

SEMI C1-90

SPECIFICATIONS FOR REAGENTS

1. Preface

1.1 In the 1950's, chemicals purchased by the electronics industry were of a quality defined by the Committee on Analytical Reagents of the American Chemical Society, or of lesser quality. With recognition of the importance of impurity content of chemicals in the manufacture of semiconductors, suppliers responded by introducing products with improved analytical characterization, notably for trace elements.

1.2 The SEMI Committee on Standards for Chemical Reagents began its efforts in the fall of 1975. With this publication, the Committee establishes the definitions, general procedures, specifications, and analytical procedures for the chemicals listed in the index.

1.3 Products within all of the requirements can be described as "meeting SEMI specifications."

1.4 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.

1.5 The Committee is continuing work on improvement of specifications and procedures and addition of other reagents and systems such as mixed etchants. The Committee welcomes comments, suggestions, and recommendations.

2. Definitions

2.1 *Accuracy and Tolerances in Measurements* - In a test procedure, unless otherwise specified, the accuracy required in the amount of sample taken shall be understood to be within 2.0% of the stated amount, whether a weight or a volume. Where a dilution is performed to a stated volume or a stated volume of a solution is taken, that volume shall be within 2.0% of the stated amount. Unless otherwise stated, a transfer by pipet shall be made by means of a volumetric pipet conforming to the tolerances established by *National Bureau of Standards Circular 602*, April 1, 1959.

2.2 *Abbreviations and Signs* - In this work abbreviations and signs used shall be restricted to those listed in Table 2. Most of the abbreviations are identical to those used in publications of the American Chemical Society as of 1982.

2.3 *Acidity and Alkalinity* - A test for acidity or alkalinity, or both, of organic liquids is common.

2.3.1 In the *acidity test* usually a stated volume of water (commonly 25 mL) is shaken in a glass-stoppered flask with a stated volume of sample (commonly 10 mL). Then 0.1 mL of phenolphthalein indicator solution is added and 0.01N sodium hydroxide until a slight pink color persists after shaking for 30 seconds. Next a stated amount of sample is added and mixed and a titration is performed with 0.01N sodium hydroxide until the pink color is reproduced; the volume of titrant required is recorded.

2.3.2 In the *alkalinity test*, a stated amount of sample is mixed with a stated volume of water (commonly 25 mL). Now 0.05 mL of methyl red indicator solution is added and the mixture is titrated with 0.01N hydrochloric acid until a slight pink color is reached; the volume of titrant required is recorded.

2.3.3 The result of such tests has often been expressed qualitatively as "passes test" or quantitatively as the content of an acid (or base) known or assumed to be present. In this work, the maximum specification limit shall be expressed in microequivalents of acid (or base) per gram of sample ($\mu\text{eq/g}$). The maximum allowed volume of titrant in a test procedure shall correspond to that specification limit.

2.4 *Apparatus* - Apparatus, unless otherwise qualified, shall be that commonly employed in the conduct of the relevant test.

2.5 *Atomic and Formula Weights* - Atomic weights (that is, atomic masses) used shall be those of the latest report of the International Commission on Atomic Weights. Formula weights shall be calculated from a given empirical (molecular) formula by addition of the stated multiples of the atomic weights. Unless otherwise stated, formula weights shall be rounded to 2 significant figures to the right of the decimal point (see *Rounding of Numbers*, Section 2.18). All relevant factors given in this work are based on the 1975 Table of Atomic Masses.

2.6 *Blank Preparation* - Where a "blank" is specified to be run, unless otherwise stated, it shall be performed with the same quantities of the same reagents and in a manner identical to that followed with the sample portion under test, but with the material itself omitted.

2.7 *Comparison of Analytical Results with Specification Limits* - In the comparison of an analytical result for a test with the numerical limit associated with the specification, the result shall be rounded to the number of significant figures indicated for that limit. (See *Rounding of Numbers*, Section 2.18.). Consequently, a specification stated

at 96% *minimum* will be met by a result as small as 95.5% and that stated as 96.0% *minimum* will be met by a result as small as 95.95%. A specification of 0.1% *maximum* will be met by a result as large as 0.14% and that of 0.10% *maximum* by a result as large as 0.105%.

2.8 Density - The density of a liquid shall be determined for the compound in air at 25°C and be expressed in grams/milliliter (g/mL). Where the specific gravity, with respect to water, is determined, it shall be expressed as density by the use of tabular values for the density of water at the relevant temperature(s).

2.9 Desiccator - A desiccator shall imply a tightly closed container charged with a suitable desiccant (commonly calcium chloride or sulfate) that allows an atmosphere of low humidity to be maintained.

2.10 Drying or Igniting to Constant Weight - A statement "dried to a constant weight" or "ignited to a constant weight" shall imply that two separate weighings differ by no more than ± 0.4 mg (unless otherwise specified), where the second weighing follows a second drying (for one hour (unless otherwise stated) or ignition for 15 minutes (unless otherwise stated) respectively.

2.11 Expression of Content and Concentration - Unless otherwise stated, a specification limit and experimental results related to it shall be expressed in units of weight by weight. The concentration of a solution of a test reagent shall be expressed either in molarity or normality or as percent weight by volume. A redox normality value shall always be followed, parenthetically, by the relevant molarity. In the approximate dilution of reagents, a parenthetical expression of two numbers with an intervening "plus" sign shall imply that the relative volume of the stated reagent given by the first number shall be admixed with the relative volume of water given by the second number. Thus, "dilute" sulfuric acid (1 + 3) directs that one volume of reagent grade sulfuric acid be added to 3 volumes of water and the mixture stirred to form a uniform solution.

2.12 Filtration - A statement to "filter", unless qualified, shall imply filtration through suitable filter paper until the filtrate is clear.

2.13 Heavy Metals (as Pb) - The test described as "Heavy Metals (as Pb)" responds to many of the metals precipitated by hydrogen sulfide. Unless otherwise stated, the test shall involve a visual comparison of the color developed by the sample preparation and a lead standard ("control"), upon treatment with hydrogen sulfide at pH 3 to 4. The color comparison shall be made with matched 50 mL Nessler tubes with vertical viewing over a white background. The treatment of the sample shall be specified in

detail in the test procedure. Unless otherwise stated, the heavy metals standard shall be prepared by diluting a solution containing 0.02 mg of lead with water to 25 mL adjusting the acidity of this solution to pH 3 to 4 (using a pH meter), and then diluting with water to 40 mL, and mixing. The test shall then be conducted by adding to that standard and to 40 mL of the stated sample solution 10 mL of freshly prepared hydrogen sulfide water with mixing. The test shall have been passed if the sample solution is no darker than the standard. This test is proximate in nature and does not imply that lead is present either alone or with other heavy metals.

2.13.1 For sodium hydroxide and potassium hydroxide, this test becomes "Heavy Metals (as Ag)" and silver replaces lead in the standard. This change is appropriate as silver and silver-clad equipment are often used in the manufacture of these caustics.

2.14 Physical Properties - Physical properties shall not usually be employed for specification purposes; for information, however, representative values for a particular chemical, as supplied, may be included as item 2 in the monograph for that chemical. Where relevant, physical properties shall be specified for 25°C.

2.15 Reagent Chemicals - Unless otherwise stated, reagents to be used in tests shall conform to the minimum standards of quality set forth in the 7th Edition of *Reagent Chemicals*, published by the American Chemical Society, and any revisions thereto.

2.16 Residue After Evaporation - A "residue after evaporation" test is often used in the assessment of organic liquids. (See Determination of Residue After Evaporation, Section 3.3.)

2.17 Residue After Ignition - A "residue after ignition" test serves to assess the amount of nonvolatile inorganic matter present in a sample. Unless otherwise stated, the ignition shall be performed at $800^\circ \pm 25^\circ\text{C}$ for 15 minutes. Where the addition of sulfuric acid is specified, the result corresponds to what is often termed "sulfated ash." The calculation of the result, expressed in parts per million ($\mu\text{g/g}$), takes the form:

ppm Residue after Ignition =

$$\frac{\text{Net weight of residue (g)} \times 10^6}{\text{Weight of sample (g)}}$$

2.18 Rounding of Numbers - The following rules for "rounding" of measured or calculated values shall be employed.

1. When the figure next beyond the last place to be retained is *less than 5*, leave unchanged the figure in the last place retained.
2. When the figure next beyond the last place to be retained is *greater than 5*, increase by 1 the figure in the last place retained.
3. When the figure next beyond the last place to be retained is 5 and there are no figures beyond this 5 or only zeroes, (a) increase by 1 the figure in the last place retained if it is odd, or leave the figure unchanged if it is even.
4. When the figure next beyond the last place to be retained is 5 and there are figures other than zeroes beyond this 5, increase by 1 the figure in the last place retained.
5. Obtain the rounded value in one step by direct rounding and not in two or more steps of successive roundings.

2.19 *Samples and Sampling* - For chemicals provided in small containers, one (or more) shall be freshly opened for testing, thereby reducing possibilities for contamination or change in composition (for example, by moisture pickup). Where the chemical is provided in larger bulk quantities, one or more drums or other containers shall be sampled appropriately and the combined sample shall be placed in a labeled, well-cleaned container that shall be tightly closed and transferred expeditiously to the testing laboratory.

2.20 *Specifications and Specification Limits* - The specifications provided by this work are intended to serve for chemicals to be used in the manufacture and processing of semiconductors and advanced electronic devices and circuits. The specifications and the associated test procedures are based on the experience of suppliers and users and also on published studies relating to chemicals of the required quality. The function of the specifications is to establish *minimum* standards of quality.

2.20.1 Where feasible, a specification of content shall be expressed as a numerical limit in units of weight by weight. For a specification that cannot be assigned such a limit, the expression "To pass test" shall be used.

2.20.2 For a major component, the value (assay, purity, etc.) shall be expressed as a *minimum* permissible limit. For an impurity, the value shall be expressed as a *maximum* permissible limit.

2.20.3 A chemical conforming to the specification will commonly contain more of the major component than the minimum permissible limit or contain less of an impurity (or several impurities) than the maximum permissible limit. In neither case shall the chemical be considered as of higher quality than that defined by the specification.

2.20.4 It is manifestly impossible in the specifications and procedures for a chemical to consider every impurity or contaminant that might be present. For certain applications, it is recognized that more stringent or additional specifications and procedures might be required. The intent of these specifications and the associated procedures is, on one hand, to assure that a chemical is suitable for the common uses to which it may be put in the manufacture and processing of semiconductor devices and, on the other hand, to be consistent with contemporary manufacturing processes for that chemical.

2.21 *Specification Parameters* - In this work, the order of statement of specification parameters in Item 1 of the monograph for a particular chemical shall be, as far as practical: 1) assay or other test assessing the content of the major component(s); 2) appearance or color; 3) acidity or alkalinity, or both, or pH range of solution; 4) residue after evaporation or ignition; 5) water content; 6) diverse general tests, arranged alphabetically; 7) tests for stated anions, arranged alphabetically (bromide, chloride, phosphate, sulfate, sulfite, etc.); 8) ammonium; 9) heavy metals; 10) arsenic and antimony; 11) tests for specific trace elements, especially metals, arranged alphabetically by name.

2.21.1 All major words in a specification parameter shall have their initial letters capitalized.

2.21.2 Following the statement of a specification parameter, where relevant, the species on which the calculation of the result is based shall be expressed parenthetically as the atomic symbol or empirical formula.

2.22 *Tared Containers* - Where the use of a tared container is specified, it shall be carried through operations identical to those used in the test procedures, including drying or ignition, or both, cooling in a desiccator, and weighing. When a new container is placed in service, special measures may be required to assure that it is brought to constant weight by the operations.

2.23 *Temperature* - Temperature values shall be expressed in degrees Celsius (°C).

2.24 *Water* - References to water in the testing procedures are understood to mean distilled or deionized water which is suitable for the intended purpose. Water meeting the requirements for Water, Reagent in *Reagent Chemicals*, ACS specifications, current edition, or Type II Reagent Water in ASTM specification D1193 may be used. In tests for nitrogen compounds, water should be "ammonia-free" or "nitrogen-free." For some tests, freshly boiled water must be used in order to ensure freedom from material absorbed from the air such as ammonia, carbon dioxide, or oxygen.

2.25 Water by Karl Fischer Titration - The Karl Fischer method for the determination of water involves a titration with the so-called Karl Fischer reagent, consisting of iodine, sulfur dioxide, pyridine, and methanol. For most relevant chemicals intended for use in semiconductor manufacture and other electronics applications, the water content is small and electrometric detection of the end point is to be preferred. Details of this method are provided by ASTM E203 and in *Reagent Chemicals*, published by the American Chemical Society.

2.26 Water and Steam Baths - A water bath, unless otherwise stated, shall imply a bath of vigorously boiling water. A steam bath (at 1 atmosphere pressure), unless otherwise qualified, shall imply either exposure to flowing steam or to another source of heat at the temperature of flowing steam.

2.27 Weights and Measures - The weights and measures used shall be, to the extent possible, those of the International System (SI), adopted by the General Conference of Weights and Measures of 1960. Some relevant quantities are listed below:

Physical Quantity	Name	Symbol	Expression in SI Base Units
length	meter	m	(base)
mass	kilogram	kg	(base)
time	second	s	(base)
electric current	ampere	A*	(base)
amount of substance	mole	mol	(base)
electric conductance	siemens	S	$\text{m}^{-2} \cdot \text{kg}^{-1} \cdot \text{s}^3 \cdot \text{A}^2$
electric potential difference	volt	V	$\text{m}^{-2} \cdot \text{kg} \cdot \text{s}^3 \cdot \text{A}^{-1}$
electric resistance	ohm	Ω	$\text{m}^2 \cdot \text{kg} \cdot \text{s}^{-3} \cdot \text{A}^{-2}$
energy, work quantity of heat	joule	J	$\text{m}^2 \cdot \text{kg} \cdot \text{s}^{-2}$
force	newton	N	$\text{m} \cdot \text{kg} \cdot \text{s}^{-2}$
frequency	hertz	Hz	s^{-1}
power, radiant flux	watt	W	$\text{m}^2 \cdot \text{kg} \cdot \text{s}^{-3}$
pressure	pascal	Pa	$\text{m}^{-1} \cdot \text{kg} \cdot \text{s}^{-2}$
quantity of electricity, electric charge	coulomb	C	$\text{s} \cdot \text{A}$

* In this work, the ampere is abbreviated amp to avoid confusion with absorbance.

3. General Procedures and Guidelines to Certain Methods

3.1 Guidelines for Assay by Packed Column Gas Chromatography - The theory of gas chromatography is given in many monographs, reviews, etc. The purpose here is to delineate some practical aspects for the assessment of volatile organic solvents by gas chromatography. No detailed procedures for the gas chromatographic assay of solvents are given since available instruments and columns vary from laboratory to laboratory.

3.1.1 Equipment - The gas chromatograph should be able to receive direct injection of the sample either into an injector block or directly onto the column. As the isothermal mode is commonly used, temperature programming is necessary only for the most retentive columns such as Porapak.

3.1.2 Sample - The sample is injected into the chromatograph by means of a syringe. The sample size selected should be small enough to avoid overloading the system. Commonly the sample size is in the range of 1-10 μL .

3.1.3 Columns - Many types of columns exist and can be used. Some that have been found useful are listed in Table 1.

3.1.4 Conditions - Appropriate conditions will vary from gas chromatograph to chromatograph and column to column; consequently, exact conditions cannot be specified. In the isothermal mode, the temperature of the column is usually maintained at 10°-20°C below the boiling point of the solvent (except for Porapak columns). The flow rate of the carrier gas is such that the major peak elutes in 5-10 minutes, and the total run lasts for at least 20 minutes. The injector port is usually maintained at 10°-20°C above the boiling point of the sample. The detector temperature is also about 20°C above the boiling point of the sample but at least 100°C.

3.1.5 Detector - The detector is a flame ionization type (FID), with the signal amplified by a stable electrometer. The signal is recorded either on a suitable recorder or with a digital integrator. If only a recorder is used, the range must be changed in the course of the chromatogram to keep all peaks on scale and to give a baseline with not more than 1% noise level for impurity peaks. For the assay of hexamethyldisilazane, a thermal conductivity detector is preferred because of the tendency to deposit silicon dioxide in a flame detector.

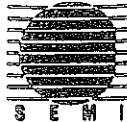


Table 1
Columns

SOLVENT	COLUMNS*	COLUMN PACKING
Acetone	4 m by 4 mm 2 m by 2 mm ss 2 m by 2 mm	30% dimethylene glycol succinate on Chromosorb® W 42/60 Porapak® R 80/100 Porapak® Q
Butyl Acetate	4 m by 2 mm ss	10% diethylene glycol succinate on Chromosorb® W AW 40/60
Dichloromethane	40 m by 0.5 mm SCOT 4 m by 2 mm ss	Carbowax® 20M 20% SP-2100 and 0.1% Carbowax® 1500 or Chromosorb®
Hexamethyldisilazane	2m by 2 mm	10-20% dimethylsilicone on W AW-DMCS Chromosorb® 80/100 or 10% Supelco® SP-2100 on Supelcoport® 100/120 deactivated with a suitable silanizing agent.
Methanol	4 m by 2 mm 2 m by 2 mm ss 2 m by 2 mm	Chromosorb® 101 Porapak® R 80/100 Porapak® Q
Methyl ethyl ketone	40 m by 0.5 mm SCOT 6 m by 2 mm	Carbowax® 20M 20% Carbowax® 1500 on Chromosorb® B 60/80
2-Propanol	2 m by 2 mm ss 2 m by 2 mm ss 2 m by 2 mm	30% diethylene glycol succinate on Chromosorb® W AW 60/80 Porapak® R 80/100 Porapak® Q
Tetrachloroethylene	2 m by 2 mm	15% UCON® LB1800X on Chromosorb® P 30/60
Toluene	40 m by 0.5 mm SCOT 3 m by 2 mm	Squalane 5% diisodecyl phthalate and 5% Bentone® 34 on Chromosorb® W 80/100
Trichloroethylene	2 m by 2 mm 4 m by 4 mm	15% UCON® LB1800X on Chromosorb® P 30/60 30% diethylene glycol succinate on Chromosorb® W 40/60
Trichlorotrifluoroethane	40 m by 0.5 mm SCOT	SE-30

* Length and diameter of column; ss = stainless steel, SCOT = support-coated open tubular.



Table 2
Abbreviations and Signs

A	=	absorbance	m.p.	=	melting point [Note 3]
Å	=	angstrom (s) [Note 1]	mv	=	millivolt(s)
a.c.	=	alternating current	mμ	=	millimicron(s) (=nm) [Note 4]
amp.	=	ampere(s) [Note 2]	N	=	normal or normality
addn.	=	addition [Note 3]	n	=	nano (10 ⁻⁹)
alc.	=	alcohol(ic) [Note 3]	ng	=	nanogram(s)
amt.	=	amount [Note 3]	nm	=	nanometer(s)
approx.	=	approximate(ly)	no.	=	number [Note 3]
aq.	=	aqueous [Note 3]	O.D.	=	outside diameter [Note 3]
atm.	=	atmosphere(s)	p	=	pico (10 ⁻¹²)
av.	=	average [Note 3]	pg	=	picogram(s)
b.p.	=	boiling point [Note 3]	powd.	=	powdered [Note 3]
ca.	=	circa (i.e., about or approximately)	ppb	=	part(s) per billion (=ng/g or ng/mL) [Note 5]
cal.	=	calorie(s)	ppm	=	part(s) per million (= μg/g or μg/mL)
cc	=	cubic centimeter(s) (mL)	ppt.	=	precipitate [Note 3]
c.d.	=	current density [Note 3]	prepn.	=	preparation [Note 3]
cm	=	centimeter(s)	psi	=	pounds per square inch
cm ²	=	square centimeter(s)	PTFE	=	poly (tetrafluoroethylene) (e.g., Teflon®)
compd.	=	compound [Note 3]	satd.	=	saturated [Note 3]
compn.	=	composition [Note 3]	SCE	=	saturated calomel electrode [Note 3]
concn.	=	concentration [Note 3]	s	=	second(s)
d	=	density (or difference in statistical analysis)	sepn.	=	separation [Note 3]
d.c.	=	direct current	soln.	=	solution [Note 3]
diam.	=	diameter [Note 3]	soly.	=	solubility [Note 3]
dil.	=	dilute [Note 3]	std.	=	standard [Note 3]
EDTA	=	ethylenediaminetetraacetate (i.e., [ethylenedinitrilo] tetraacetate)	T	=	transmittance
equiv.	=	equivalent(s)	temp.	=	temperature [Note 3]
f.p.	=	freezing point [Note 3]	TLC	=	thin-layer chromatography (or chromatographic)
FW	=	formula weight	titm.	=	titration [Note 3]
g	=	gram(s)	UV	=	ultraviolet [Note 3]
GC	=	gas chromatography (or chromatographic)	v	=	volts [Note 3]
GLC	=	gas-liquid chromatography (or chromatographic)	vol.	=	volume [Note 3]
hr.	=	hour [Note 3]	W	=	watts [Note 3]
I.D.	=	inside diameter [Note 3]	wt.	=	weight [Note 3]
insol.	=	insoluble [Note 3]	μ	=	micron(s) (= μm) or micro (10 ⁻⁶) [Note 4]
ir	=	infrared [Note 3]	μa	=	microampere(s)
kg	=	kilogram(s)	μeq	=	microequivalent(s)
L	=	liter(s)	μg	=	microgram(s)
m	=	meter(s) or milli (10 ⁻³)	μL	=	microliter
M	=	molar or molarity	μm	=	micrometer(s)
ma	=	milliampere(s)	μM	=	micromolar
max.	=	maximum (or maxima)	μmol	=	micromole(s)
meq	=	millequivalent(s)	Ω	=	ohm(s)
mg	=	milligram(s)	°C	=	degrees Celsius
min	=	minute(s)	~	=	circa (about or approximately)
min.	=	minimum	%	=	percent
mixt.	=	mixture [Note 3]	>	=	greater than
mL	=	milliliter(s)	≥	=	greater than or equal to
mm	=	millimeter(s)	<	=	less than
mM	=	millimolar (or millimolarity)	≤	=	less than or equal to
mmol	=	millimole			
mol	=	mole [Note 3]			