

SEMI F75-0617

GUIDE FOR QUALITY MONITORING OF ULTRAPURE WATER USED IN SEMICONDUCTOR MANUFACTURING

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NOTICE: This Document was completely rewritten in 2017.

1 Purpose

1.1 This Guide describes potential sources of contaminants, their impact on semiconductor manufacturing and available options for monitoring these contaminants. This Guide should be used in conjunction with SEMI F61 and SEMI F63. Together these Guides provide recommendations for facility engineers and other manufacturing and quality professionals who are responsible for establishing programs to monitor and control the quality of their ultrapure water (UPW) systems, through to point of use (POU). These Guides may be used to help determine the parameters that should be monitored for UPW that is produced, distributed and used throughout the manufacturing facility, and the frequency and location of testing.

NOTE 1: These suggested guides are published as technical information and are intended for informational purposes only.

2 Scope

2.1 UPW is used extensively in the production of semiconductor devices for all wet-processing steps. Ultrapure water systems need to be tested and monitored to ensure that the UPW being produced matches the specifications established by the manufacturing process. The purity of the UPW may affect device yield unless a wide range of parameters are closely controlled at the point of distribution (POD). Semiconductor devices are currently being designed with smaller linewidths (<65 nm) and are therefore more susceptible to low level impurities.

2.2 UPW systems are monitored for continuous performance for desired and achievable levels of quality. Action limits are generally set to determine when system performance data warrants that corrective action is needed. Table 1, Parameters and Range of Performance, in SEMI F63 may be a useful reference for establishing quality levels.

2.3 In more critical processes, the quality of the UPW also needs to be monitored at the POU where the UPW is in contact with the wafer. The quality of the UPW should not be expected to be identical to the quality of the UPW being produced at final filter (FF), which is not subject to conditions within the tool or distribution system.

2.4 This Guide (SEMI F75) is the third in a series of SEMI Guides developed for UPW which include SEMI F61, a Standard defining the performance of a UPW system, and SEMI F63, a Standard defining the quality of UPW.

2.5 This Guide provides information about the frequency and location of sampling for those parameters that are not available from online analyzers. Frequency of sampling should be based on the specifications set by manufacturing for the quality of the POD UPW, the number and locations of online analyzers, the stability of the incoming feed water to the system, and the historical performance of the UPW system over time.

2.6 The SEMI Guides may also be used to establish process control criteria for the incoming feedwater, performance of UPW system components and POU rinse baths.

NOTICE: SEMI Standards and Safety Guidelines do not purport to address all safety issues associated with their use. It is the responsibility of the users of the Documents to establish appropriate safety and health practices, and determine the applicability of regulatory or other limitations prior to use.

3 Limitations

3.1 The SEMI Guides have been developed with consideration of various other relevant sources but they are not intended to be identical to, or consistent with, any other industry document or standard.

3.2 The SEMI Guides do not specifically address monitoring and testing of recycled or reclaimed water systems; additional test parameters, such as quantification and identification of organic species in reclaim water, should be added to monitoring programs for reclaim and reuse waters.

3.3 Measuring the purity of UPW can be challenging. Many online instruments (such as sodium analyzers, TOC analyzers, silica analyzers, optical particle counters (OPC), and nonvolatile residue (NVR) analyzers) provide very low limits of detection but may not be capable of being calibrated in the range of detection or may have very poor accuracy at low levels therefore online analyzers should primarily be used for trend analysis. Many tests can still be performed more accurately and reproducibly in a laboratory environment but taking batch samples can prove time-consuming and be prone to sampling error.

3.4 To maintain their relevance, SEMI Documents must be updated on a regular basis. This Guide, SEMI F61 and SEMI F63 should all be updated at the same time in order to ensure continuity for the users of all three Documents. All three Documents will be updated on a two-year cycle.

4 Referenced Standards and Documents

4.1 SEMI Standards and Safety Guidelines

SEMI F57 — Specification for Polymer Materials and Components Used in Ultrapure Water and Liquid Chemical Distribution Systems

SEMI F61 — Guide for Ultrapure Water System Used in Semiconductor Processing

SEMI F63 — Guide for Ultrapure Water Used in Semiconductor Processing

4.2 ASTM Standards¹

ASTM D859 — Standard Test Method for Silica in Water

ASTM D4327 — Standard Test Method for Anions in Water by Chemically Suppressed Ion Chromatography

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

ASTM D5173 — Standard Test Method for On-Line Monitoring of Carbon Compounds in Water by Chemical Oxidation, by UV Light Oxidation, by Both, or by High Temperature Combustion Followed by Gas Phase NDIR or by Electrolytic Conductivity

ASTM D5391 — Standard Test Method for Electrical Conductivity and Resistivity of a Flowing High Purity Water Sample

ASTM D5462 — Standard Test Method for On-Line Measurement of Low-Level Dissolved Oxygen in Water

ASTM D5544 — Standard Test Method for On-Line Measurement of Residue After Evaporation of High-Purity Water

ASTM D6317 — Standard Test Method for Low Level Determination of Total Carbon, Inorganic Carbon and Organic Carbon in Water by Ultraviolet, Persulfate Oxidation, and Membrane Conductivity Detection

ASTM D7126 — Standard Test Method for On-Line Colorimetric Measurement of Silica

ASTM F1094 — Test Method for Microbiological Monitoring of Water Used for Processing Electron and Microelectronic Devices by Direct- Pressure Tap Sampling Valve and by the Pre-Sterilized Plastic Bag Method

4.3 ISO Standard²

ISO/IEC 17025:2005 — General Requirements for the Competence of Testing and Calibration Laboratories

4.4 Other Documents

Libman S. and Huber S. “An Overview of LC-OCD – Organic Speciation For Critical Analytical Tasks In the Semiconductor Industry.” *Ultrapure Water Journal*, Volume 31, Number 3, May/June 2014, pp. 10–16.

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

¹ ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959, USA; Telephone: +1.610.832.9585, Fax: +1.610.832.9555, <http://www.astm.org>

² International Organization for Standardization, ISO Central Secretariat, 1, ch. de la Voie-Creuse, CP 56, CH-1211 Geneva 20, Switzerland; Telephone: +41.22.749.01.11, Fax: +41.22.733.34.30, <http://www.iso.org>

5 Terminology

5.1 Abbreviations and Acronyms

NOTE 2: All other abbreviations and acronyms are defined in the SEMI International Standards: Compilation of Terms available at Web site, <http://www.semi.org/>.

- 5.1.1 *CFU* — colony-forming units
- 5.1.2 *DO* — dissolved oxygen
- 5.1.3 *EDI* — electro-deionization
- 5.1.4 *EDX* — energy dispersive x-ray microanalysis
- 5.1.5 *FF* — final filter
- 5.1.6 *IC* — ion chromatography
- 5.1.7 *LC-OCD* — liquid chromatography with organic carbon detector
- 5.1.8 *NDIR* — non-dispersive infrared analysis
- 5.1.9 *OPC* — optical particle counters
- 5.1.10 *POD* — point of distribution
- 5.1.11 *POU* — point of use
- 5.1.12 *RO* — reverse osmosis
- 5.1.13 *TDS* — total dissolved solids
- 5.1.14 *THM* — trihalomethanes

6 Units

- 6.1 Parts per million (ppm) is equivalent to $\mu\text{g/mL}$ or mg/L .
- 6.2 Parts per billion (ppb) is equivalent to ng/mL or $\mu\text{g/L}$.
- 6.3 Parts per trillion (ppt) is equivalent to pg/mL or ng/L .

7 Use of the Guides

- 7.1 Monitoring programs should reflect the age and complexity of the UPW equipment and the needs of the manufacturing process.
- 7.2 The quality of UPW at the POU may be negatively impacted by contamination sources within a tool, the design of the tool, the materials of construction of the tool and piping distribution, and contamination loading in the bath from build-up after multiple rinse cycles.
- 7.3 Sampling methods and contamination control are of paramount importance when attempting to measure the listed parameters at very low levels of sensitivity.
- 7.4 The quality of the data measured may depend on which testing methods and calibration techniques are used. Consequently, trends observed in the values may be more meaningful than absolute values, especially for certain online monitors calibrated for ultrasensitive detection. In addition, online and off-line measurements may not correlate depending on the measurement technique and level of sensitivity of the measurement.

8 Tests for Monitoring UPW Production and Distribution

NOTE 3: Since SEMI Guides do not require analytical data or methods to support them, the recommendations of specific analytical methods are only for informational purposes. Alternative methods may also be applicable.

NOTE 4: See Table 1, § 9, for a summary of recommended testing frequency and sampling points.

8.1 Resistivity (megohm-centimeters [$m\Omega\cdot cm$])

8.1.1 Resistivity (the inverse of conductivity and a general measure of ionic activity) is measured by an online meter. The resistivity of UPW should be approximately $18.2 m\Omega\cdot cm$ depending on the resolution of the instrument.

NOTE 5: $18.18 M\Omega\cdot cm$ is the theoretical upper limit for pure water at $25^{\circ}C$.

8.2 Total Oxidizable (Organic) Carbon (TOC) (ppb)

8.2.1 Carbon Sources in Water Supplies

8.2.1.1 Incoming feed water contains both inorganic and organic carbon. Inorganic carbon as dissolved carbon dioxide (CO_2), bicarbonate, and carbonate can be present at high ppm levels according to the geology of the water supply. Organic carbon includes natural organic matter (NOM) input and man-made (synthetic) contaminants such as pesticides and fertilizers. Ground waters normally have significantly lower organic content than surface waters. To remove the majority of organics, most UPW systems employ reverse osmosis (RO), anion exchange resin, and ultraviolet (UV) destruction. Some volatile organics, such as trihalomethanes (THM), may be reduced by the use of vacuum degasification. The control of organics is essential for preventing organic fouling and maintaining treatment at high efficiency. In addition, reduced organic matter will limit the nutrients available for bacteria growth. Increasing TOC values at the POD may be due to deterioration of the incoming water quality, degradation of system components, contamination from routine operational maintenance, or return contamination from the factory.

8.2.2 Method of TOC Measurement for Source Water

8.2.2.1 There are various methods for measuring TOC and several TOC analyzers are available. TOC measurement generally involves the oxidation of organic materials by means of temperature, UV radiation, and/or chemicals. The CO_2 produced by these reactions can be measured by non-dispersive infrared analysis (NDIR) or conductivity (resistivity) differential. The exact method used varies depending upon the TOC instrumentation employed. Different methods have different recoveries of various organics and therefore affect the TOC readings. Some instruments require the use of a carrier gas such as air or nitrogen while others measure TOC directly.

8.2.2.2 Special organic speciation may be required to identify the sources of the contamination and define adequate measures for correcting TOC levels. Liquid chromatography with organic carbon detector (LC-OCD) is recommended for such troubleshooting. This method can be used for both high ppm and low ppb levels of TOC speciation.

8.2.3 Monitoring TOC in the UPW System

8.2.3.1 Refer to ASTM D5173 and ASTM D6317 for TOC analysis in UPW.

8.2.3.2 TOC is a useful test to measure the organic removal effectiveness of the UPW system components including carbon, RO, degasification, and ion exchange. After the RO, TOC typically drops from low ppm levels in the source water to mid ppb range, and to single digit ppb levels after the mixed resin beds and UV TOC reduction units.

8.2.3.3 TOC may be measured at the point-of-use to determine quality changes from the distribution system and the manufacturing tool. Short wavelength UV (185 nm) is capable of breaking up residual organics into charged organic molecules. TOC that survives to the POU in a UPW system is typically either 'light' molecules or small fragments of larger molecules such as acetate and formate. While low TOC means that the UPW system is working effectively to eliminate the source water organic load, this test is not an accurate measure of sterility of a UPW system. In addition, TOC levels at POU can also reflect carryover from chemical baths and contaminants in cleanroom air.

8.3 Dissolved Oxygen (DO) (ppb)

8.3.1 Unless DO content is controlled, rinsing hydrogen-passivated silicon wafer surfaces with high DO UPW can result in etching of the silicon by the oxygenated UPW and loss of control of gate oxide thickness. DO is measured online by two basic technologies: electrochemical cell or optical fluorescence. Traditional electrochemical measurement uses a sensor with a gas-permeable membrane. Behind the membrane, electrodes immersed in an electrolyte develop an electric current directly proportional to the oxygen partial pressure of the sample. The signal is temperature compensated for the oxygen solubility in water, the electrochemical cell output and the diffusion rate of oxygen through the membrane. Optical fluorescent DO sensors use a light source, a fluorophore and an optical detector. The fluorophore is immersed in the sample. Light is directed at the fluorophore which absorbs energy and then re-emits light at a longer wavelength. The duration and intensity of the re-emitted light is related to the DO partial pressure by the Stern-Volmer relationship. The signal is temperature compensated for the solubility of oxygen in water and the fluorophore characteristics to obtain the DO concentration value. Refer to ASTM D5462 for DO testing.