in ASTM D5127.

11.2.2.3 *Potassium Carbonate Solution* — Prepare a solution containing 500 mg of reagent grade potassium carbonate (K_2CO_3) in 100 mL of water meeting the criteria for Type E1.1 in ASTM D5127.

11.2.3 Sample Preparation

11.2.3.1 In a clean environment, place 200 g of sample into a clean beaker. Add 1 mL of a 5 mg/mL potassium carbonate solution and evaporate carefully (at 100°C) to a volume of 0.5 mL. Dilute with water meeting the criteria for Type E1.1 in ASTM D5127 to a final volume of 20 mL.

11.2.4 Analysis

11.2.4.1 Using the prepared solutions and blanks, analyze chloride, nitrate, phosphate, and sulfate by ion chromatography. Run a reagent blank. Samples and reagent blanks should be prepared and analyzed in triplicate.

11.2.4.2 *Columns* — Precolumn should be AG4-A (Dionex) or equivalent, and separation column should be AS4-A (Dionex) or equivalent.

11.3 Trace Metals Analysis

11.3.1 The following method has given satisfactory results in determining metal ion impurities at the values specified for each of the following metals: aluminum (Al), antimony (Sb), arsenic (As), 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 a recovery between 75–125% of a known sample spike for half of the value of each specified element.

11.3.2 Special Reagents

11.3.2.1 *Nitric Acid, Ultrapure* — Use nitric acid of low metal ion content.

11.3.2.2 *2% Nitric Acid Solution* — Dilute ultrapure nitric acid with water meeting the criteria for Type E1.1 in ASTM D5127.

11.3.2.3 *Water* — The water used for dilution, calibration, and standards should meet, at a minimum, the criteria for Type E1.1 in ASTM D5127 in regard to cation analysis.

11.3.2.4 *Internal Standard Solution* — Make up an internal standard solution to a concentration of 1000 $\mu\text{g}/\text{mL}$ from appropriate concentrated scandium, yttrium, indium, thulium, and thorium standard solutions.

11.3.3 Sample Preparation

11.3.3.1 In a clean environment, in a teflon bottle, evaporate a 50.0 g sample at low heat until approximately 5 g of the sample remains. Cool to room temperature, add 100 μL of the internal standard solution, and dilute with 2% nitric acid to a final weight of 10.0 g.

11.3.4 Analysis

11.3.4.1 Using the prepared solutions and blanks, calibrate the instrument and analyze calcium, iron, sodium, and potassium by cool plasma inductively coupled plasma mass spectrometry (ICP-MS) and the remaining elements by normal plasma ICP-MS.

11.3.4.2 *Calculations* — All data were reported relative to an appropriate 1.0 $\mu\text{g}/\text{L}$ standard and corresponding blank solution. Internal standard corrections were applied to the data.

12 Grade 5 Procedures

12.1 This section does not apply to this chemical.

13 VLSI Grade Procedures

13.1 Specific procedures for this grade do not exist. Refer to Sections 8 and 9 for available procedures.

14 Tier A Procedures

14.1 This section does not apply to this chemical.

15 Tier B Procedures

15.1 This section does not apply to this chemical.

16 Tier C Procedures

16.1 This section does not apply to this chemical.

17 Tier D Procedures

17.1 Standardized test methods are being developed for all parameters at the purity levels indicated. The Process Chemicals Committee considers a test method to be valid if there is a documented recovery study showing a recovery of 75–125%. Recovery is for a known sample spike at 50% of the specified level.

Table 1 Impurity Limits and Other Requirements for Ammonium Hydroxide

Previous SEMI Reference #	C1.4-95	C7.1-96	C8.1-0298	C17.1-0298	C11.1-94	--
	Grade 1 (Specification)	Grade 2 (Specification)	Grade 3 (Specification)	Grade 4 (Specification)	VLSI Grade (Guideline)	Tier D (Guideline)
Assay (as NH ₃)	28.0 - 30.0%	28.0 - 30.0%	28.0 - 30.0%	28.0 - 30.0%	25.0 - 27.0% or 28.0 - 30.0%	28.0 - 30.0%
Appearance	To pass test	--	--	--	--	--
Color (APHA)	10 max	10 max				
Residue after Ignition	--	--	--	--	2 ppm max	--
Residue after Evaporation	--	--	--	--	10 ppm max	--
Substances Reducing KMnO ₄ (as O)	--	--	--	--	5 ppm max	--
Substances Reducing Permanganate	To pass test	To pass test	To pass test	To pass test	--	--
Carbon Dioxide (CO ₂)	20 ppm max	20,000 ppb max	20 ppm max	20 ppm max	--	20 ppm max
Carbonate (CO ₃)	--	--	--	--	10 ppm max	--
Chloride (Cl)	0.5 ppm max	200 ppb max	100 ppb max	50 ppb max	0.5 ppm max	30 ppb max
Nitrate (NO ₃)	--	400 ppb max	100 ppb max	50 ppb max	--	30 ppb max
Phosphate (PO ₄)	0.5 ppm max	200 ppb max	100 ppb max	40 ppb max	0.2 ppm max	30 ppb max
Silica (SiO ₂)	--	--	--	--	0.2 ppm max	--
Sulfide (S)	--	--	--	--	0.2 ppm max	--
Sulfate (SO ₄)	--	200 ppb max	100 ppb max	50 ppb max	2 ppm max	30 ppb max
Total Sulfur (SO ₄)	1 ppm max	--	--	--	--	--
Aluminum (Al)	0.3 ppm max	10 ppb max	1 ppb max	100 ppt max	0.05 ppm max	10 ppt max
Antimony (Sb)	--	5 ppb max	1 ppb max	100 ppt max	--	10 ppt max
Arsenic (As)	--	5 ppb max	1 ppb max	100 ppt max	--	10 ppt max
Arsenic and Antimony (as As)	0.05 ppm max	--	--	--	0.05 ppm max	--
Barium (Ba)	--	--	--	--	0.01 ppm max	10 ppt max
Beryllium (Be)	--	--	--	--	0.01 ppm max	--
Bismuth (Bi)	--	--	--	--	0.02 ppm max	--
Boron (B)	0.1 ppm max	10 ppb max	1 ppb max	100 ppt max	0.01 ppm max	10 ppt max
Cadmium (Cd)	--	--	--	--	0.01 ppm max	10 ppt max
Calcium (Ca)	0.3 ppm max	10 ppb max	1 ppb max	100 ppt max	0.1 ppm max	10 ppt max
Chromium (Cr)	0.2 ppm max	10 ppb max	1 ppb max	100 ppt max	0.01 ppm max	10 ppt max
Cobalt (Co)	--	--	--	--	0.01 ppm max	--
Copper (Cu)	0.1 ppm max	10 ppb max	1 ppb max	100 ppt max	0.01 ppm max	10 ppt max
Gallium (Ga)	--	--	--	--	0.01 ppm max	--
Germanium (Ge)	--	--	--	--	0.05 ppm max	--
Gold (Au)	0.3 ppm max	10 ppb max	1 ppb max	100 ppt max	0.02 ppm max	--

Previous SEMI Reference #	C1.4-95	C7.1-96	C8.1-0298	C17.1-0298	C11.1-94	--
	Grade 1 (Specification)	Grade 2 (Specification)	Grade 3 (Specification)	Grade 4 (Specification)	VLSI Grade (Guideline)	Tier D (Guideline)
Indium (In)	--	--	--	--	0.01 ppm max	--
Iron (Fe)	0.1 ppm max	10 ppb max	1 ppb max	100 ppt max	0.05 ppm max	10 ppt max
Lead (Pb)	0.2 ppm max	10 ppb max	1 ppb max	100 ppt max	0.01 ppm max	10 ppt max
Lithium (Li)	--	--	--	--	0.01 ppm max	--
Magnesium (Mg)	0.3 ppm max	10 ppb max	1 ppb max	100 ppt max	0.05 ppm max	10 ppt max
Manganese (Mn)	0.2 ppm max	10 ppb max	1 ppb max	100 ppt max	0.01 ppm max	10 ppt max
Molybdenum (Mo)	--	--	--	--	0.01 ppm max	--
Nickel (Ni)	0.1 ppm max	10 ppb max	1 ppb max	100 ppt max	0.01 ppm max	10 ppt max
Platinum (Pt)	--	--	--	--	0.02 ppm max	--
Potassium (K)	0.3 ppm max	10 ppb max	1 ppb max	100 ppt max	0.1 ppm max	10 ppt max
Silver (Ag)	--	--	--	--	0.01 ppm max	--
Sodium (Na)	0.3 ppm max	10 ppb max	1 ppb max	100 ppt max	0.2 ppm max	10 ppt max
Strontium (Sr)	--	--	--	--	0.01 ppm max	--
Thallium (Tl)	--	--	--	--	0.02 ppm max	--
Tin (Sn)	0.3 ppm max	10 ppb max	1 ppb max	100 ppt max	0.02 ppm max	10 ppt max
Titanium (Ti)	0.3 ppm max	10 ppb max	1 ppb max	100 ppt max	0.01 ppm max	10 ppt max
Vanadium (V)	--	--	--	--	0.01 ppm max	--
Zinc (Zn)	0.3 ppm max	10 ppb max	1 ppb max	100 ppt max	0.05 ppm max	10 ppt max
Zirconium (Zr)	--	--	--	--	0.01 ppm max	--
Particles in bottles: size, #/mL	≥ 1.0 µm, 25 max	≥ 0.5 µm, 25 max	≥ 0.5 µm, 25 max	≥ 0.5 µm, 25 max (see NOTE 1)	≥ 0.5 µm, 250 max	(See NOTE 2.)

NOTE 1: Care must be taken in analyzing particles because of the potential formation of microbubbles.

NOTE 2: Due to the limitations of current particle counters, particle size and number are to be agreed upon between supplier and user. See SEMI C1, Section 3.9 for particle counting methodology.

NOTICE: These standards do not purport to address safety issues, if any, associated with their use. It is the responsibility of the user of these standards to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. SEMI makes no warranties or representations as to the suitability of the standards set forth herein for any particular application. The determination of the suitability of the standard is solely the responsibility of the user. Users are cautioned to refer to manufacturer's instructions, product labels, product data sheets, and other relevant literature respecting any materials mentioned herein. These standards are subject to change without notice.

The user's attention is called to the possibility that compliance with this standard may require use of copyrighted material or of an invention covered by patent rights. By publication of this standard, SEMI takes no position respecting the validity of any patent rights or copyrights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of any such patent rights or copyrights, and the risk of infringement of such rights, are entirely their own responsibility.

SEMI C22-0699

GUIDELINE FOR BORON TRIBROMIDE

This guideline 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 C7.17 in its entirety. Originally published in 1994.

1 Purpose

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

3 Limitations

3.1 None.

4 Referenced Documents

4.1 None.

5 Terminology

5.1 None.

6 Physical Property (for information only)

Clear Colorless Liquid Density at 20°C	2.54 g/mL
--	-----------

7 Requirements

7.1 The requirements for boron tribromide for Tier A are listed in Table 1.

8 Grade 1 Procedures

8.1 This section does not apply to this chemical.

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.

14 Tier A Procedures

14.1 Standardized test methods are being developed for all parameters at the purity levels indicated. Until standardized test methods are published, test methodology shall be determined by user and producer. The Process Chemicals Committee considers a test method to be valid only if there is a documented recovery study showing a recovery of 75 - 125%. Recovery is for a known sample spike at 50% of the specified level.

15 Tier B Procedures

15.1 This section does not apply to this chemical.

16 Tier C Procedures

16.1 This section does not apply to this chemical.

17 Tier D Procedures

17.1 This section does not apply to this chemical.

Table 1 Impurity Limits and Other Requirements for Boron Tribromide

Previous SEMI Reference #	C7.17-94
	Tier A
	(Guideline)
Color (APHA)	60 max
Aluminum (Al)	5 ppb max
Antimony (Sb)	5 ppb max
Arsenic (As)	10 ppb max
Barium (Ba)	5 ppb max
Bismuth (Bi)	5 ppb max
Calcium (Ca)	10 ppb max
Chromium (Cr)	5 ppb max
Cobalt (Co)	5 ppb max
Copper (Cu)	5 ppb max
Gallium (Ga)	5 ppb max
Gold (Au)	5 ppb max
Iron (Fe)	10 ppb max
Lead (Pb)	5 ppb max
Lithium (Li)	5 ppb max
Magnesium (Mg)	10 ppb max
Manganese (Mn)	5 ppb max
Mercury (Hg)	10 ppb max
Nickel (Ni)	5 ppb max
Potassium (K)	5 ppb max
Silver (Ag)	5 ppb max
Sodium (Na)	5 ppb max
Strontium (Sr)	5 ppb max
Tin (Sn)	5 ppb max
Titanium (Ti)	5 ppb max
Zinc (Zn)	5 ppb max
Particles in bottles: size, #/mL	≥0.5 µm, 25 max

NOTICE: These standards do not purport to address safety issues, if any, associated with their use. It is the responsibility of the user of these standards to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. SEMI makes no warranties or representations as to the suitability of the standards set forth herein for any particular application. The determination of the suitability of the standard is solely the responsibility of the user. Users are cautioned to refer to manufacturer's instructions, product labels, product data sheets, and other relevant literature respecting any materials

mentioned herein. These standards are subject to change without notice.

The user's attention is called to the possibility that compliance with this standard may require use of copyrighted material or of an invention covered by patent rights. By publication of this standard, SEMI takes no position respecting the validity of any patent rights or copyrights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of any such patent rights or copyrights, and the risk of infringement of such rights, are entirely their own responsibility.



SEMI C23-0301

SPECIFICATIONS FOR BUFFERED OXIDE ETCHANTS

These specifications 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 October 17, 1999. Initially available at www.semi.org February 2001; to be published March 2001. This document replaces SEMI C2.2 and C7.23 in their entirety. Originally published in 1981 and 1997 respectively; previously published June 1999.

1 Purpose

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

2.2 These standards do not purport to address safety issues, if any, associated with their use. It is the responsibility of the user of these standards to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

3 Limitations

3.1 None.

4 Referenced Documents

4.1 SEMI Standards

SEMI C1 — Specifications for Reagents

4.2 ASTM Standards¹

ASTM D5127 — Standard Guide for Ultra Pure Water Used in the Electronics and Semiconductor Industry

NOTE 1: As listed or revised, all documents cited shall be the latest publications of adopted standards.

5 Terminology

5.1 *buffered oxide etchant* — any combination of ammonium fluoride and hydrofluoric acid in which the concentrations are expressed in terms of the equivalent

¹ American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, Pennsylvania 19428-2959, USA. Telephone: 610.832.9585, Fax: 610.832.9555. Website: www.astm.org

relative volumes of 40% ammonium fluoride solution and 49% hydrofluoric acid. In the expression, the relative volumes shall be reduced to a ratio of the smallest whole numbers which properly describes the composition. For example, a 7:1 buffered oxide etchant contains the equivalent of 7 volumes of 40.0% ammonium fluoride and 1 volume of 49% hydrofluoric acid.

NOTE 2: Density at temperature.

6 Composition

6.1 For analytical purposes, the absolute concentrations of ammonium fluoride and hydrofluoric acid corresponding to the above definition shall be calculated according to the following equations.

$$\text{Weight \% } \text{NH}_4\text{F} =$$

$$\frac{(\text{volume} \times \text{density} \times \text{concentration}) \text{NH}_4\text{F}}{(\text{volume} \times \text{density}) \text{NH}_4\text{F} + (\text{volume} \times \text{density}) \text{HF}}$$

$$\text{Weight \% HF} =$$

$$\frac{(\text{volume} \times \text{density} \times \text{concentration}) \text{HF}}{(\text{volume} \times \text{density}) \text{NH}_4\text{F} + (\text{volume} \times \text{density}) \text{HF}}$$

where volume and density are expressed in consistent units and concentration is in weight percent to three significant figures.

6.2 Sample calculation for 7:1 buffered oxide etchant using 40.0% ammonium fluoride, density 1.111 g/mL, and 49.0% hydrofluoric acid, density 1.153 g/mL. The absolute percentage concentration of each component follows:

$$\text{Weight \% } \text{NH}_4\text{F} = \frac{7 \times 1.111 \times 40.0}{7 \times 1.111 + 1 \times 1.153} = 34.8\%$$

$$\text{Weight \% HF} = \frac{1 \times 1.153 \times 49.0}{7 \times 1.111 + 1 \times 1.153} = 6.33\%$$

7 Tolerances

7.1 The tolerances allowed for the absolute percentage of each of the components of a buffered oxide etchant shall be:

Ammonium Fluoride:	± 0.5%
Hydrofluoric Acid:	± 0.15%

7.2 For the example above, the permissible range of concentration for ammonium fluoride shall be $34.8 \pm 0.5\%$ and for hydrofluoric acid $6.33 \pm 0.15\%$.

8 Requirements

8.1 The requirements for buffered oxide etchants for Grades 1 and 2 are listed in Table 1.

9 Grade 1 Procedures

9.1 *Hydrofluoric Acid* — Weigh accurately approximately 4.0 grams of sample, transfer to a polyethylene beaker, and dilute with water to about 100 mL. Titrate with standardized 1 N sodium hydroxide. The endpoint may be detected colorimetrically by adding 3 drops of methyl red indicator solution and titrating to a definite yellow (no orange) endpoint. As an alternate method, the endpoint may be detected potentiometrically using an HF resistant pH electrode previously standardized in pH 4 and pH 7 buffers. Titrate to pH 6.5 with continuous stirring. Save the solution for the determination of ammonium fluoride.

$$\% \text{ Hydrofluoric Acid} = \frac{\text{mL} \times \text{N of NaOH} \times 2.001}{\text{Weight of sample (g)}}$$

9.2 *Ammonium Fluoride* — Add 40 mL of neutralized formaldehyde solution (see Section 9.2.1) to the solution from the preceding test and stir magnetically for 30 minutes. Titrate with standardized 1 N sodium hydroxide. The endpoint may be detected colorimetrically using 10 drops of phenolphthalein indicator and titrating to a stable pink end point. As an alternative method, the endpoint may be detected potentiometrically using an HF resistant electrode previously standardized in pH 7 and 9 buffers. Titrate to pH 8.5 with continuous stirring.

$$\% \text{ Ammonium Fluoride} = \frac{\text{mL} \times \text{N of NaOH} \times 3.704}{\text{Weight of sample (g)}}$$

9.2.1 *Neutralized Formaldehyde Solution* — Dilute 20 mL of 37% formaldehyde solution with 20 mL of water and neutralize with 0.1 N sodium hydroxide solution to the phenolphthalein endpoint.

9.3 *Arsenic and Antimony (as As)* — To 30 mL (33 g) of sample in a polyfluorocarbon dish, add 20 mL of nitric acid and 5 mL of hydrochloric acid and evaporate in a sand bath in a hood to dryness. Completely volatilize the ammonium fluoride, but do not bake. Add 10 mL of water and 5 mL of sulfuric acid and evaporate to dense fumes of sulfur trioxide. Cool, cautiously add 10 mL of water, and reevaporate 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 in the standard containing 0.001 mg of arsenic ion (As).

9.4 *Trace Element Contents* — Determine the levels of specified trace elements and establish that they do not exceed the specification limits using a suitable emission spectrographic procedure (see SEMI C1, Section 3.5, Guidelines for Determination of Trace Elements by Emission Spectrography).

10 Grade 2 Procedures

NOTE 1: Each laboratory is responsible for verifying the validity of the method within its own operation.

10.1 *Hydrofluoric Acid* — Weigh accurately approximately 4.0 grams of sample, transfer to a polyethylene beaker, and dilute with water to about 100 mL. Titrate with standardized 1 N sodium hydroxide. The endpoint may be detected colorimetrically by adding 3 drops of methyl red indicator solution and titrating to a definite yellow (no orange) endpoint. As an alternate method, the endpoint may be detected potentiometrically using an HF resistant pH electrode previously standardized in pH 4 and pH 7 buffers. Titrate to pH 6.5 with continuous stirring. Save the solution for the determination of ammonium fluoride.

$$\% \text{ Hydrofluoric Acid} = \frac{\text{mL} \times \text{N of NaOH} \times 2.001}{\text{Weight of sample (g)}}$$

10.2 *Ammonium Fluoride* — Add 40 mL of neutralized formaldehyde solution (see Section 10.2.1) to the solution from the preceding test and stir magnetically for 30 minutes. Titrate with standardized 1 N sodium hydroxide. The endpoint may be detected colorimetrically using 10 drops of phenolphthalein indicator and titrating to a stable pink endpoint. As an alternative method, the endpoint may be detected potentiometrically using an HF resistant electrode previously standardized in pH 7 and 9 buffers. Titrate to pH 8.5 with continuous stirring.

$$\% \text{ Ammonium Fluoride} = \frac{\text{mL} \times \text{N of NaOH} \times 3.704}{\text{Weight of sample (g)}}$$

10.2.1 *Neutralized Formaldehyde Solution* — Dilute 20 mL of 37% formaldehyde solution with 20 mL of water and neutralize with 0.1 N sodium hydroxide solution to the phenolphthalein endpoint.

10.3 *Chloride* — Mix 2.2 mL (2.5 g) of sample with 20 mL of water containing 0.5 g of boric acid. Add 1 mL of nitric acid and 1 mL of silver nitrate reagent solution, and allow to stand for 5 minutes. Any turbidity produced should be no greater than that

produced when 0.01 mg of chloride ion (Cl) is treated as the sample.

10.4 Nitrate — To 2 mL of water in a white plastic beaker, add 0.9 mL (1g) of sample, 1 mL of sulfuric acid, 0.05 mL of 0.01 N (0.002 M) potassium permanganate, mix, and decolorize with sodium arsenite reagent solution. Dilute to 50 mL with brucine sulfate reagent solution and mix. Heat the solution in a preheated (boiling water) bath for 10 minutes. Cool rapidly in an ice bath to room temperature. The yellow color of the sample should be no greater than that produced when 0.01 mg of nitrate ion (NO₃) is treated as the sample.

10.5 Phosphate — To a 9 mL (10 g) sample in a platinum dish, add 1 mL of sodium carbonate reagent solution and 40 mL of nitric acid. Evaporate carefully, to prevent spattering, to near dryness. Cool, wash down the sides of the dish with 5 mL of nitric acid, and evaporate to dryness. Repeat the evaporation with nitric acid two times to ensure complete removal of all the fluoride. To the cooled dish, add 25 mL of 0.5 N sulfuric acid to dissolve the residue, warming if necessary. Cool, transfer to a color comparison tube, and add 1 mL of ammonium molybdate reagent solution, 1 mL of p-(methylamino)phenol sulfate reagent solution, and allow to stand at room temperature for 2 hours. Any blue color should be no greater than that produced when 0.01 mg of phosphate ion (PO₄) is treated as the sample.

10.6 Sulfate — To 23 mL (25 g) of sample, add 10 mL of sodium carbonate reagent solution and heat gently until sample has been volatilized. To the residue, add 5 mL of hydrochloric acid and evaporate to dryness in a hood. Dissolve the residue in 10 mL of water and 1 mL of dilute hydrochloric acid (1 + 19); filter if necessary. Add 1 mL of barium chloride reagent solution, mix, and allow to stand for 10 minutes. Any turbidity developed should be no greater than that produced when 0.05 mg of sulfate ion (SO₄) solution is treated as the sample.

10.7 Trace Metals Analysis

10.7.1 The following method has given satisfactory results in determining metal ion impurities at the values specified for each of the following metals: aluminum (Al), antimony (Sb), arsenic (As), boron (B), calcium (Ca), chromium (Cr), copper (Cu), gold (Au), iron (Fe), lead (Pb), magnesium (Mg), manganese (Mn), nickel (Ni), potassium (K), silver (Ag), sodium (Na), tin (Sn), titanium (Ti), and zinc (Zn). Alternate methods may be used as long as appropriate studies demonstrate a recovery between 75–125% of a known sample spike for half of the value of each specified element.

10.7.2 Special Reagents

10.7.2.1 Nitric Acid, Ultrapure — Use nitric acid specified for low metal ion content.

10.7.2.2 4% Nitric Acid Solution — Dilute 40 mL of ultrapure nitric acid to 1 L using water meeting the criteria for Type E1.1 in ASTM D5127.

10.7.2.3 Water — The water used for all the dilution, calibration, and standards should meet at a minimum the criteria for Type E1.1 in ASTM D5127 in regard to cation analysis.

10.7.2.4 Indium Internal Standard — Make up a indium internal standard solution to a concentration of 20 µg/mL (ppm) from an appropriate concentrated indium standard solution.

10.7.3 Sample Preparation

10.7.3.1 In a clean environment, weigh 10.0 g sample into a cleaned Teflon beaker and evaporate the sample on a 250°C hotplate to near dryness. Carefully add 1 mL of the ultrapure nitric and 3 mL of water and gently warm for several minutes. Cool to room temperature, add 25 µL of the indium internal standard, and dilute with Type E1.1 water to a final weight of 25.0 g.

10.7.4 Analysis

10.7.4.1 Using the prepared solutions and blanks, analyze sodium, potassium, calcium, and iron by graphite furnace atomic absorption (GFAA) and the remaining elements by inductively coupled plasma mass spectrometry (ICP/MS). For calibration, the standards are made up in 4% nitric acid solution with final concentration of 20 ng/g of the indium internal standard. Run a reagent blank.

11 Grade 3 Procedures

11.1 This section does not apply to this chemical.

12 Grade 4 Procedures

12.1 This section does not apply to this chemical.

13 Grade 5 Procedures

13.1 This section does not apply to this chemical.

14 VLSI Grade Procedures

14.1 This section does not apply to this chemical.

15 Tier A Procedures

15.1 This section does not apply to this chemical.

16 Tier B Procedures

16.1 This section does not apply to this chemical.



17 Tier C Procedures

17.1 This section does not apply to this chemical.

18 Tier D Procedures

18.1 This section does not apply to this chemical.

Table 1 Impurity Limits and Other Requirements for Buffered Oxide Etchants

Previous SEMI Reference #	C2.2-95	C7.23-0697
	Grade 1	Grade 2
	(Specification)	(Specification)
Chloride (Cl)	--	4 ppm max
Nitrate (NO ₃)	--	10 ppm max
Phosphate (PO ₄)	--	1 ppm max
Sulfate (SO ₄)	--	2 ppm max
Aluminum (Al)	0.2 ppm max	10 ppb max
Antimony (Sb)	--	10 ppb max
Arsenic (As)	--	10 ppb max
Arsenic and Antimony (as As)	0.03 ppm max	--
Boron (B)	0.2 ppm max	20 ppb max
Calcium (Ca)	0.2 ppm max	10 ppb max
Chromium (Cr)	0.1 ppm max	5 ppb max
Copper (Cu)	0.1 ppm max	5 ppb max
Gold (Au)	0.3 ppm max	10 ppb max
Iron (Fe)	0.2 ppm max	5 ppb max
Lead (Pb)	0.3 ppm max	10 ppb max
Magnesium (Mg)	0.2 ppm max	10 ppb max
Manganese (Mn)	0.2 ppm max	10 ppb max
Nickel (Ni)	0.2 ppm max	10 ppb max
Potassium (K)	0.3 ppm max	5 ppb max
Sodium (Na)	0.3 ppm max	5 ppb max
Tin (Sn)	0.3 ppm max	10 ppb max
Titanium (Ti)	0.3 ppm max	10 ppb max
Zinc (Zn)	0.3 ppm max	5 ppb max
Particles in bottles: size, #/mL	≥ 1.0 µm, 25 max	≥ 0.5 µm, 150 max

NOTICE: SEMI makes no warranties or representations as to the suitability of the standards set forth herein for any particular application. The determination of the suitability of the standard is solely the responsibility of the user. Users are cautioned to refer to manufacturer's instructions, product labels, product data sheets, and other relevant literature respecting any materials mentioned herein. These standards are subject to change without notice.

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SEMI C24-0301

SPECIFICATION FOR n-BUTYL ACETATE

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 October 17, 1999. Initially available at www.semi.org February 2001; to be published March 2001. This document replaces SEMI C1.5 in its entirety. Originally published in 1978; previously published June 1999.

1 Purpose

1.1 The purpose of this document is to standardize requirements for n-butyl acetate 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 n-butyl acetate 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 n-butyl acetate used in the semiconductor industry.

2.2 These standards do not purport to address safety issues, if any, associated with their use. It is the responsibility of the user of these standards to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

3 Limitations

3.1 None.

4 Referenced Standards

4.1 SEMI Standards

SEMI C1 — Specifications for Reagents

4.2 ASTM Standards¹

ASTM D5127 — Standard Guide for Ultra Pure Water Used in the Electronics and Semiconductor Industry

NOTE 1: As listed or revised, all documents cited shall be the latest publications of adopted standards.

5 Terminology

5.1 None.

¹ American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, Pennsylvania 19428-2959, USA. Telephone: 610.832.9585, Fax: 610.832.9555. Website: www.astm.org

6 Physical Property (for information only)

Density at 25°C	0.88 g/mL
Boiling Point	126.5°C

7 Requirements

7.1 The requirements for n-butyl acetate for Grade 1 are listed in Table 1.

8 Grade 1 Procedures

NOTE 2: 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):	
Butyl Acetate	8.0

8.2 *Color* — Dilute 3.0 mL of platinum-cobalt stock solution (APHA No. 500) to 100 mL with water. Compare this standard (APHA No. 15) 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 57 mL (50 g) of sample in a 250 mL conical flask, add 0.5 mL of phenolphthalein indicator solution and titrate with 0.1 N alcoholic potassium hydroxide until a slight pink color persists for at least

15 seconds. Not more than 1.0 mL of the potassium hydroxide solution should be required.

8.4 Residue after Evaporation — Evaporate 90 mL (80 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 25 mL (22 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.

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

8.6 Phosphate — To 11 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 should be no greater than that produced when 0.01 mg of phosphate ion (PO_4^{3-}) is treated as the sample.

8.7 Arsenic and Antimony (as As) — Evaporate 45 mL (40 g) of sample in a 150 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 of the sample should 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), 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.

8.8.1 Special Reagents

8.8.1.1 Solution A — Glycerol (ACS Reagent Grade) 10 g, Adipic Acid (99 + %) 1 g, EDTA Acid (ACS Reagent Grade) 0.1 g. Dilute to 1 L using water meeting the criteria for Type E1.1 in ASTM D5127.

8.8.1.2 Nitric Acid, Ultra Pure — Use 70% nitric acid specified for ultra low metal ion content.

8.8.1.3 2% Nitric Acid Solution — Dilute 20 mL of ultra pure nitric acid to 1 L using water meeting the criteria for Type E1.1 in ASTM D5127.

8.8.2 Sample Preparation

8.8.2.1 In a clean environment, place 250 g of sample in a PTFE dish. Add 50 mL of Solution A. Slowly evaporate in a hot plate avoiding loss of sample by effervescence or spattering until there is no further loss of liquid. Cool. Add 1 mL of ultra pure, 70% nitric acid. While maintaining volume, carefully warm several minutes to dissolve any residue. Cool. Transfer quantitatively to a 50 mL volumetric flask using 2% nitric acid for rinsing and dilution to volume. Run a reagent blank.

8.8.3 Analysis

8.8.3.1 Using the prepared sample, analyze group I elements by flame atomic absorption spectroscopy and all other elements by plasma emission spectroscopy. Apply, if necessary, a reagent blank correction to the final determined value of the sample.

NOTE 3: Repeat analysis for tin using larger sample size if the instrument sensitivity is insufficient at the specified limit.

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.

14 Tier A Procedures

14.1 This section does not apply to this chemical.

15 Tier B Procedures

15.1 This section does not apply to this chemical.

17 Tier D Procedures

17.1 This section does not apply to this chemical.

16 Tier C Procedures

16.1 This section does not apply to this chemical.

Table 1 Impurity Limits and Other Requirements for n-Butyl Acetate

Previous SEMI Reference #	C1.5-96
	Grade 1
	(Specification)
Assay ($C_6H_{12}O_2$)	99.0% min
Color (APHA)	15 max
Acidity	2.0 μ eq/g max
Residue after Evaporation	10 ppm max
Water (H_2O)	0.05% max
Phosphate (PO_4)	1 ppm max
Aluminum (Al)	0.1 ppm max
Arsenic and Antimony (as As)	0.01 ppm max
Boron (B)	0.1 ppm max
Calcium (Ca)	0.1 ppm max
Chromium (Cr)	0.1 ppm max
Copper (Cu)	0.1 ppm max
Gold (Au)	0.1 ppm max
Iron (Fe)	0.1 ppm max
Lead (Pb)	0.1 ppm max
Magnesium (Mg)	0.1 ppm max
Manganese (Mn)	0.1 ppm max
Nickel (Ni)	0.1 ppm max
Potassium (K)	0.1 ppm max
Sodium (Na)	0.1 ppm max
Tin (Sn)	0.1 ppm max
Titanium (Ti)	0.1 ppm max
Zinc (Zn)	0.1 ppm max
Particles in bottles: size, #/mL	$\geq 1.0 \mu m$, 10 max

NOTICE: SEMI makes no warranties or representations as to the suitability of the standards set forth herein for any particular application. The determination of the suitability of the standard is solely the responsibility of the user. Users are cautioned to refer to manufacturer's instructions, product labels, product data sheets, and other relevant literature respecting any materials mentioned herein. These standards are subject to change without notice.

The user's attention is called to the possibility that compliance with this standard may require use of copyrighted material or of an invention covered by patent rights. By publication of this standard, SEMI takes no position respecting the validity of any patent rights or copyrights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of any such patent rights or copyrights, and the risk of infringement of such rights, are entirely their own responsibility.

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.

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

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 (PO₄³⁻) 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 (Pb²⁺) 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 or 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.

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.

14 Tier A Procedures

14.1 This section does not apply to this chemical.

15 Tier B Procedures

15.1 This section does not apply to this chemical.

16 Tier C Procedures

16.1 This section does not apply to this chemical.

17 Tier D Procedures

17.1 This section does not apply to this chemical.

Table 1 Impurity Limits and Other Requirements for Dichloromethane (Methylene Chloride)

Previous SEMI Reference #	C1.6-96
	<i>Grade 1</i>
	(Specification)
Assay (CH_2Cl_2)	98.0% min
Color (APHA)	10 max
Acidity	0.2 $\mu\text{eq/g}$
Residue after Evaporation	10 ppm max
Chloride (Cl)	0.5 ppm max
Heavy Metals (as Pb)	0.2 ppm max
Phosphate (PO_4)	1 ppm max
Water (H_2O)	0.01% max
Aluminum (Al)	1 ppm max
Arsenic and Antimony (as As)	0.01 ppm max
Barium (Ba)	1 ppm max
Boron (B)	0.2 ppm max
Cadmium (Cd)	1 ppm max
Calcium (Ca)	1 ppm max
Chromium (Cr)	0.5 ppm max
Cobalt (Co)	0.1 ppm max
Copper (Cu)	0.1 ppm max
Gallium (Ga)	0.5 ppm max
Germanium (Ge)	1 ppm max
Gold (Au)	0.5 ppm max
Iron (Fe)	1 ppm max

Previous SEMI Reference #	C1.6-96
	<i>Grade 1</i>
	(Specification)
Lithium (Li)	1 ppm max
Magnesium (Mg)	1 ppm max
Manganese (Mn)	1 ppm max
Nickel (Ni)	0.1 ppm max
Potassium (K)	1 ppm max
Silicon (Si)	1 ppm max
Silver (Ag)	0.5 ppm max
Sodium (Na)	1 ppm max
Strontium (Sr)	1 ppm max
Tin (Sn)	1 ppm max
Zinc (Zn)	1 ppm max

NOTE: Dichloromethane contains 0.0025–0.05% ethanol, cyclohexane, or mixed pentenes as stabilizer.

NOTICE: These standards do not purport to address safety issues, if any, associated with their use. It is the responsibility of the user of these standards to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. SEMI makes no warranties or representations as to the suitability of the standards set forth herein for any particular application. The determination of the suitability of the standard is solely the responsibility of the user. Users are cautioned to refer to manufacturer's instructions, product labels, product data sheets, and other relevant literature respecting any materials mentioned herein. These standards are subject to change without notice.

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SEMI C26-0699^E

SPECIFICATION AND GUIDELINE FOR HEXAMETHYLDISILAZANE (HMDS)

This specification and 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.

^E This document was editorially modified in April 2000 to correct a formatting error. Changes were made to Table 1.

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)=

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

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.

14 Tier A Procedures

14.1 Standardized test methods are being developed for all parameters at the purity levels indicated. Until standardized test methods are published, test methodology shall be determined by user and producer. The Process Chemicals Committee considers a test

method to be valid only if there is a documented recovery study showing a recovery of 75 - 125%. Recovery is for a known sample spike at 50% of the specified level.

15 Tier B Procedures

15.1 This section does not apply to this chemical.

16 Tier C Procedures

16.1 This section does not apply to this chemical.

17 Tier D Procedures

17.1 This section does not apply to this chemical.

Table 1 Impurity Limits and Other Requirements for Hexamethyldisilazane

Previous SEMI Reference #	C1.23-94	C7.10-94
Grade 1	Tier A	
(Specification)	(Guideline)	
Assay	99.0%	99.5% min
Color (APHA)	10 max	10 max
Trailing Impurities (area % max)	0.1%	0.2%
Residue after Evaporation	10 ppm max	10 ppm max
UV absorbance units at 270 nm	0.25 max	0.25 max
Turbidity	1.0 NTU units	1.0 NTU units max
Chloride (Cl)	2 ppm max	0.3 ppm max
Aluminum (Al)	0.1 ppm max	10 ppb max
Antimony (Sb)	--	10 ppb max
Arsenic (As)	--	10 ppb max
Arsenic and Antimony (as As)	10 ppb max	--
Barium (Ba)	--	10 ppb max
Beryllium (Be)	--	10 ppb max
Bismuth (Bi)	--	10 ppb max
Boron (B)	0.1 ppm max	10 ppb max
Cadmium (Cd)	--	10 ppb max
Calcium (Ca)	0.1 ppm max	10 ppb max
Chromium (Cr)	--	10 ppb max
Cobalt (Co)	--	10 ppb max
Copper (Cu)	0.1 ppm max	10 ppb max
Gallium (Ga)	0.1 ppm max	10 ppb max
Germanium (Ge)	0.1 ppm max	10 ppb max
Gold (Au)	0.1 ppm max	10 ppb max
Iron (Fe)	0.05 ppm max	10 ppb max
Lead (Pb)	0.1 ppm max	10 ppb max
Lithium (Li)	0.1 ppm max	10 ppb max
Magnesium (Mg)	0.1 ppm max	10 ppb max
Manganese (Mn)	--	10 ppb max
Molybdenum (Mo)	--	10 ppb max
Nickel (Ni)	0.1 ppm max	10 ppb max
Potassium (K)	0.1 ppm max	10 ppb max

Previous SEMI Reference #	C1.23-94	C7.10-94
	Grade 1 (Specification)	Tier A (Guideline)
Silver (Ag)	0.1 ppm max	10 ppb max
Sodium (Na)	0.5 ppm max	10 ppb max
Strontium (Sr)	0.1 ppm max	10 ppb max
Tantalum (Ta)	0.1 ppm max	10 ppb max
Thallium (Tl)	--	10 ppb max
Tin (Sn)	--	10 ppb max
Titanium (Ti)	--	10 ppb max
Vanadium (V)	--	10 ppb max
Zinc (Zn)	--	10 ppb max
Zirconium (Zr)	--	10 ppb max

NOTICE: These standards do not purport to address safety issues, if any, associated with their use. It is the responsibility of the user of these standards to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. SEMI makes no warranties or representations as to the suitability of the standards set forth herein for any particular application. The determination of the suitability of the standard is solely the responsibility of the user. Users are cautioned to refer to manufacturer's instructions, product labels, product data sheets, and other relevant literature respecting any materials mentioned herein. These standards are subject to change without notice.

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SEMI C27-0301

SPECIFICATIONS AND GUIDELINES FOR HYDROCHLORIC ACID

These specifications and guidelines 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 by letter ballot dated October 17, 1999. Initially available at www.semi.org February 2001; to be published March 2001. This document replaces SEMI C1.7, C7.2, C8.2, C11.6, and C12.2 in their entirety. Originally published in 1978, 1990, 1992, 1996, and 1995 respectively; previously published June 2000.

1 Purpose

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

2.2 The VLSI grade purity level is typically required by semiconductor devices with geometries of 0.8–1.2 microns.

2.3 These specifications and guidelines do not purport to address safety issues, if any, associated with their use. It is the responsibility of the users of these specifications and guidelines to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

3 Limitations

3.1 None.

4 Referenced Standards

4.1 SEMI Standards

SEMI C1 — Specifications for Reagents

4.2 ASTM Standards¹

ASTM D5127 — Standard Guide for Ultra Pure Water Used in the Electronics and Semiconductor Industry

NOTE 1: As listed or revised, all documents cited shall be the latest publications of adopted standards.

¹ American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, Pennsylvania 19428-2959, USA. Telephone: 610.832.9585, Fax: 610.832.9555. Website: www.astm.org

5 Terminology

5.1 None.

6 Physical Property (for information only)

Density at 25°C	1.19 g/mL
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7 Requirements

7.1 The requirements for hydrochloric acid for Grades 1 and 2, VLSI Grade, and Tiers B and C are listed in Table 1.

8 Grade 1 Procedures

NOTE 2: Each laboratory is responsible for verifying the validity of the method within its own operation.

8.1 *Assay* — Accurately weigh a glass-stoppered conical flask containing about 30 mL of water. Deliver from a pipet about 3 mL of sample near the water surface, stopper immediately, and reweigh. Dilute to about 50 mL with water, add methyl orange indicator solution, and titrate with standardized 1 N sodium hydroxide to a red-to-yellow color change.

$$\% \text{ Assay} = \frac{\text{mL} \times \text{N of NaOH} \times 3.646}{\text{Weight of sample (g)}}$$

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 *Extractable Organic Substances* — Cool 110 mL of sample in an ice bath. Add 5 mL of 2,2,4-trimethylpentane and 100 mL of water to each of two 250 mL separatory funnels. To a third funnel add 100 mL of water and 5 mL of the standard (see below). To the first funnel add 100 mL of the cooled sample, and 100 mL of water to each of the remaining two. Stopper, shake well, and allow the layers to separate. Inject 1.0 μL of each of the 2,2,4-trimethylpentane extracts into a gas chromatograph with a flame ionization detector. The following conditions have been found to be satisfactory: Column — 20% Carbowax® 20 M on