

SEMI F121-0923

GUIDE FOR EVALUATING METROLOGY FOR PARTICLE PRECURSORS IN ULTRAPURE WATER

This Standard was technically approved by the Liquid Chemicals Global Technical Committee. This edition was approved for publication by the global Audits and Reviews Subcommittee on August 21, 2023. Available at www.semiviews.org and www.semi.org in September 2023.

NOTICE: The section symbol (§) is used to reference a numbered section, paragraph, or header and all subordinate paragraphs, headers, and embedded material (i.e., EXCEPTIONs, lists) therein. The paragraph symbol (§) is used to reference a particular numbered paragraph and embedded material therein. When duplicated (i.e., §§ and §§§) the symbols are used to reference more than one section or paragraph, respectively.

NOTICE: Paragraphs entitled ‘NOTE:’ are not an official part of this Standard or Safety Guideline and are not intended to modify or supersede the official Standard or Safety Guideline. These have been supplied by the global technical committee to enhance the usage of the Standard or Safety Guideline.

1 Purpose

1.1 This Guide provides a performance-based definition of metrology that can be used to measure particle precursors in ultrapure water (UPW). This Guide includes a testing methodology and criteria for qualifying measurement techniques for quantifying particle precursor concentrations in UPW. Particle precursors are defined as dissolved compounds that can form particles when dried on a wafer surface. This definition was developed by the UPW International Roadmap for Devices and Systems (IRDS). Particle precursors can originate from UPW system components, such as ion exchange resin (IX resin).

1.2 Critical dimensions in semiconductor manufacturing have reached levels susceptible to particle sizes and types that are currently difficult to detect. Particle precursors can form particles at those sizes, as demonstrated by a recent IRDS study. The industry requires proactive measures to prevent contamination and risk to yield, and, therefore, this Guide was developed to address the gap in metrology available for measurement of particle precursors.

2 Scope

2.1 This Guide recommends a testing methodology to qualify metrology for the measurement of particle precursors in UPW. Performance criteria include:

- Accuracy in particle sizing,
- Repeatability in particle sizing and concentration,
- Dynamic range, and
- Noise.

2.2 Performance criteria testing materials include:

- A traceable reference nanomaterial standard used for particle sizing validation,
- A dissolved standard for concentration calibration, noise, and dynamic range, and
- A real-world demonstration using IX resin extract to evaluate particle formation from a known particle precursor source relevant to the semiconductor industry.

2.3 Test procedures and success criteria are applicable to both online and offline sample measurement techniques.

2.4 A key assumption of this Guide is that one step in the analytical process is a drying step, such as nebulization or atomization, to form a particle from a dissolved species.

2.5 The intended users of this Guide are instrument manufacturers and instrument users. The number of replicates and duration of performance criteria testing are provided in the Guide as recommended minimum values. However, instrument manufacturers can choose to run additional replicates over an extended period of time to further demonstrate instrument capabilities and performance.

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 This Guide defines success criteria for analyzing particle precursors only in UPW. The concern of metrology for particle precursors in other liquid chemicals is still being determined and, if a need is determined, can be considered in future revisions.

3.2 This Guide focuses on qualifying metrology for measuring high molecular weight organic particle precursors that can leach from IX resin. Silicic acid as a particle precursor for colloidal silica formation is not evaluated in this Guide but can be included in future revisions.

3.3 This Guide considers the measurement of particle precursors only in UPW and does not address the quantification of particles formed on a product wafer surface.

3.4 The analysis of particle precursors described in this Guide is an indirect measurement because dissolved particle precursors are being measured as particles after a drying step in the analytical process.

3.5 The measurement of contaminants that can form films on a wafer surface is not considered in this Guide, which focuses on only particle precursors that can form particles on a wafer surface.

3.6 Currently no single technique or technology can provide information for particle number, size distribution, and chemical composition. Therefore, this Guide does not include any performance criteria related to chemical composition data. Chemical information of particular interest includes organic molecular structure and functional group identification. Complementary techniques that can provide this information are important for understanding sources and control of particle precursors.

4 Referenced Standards and Documents

4.1 SEMI Standards and Safety Guidelines

SEMI C93 — Guide for Determining the Quality of Ion Exchange Resin Used in Polish Applications of Ultrapure Water System

SEMI F63 — Guide for Ultrapure Water Used in Semiconductor Processing

4.2 ISO® Standards¹

ISO Guide 35:2017 — Reference Materials – Guidance for Characterization and Assessment of Homogeneity and Stability

4.3 Other Documents

BAM-N008 — Size Distribution and Concentration of Silver Nanoparticles Calculated from Small-Angle X-Ray Scattering (SAXS)²

RM 8012 — Gold Nanoparticles, Nominal 30 nm Diameter³

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

5 Terminology

5.1 Abbreviations and Acronyms

5.1.1 CPC — condensation particle counter

¹ International Organization for Standardization, ISO Central Secretariat, Chemin de Blandonnet 8, CP 401-1214 Vernier, Geneva, Switzerland; Telephone: +41.22.749.01.11, Fax: +41.22.733.34.30, <http://www.iso.org>. ISO trademark is owned by International Organization for Standardization.

² Bundesanstalt für Materialforschung und -prüfung, German Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany; Telephone: +49.30.8104.0, Fax: +49.30.8104.7.2222, <https://rrr.bam.de/>

³ National Institute of Standards and Technology, 100 Bureau Drive, Stop 3460, Gaithersburg, MD 20899-3460, USA; Telephone: +1.301.975.2000, <http://www.nist.gov>. NIST trademark is owned by National Institute of Standards and Technology.

- 5.1.2 *DLS* — dynamic light scattering
- 5.1.3 *DMA* — differential mobility analyzer
- 5.1.4 *HDPE* — high-density polyethylene
- 5.1.5 *IC* — ion chromatography
- 5.1.6 *IX resin* — ion exchange resin
- 5.1.7 *LNS* — liquid nanoparticle sizer
- 5.1.8 *MB* — mixed bed
- 5.1.9 *ppb* — parts per billion, ng/mL or µg/L
- 5.1.10 *ppm* — parts per million, µg/mL or mg/L
- 5.1.11 *ppt* — parts per trillion, pg/mL or ng/L
- 5.1.12 *RSD* — relative standard deviation
- 5.1.13 *SAXS* — small angle X-ray scattering
- 5.1.14 *STPC* — scanning threshold particle counter
- 5.1.15 *UF* — ultrafilter
- 5.1.16 *UPW* — ultrapure water

5.2 Definitions

- 5.2.1 *noise* — the fluctuation in the instrument background signal.
- 5.2.2 *particle precursor* — a dissolved compound that can form particles when dried on a wafer surface.

6 Use of the Guide

6.1 This Guide is intended to be used by instrument manufacturers and instrument users to demonstrate the ability to measure particle precursors by achieving the performance criteria described in § 7, which includes three steps.

6.1.1 Step 1 is used to evaluate particle sizing accuracy and repeatability using a traceable reference material. The standard should meet the following criteria:

- Size reference material that is traceable to a standards organization,
- Particle with a nominal diameter between 3 to 10 nm,
- Diameter-weighted geometric standard deviation less than 1.25, and
- Stable in UPW.

NOTE 1: The reference material for Step 1 does not need to be a concentration standard. To our knowledge, no such concentration reference material exists in the particle size range of interest (three to ten nm). This step focuses on size validation, and Step 2 addresses accuracy of concentration measurement.

6.1.2 Step 2 tests the ability of an instrument to repeatably form particles from a dissolved standard over a range of concentrations, because one of the assumptions is that the measurement technique includes a drying step. Note that potassium chloride (KCl) is not a particle precursor of concern in the semiconductor industry but is used in this Guide because it can form a particle during the drying step and its concentration can be accurately measured by ion chromatography (IC).

6.1.3 The purpose of Step 3 is to demonstrate repeatability in particle size and concentration measurement using a known particle precursor source relevant to the semiconductor industry, leachate from a polish mixed bed (MB) IX resin.

6.1.4 A summary of the measurement performance criteria testing is shown in Figure 1.

6.2 Instrument-to-instrument performance should be evaluated (i.e., each individual instrument should be qualified using the performance criteria defined in this Guide, not just one representative model from a manufacturer).

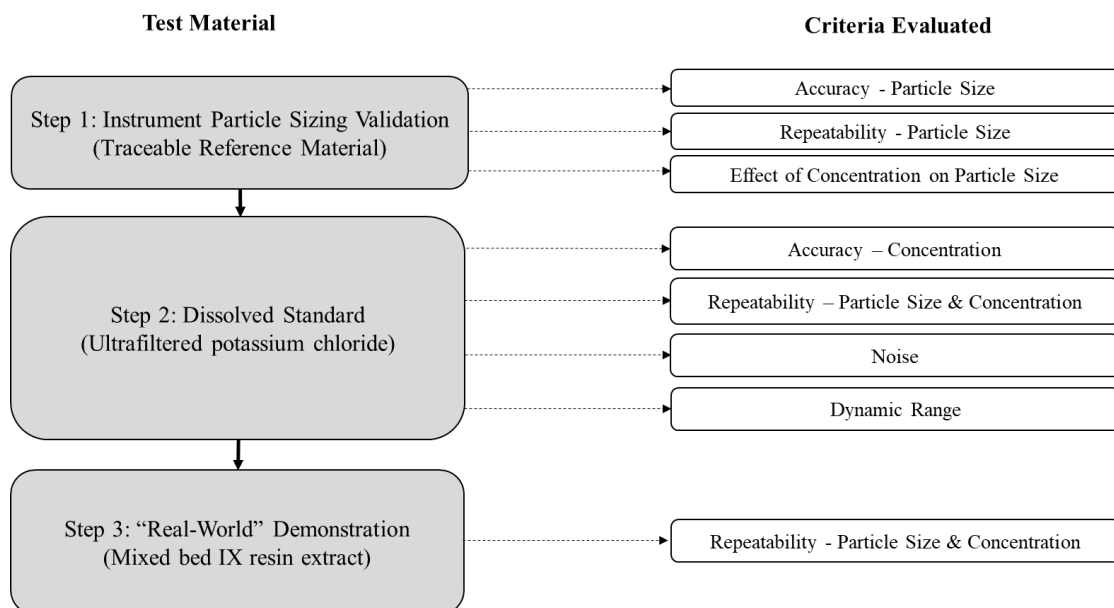


Figure 1
Particle Precursor Measurement Performance Criteria Schematic

7 Measurement Performance Criteria

7.1 Step 1: Instrument Particle Sizing Validation (Traceable Reference Nanomaterial)

7.1.1 Initial Particle Sizing Accuracy — The average reported particle diameter (number-weighted peak diameter) for five replicate measurements of the reference nanomaterial should be between 5.3 and 9.3 nm. The replicates should be measured once per day for five consecutive days. This validation step is only for sizing, not concentration, so a recommended concentration is intentionally not defined here. The user should select a concentration appropriate for the instrument being evaluated.

7.1.1.1 To the knowledge of the task force that developed this Guide, the only available standard that meets the criteria described in § 6.1.1 is BAM-N008⁴, a 6 nm nominal diameter silver nanoparticle reference nanomaterial that is expected to be available for at least 8 years at the time of publishing this Guide from Bundesanstalt für Materialforschung und-prüfung (BAM), the German Federal Institute for Materials Research and Testing. Therefore, the acceptable size range criteria for particle sizing accuracy is based on BAM-N008. Refer to Appendix 1 for basis of this range including validation data.

NOTE 2: The reported average particle size is known to vary slightly depending on the measurement technique used (e.g., scanning electron microscopy vs. differential mobility analysis vs. dynamic light scattering vs. small-angle x-ray scattering [SAXS]). The BAM-N008 reference nanomaterial certification report includes sizing only by SAXS. Therefore, the anticipated variability in reported size based on metrology type is included in the upper and lower limits of the sizing accuracy criteria.

7.1.2 Particle Sizing Repeatability — The relative standard deviation (RSD) of the average particle diameter should be less than 15% for five replicate measurements of the reference nanomaterial. The replicates should be measured over the duration of the calibration interval defined by the manufacturer.

NOTE 3: The duration of repeatability testing should be within the stability time of the reference standard. Preliminary testing has demonstrated stability of a diluted BAM-N008 standard for at least one month (refer to Appendix 1).

7.1.3 Concentration Effect on Sizing — The reported particle diameter for five replicate measurements at two additional concentrations should be within $\pm 5\%$ of the averaged value measured in ¶ 7.1.1. The additional

⁴ https://rrr.bam.de/RRR/Content/EN/Downloads/RM-Certificates/RM-nanomaterials/bam_n008_repe.html

concentrations should be approximately $1/3\times$ and $3\times$ the concentration used for initial particle sizing accuracy in ¶ 7.1.1.

NOTE 4: After instrument particle sizing is validated by Step 1, it is recommended that sizing confirmation is performed on a regular basis at an appropriate frequency (e.g., daily, weekly, monthly) defined by the instrument manufacturer to ensure instrument performance. A non-traceable reference nanoparticle standard (e.g., diafiltered 10 nm gold) can be used for ongoing size confirmation if it is first correlated to the traceable reference standard. The ongoing size confirmation should meet the criteria defined in § 7.1.

7.2 Step 2: Dissolved Standard Particle Precursor Measurement (Ultrafiltered Potassium Chloride Solution)

7.2.1 *Concentration Accuracy* — The average response of the instrument being evaluated for particle precursor measurement for five replicate measurements (once per day for five consecutive days) of the dissolved standard (ultrafiltered potassium chloride) should be within $\pm 10\%$ of the expected mass concentration value. The expected concentration should be validated using IC analysis for Cl^- .

7.2.2 *Particle Formation Repeatability* — The RSD of five replicate measurements (once per day for five consecutive days) of the dissolved standard should be less than 15% for size and concentration.

7.2.3 *Noise* — The noise of the instrument output should be no larger than 30% of the background concentration reported by the instrument while measuring the method blank (UPW used to prepare the standards).

7.2.3.1 The recommended method for calculating the root mean square (RMS) noise level is shown in Equation 1:

$$Noise_{RMS} = \sqrt{\sum_{i=1}^n \frac{(Conc_i - Conc_{Avg})^2}{n}} \quad (1)$$

where:

$Conc_i$ = the concentration calculated from instrument response at regular intervals with the length of the regular interval defined by the user of the Standard, and

$Conc_{Avg}$ = the average concentration calculated from instrument response of n measurements.

NOTE 5: For statistical accuracy, it is recommended that n is greater than or equal to 30.

7.2.3.2 The background concentration is defined as:

$$Conc_{Avg} = \sum_{i=1}^n \frac{Conc_i}{n} \quad (2)$$

NOTE 6: The background concentration should be established while challenging the instrument with a method blank with the UPW used to prepare the standards.

7.2.3.3 *Detection Efficiency* — The detection efficiency for particle metrology is defined as the number of particles detected/unit volume divided by the number of actual particles/unit volume for the dissolved standard. For dissolved species, the detection efficiency is defined as detected quantity/unit volume divided by actual quantity/unit volume for the applicable standard. No minimum detection efficiency is defined here, but the detection efficiency of the technique should be reported as part of the metrology evaluation.

7.2.4 *Dynamic Range* — The dynamic range is evaluated by analyzing standards for at least three concentrations spanning $10\times$ to $100\times$ the reported background concentration and plotting log of the measured values versus the log of expected values. Linearity is confirmed if the square of the correlation coefficient (R^2) is greater than 0.95.

7.3 Step 3: Real-World Demonstration with Mixed Bed Ion Exchange Resin Extract

7.3.1 *Measurement Repeatability* — The relative standard deviation of three replicate measurements each at three different concentrations of the ion exchange extract (prepared following SEMI C93 procedure for static leach grab sample) should be less than 15% for size and concentration. Three concentrations of the ion exchange extract should be measured: 100%, 30%, and 10%. If the concentration of the undiluted extract (100% concentration) is higher than the maximum analytical limit, then the dilutions should be prepared at 80%, 24%, and 8% of the maximum analytical limit of the instrument.

7.4 Table 1 summarizes the performance criteria values.

Table 1 Particle Precursor Measurement Performance Criteria Summary

Performance Criteria (Units)	Value	Criteria Evaluated Using		
		Step 1 (Traceable Size Reference Material – Silver Nanoparticle)	Step 2 (Dissolved Standard – Ultrafiltered KCl)	Step 3 (Real-World Demonstration – MB IX Resin Extract)
Particle size accuracy to certified value (nm)	Average size between 5.3–9.3 nm	X		
Particle size repeatability (% RSD)	<15	X	X	X
Particle concentration repeatability (% RSD)	<15		X	X
Concentration effect on particle sizing (1/3× and 3× concentration)	Within ±5% of the average value for sizing accuracy	X		
Concentration accuracy (%)	±10		X	
Noise/Background (%)	<30		X	
Dynamic Range: R ² for log measured values vs. log expected values, three concentrations between 10×–100× background level	>0.95		X	

8 Analytical Testing Materials and Methodology

8.1 Materials

8.1.1 *UPW for Standards Preparation* — The UPW used to prepare all standards should meet the criteria of SEMI F63.

8.1.2 *Container Material* — For general sample preparation (silver reference nanomaterial, KCl, and IX resin extract), high-density polyethylene (HDPE) is recommended due to low particle precursor extraction at room temperature and reduced risk of particle losses to the wall of the container. Refrigerated storage of the samples when not in use and shielding from light is recommended.

8.1.2.1 The container should be pre-cleaned and qualified for the intended tests to be conducted. The criteria for the qualification are that the parameters tested in the container filled with UPW should be either less than detection limits or significantly lower than the value of the test results. Dedicate standards containers to specific test materials and concentrations.

8.1.3 Stability of Materials (Based on Preliminary Testing Observations)

8.1.3.1 *Step 1: Traceable reference nanomaterial* — Dilution of BAM-N008 observed to be stable at least one month.

8.1.3.2 *Step 2: Ultrafiltered KCl* — Stable greater than 6 months.

8.1.3.3 *Step 3: IX resin extract* — Stable for at least one month when stored in a refrigerator.

NOTE 7: Solution was considered stable if concentration did not vary by more than 10% of initial value.

8.2 Step 1: Instrument Particle Sizing Validation (Traceable Reference Nanomaterial)

8.2.1 BAM-N008 certified reference material can be purchased from the German Federal Institute for Materials Research and Testing. The standard contains a 5 mL aqueous suspension of nominal 6 nm diameter silver nanoparticles.

8.2.2 Depending on the operation of the instrument, the reference material can be used as received or with diafiltration. The optional diafiltration step reduces the level of dissolved material in the solution and can help to provide a more accurate and repeatable size measurement. A procedure that has been used successfully with the 6 nm silver reference material is provided in Appendix 2.

8.2.3 Measure particle size on five replicate measurements of the reference silver nanoparticles solution. For particle size accuracy, replicates should be measured once per day for five days. For particle sizing repeatability, replicates should be measured over the duration of calibration interval defined by the manufacturer. The concentration of the reference nanoparticle is not a certified value, and the user should determine an appropriate dilution to use. Refer to Appendix 1 for example data including dilution information.

8.2.4 Prepare two additional solutions of the reference silver nanoparticles at $1/3\times$ and $3\times$ the concentration used for particle sizing accuracy above. Measure particle size on five replicates of each to determine the effect of concentration on particle sizing.

8.3 Step 2: Dissolved Standard Particle Precursor Measurement (Ultrafiltered Potassium Chloride Solution)

8.3.1 Preparation Procedure

8.3.1.1 Prepare 1 mg/g KCl solution using high-purity (ACS reagent grade, >99% purity, or better) anhydrous KCl in UPW (1 g KCl in UPW to make 1000 g of solution). Gravimetric accuracy should be $\pm 1\%$.

8.3.1.2 Calculate the concentration of KCl using Equation 3 and record it.

$$C_{KCl} = \frac{\text{Mass of KCl (g)}}{\text{Mass of KCl (g)} + \text{Mass of Water (g)}} \quad (3)$$

8.3.1.3 Agitate on shaker table for 12 hours.

8.3.1.4 Pre-rinse a 3,000 to 6,000 molecular weight cutoff ultrafilter (UF) with UPW. Monitor with particle precursor measurement instrument. Continue rinsing until the concentration of the filtrate is comparable with incoming UPW.

8.3.1.5 Filter the prepared solution with the pre-rinsed UF. Discard the first 100 mL of filtrate and then collect filtrate in a clean HDPE container per § 8.1.2.

8.3.1.6 Analyze solution aliquot by IC to determine Cl^- concentration. The value should be within $\pm 5\%$ of the concentration calculated in ¶ 8.3.1.2.

8.3.1.7 Prepare a stock solution by diluting to 100 ppm nominal concentration with UPW based on concentration calculated in ¶ 8.3.1.2. Prepare additional solution as needed using offline or online dilution techniques as appropriate for the instrument.

8.3.1.8 Multiple concentrations of the KCl solutions should be run to characterize the response of the instrument. The number of concentrations measured is at the discretion of the user.

8.3.1.9 The recommended KCl concentration range during testing is 1 ppt to 100 ppb. This range can be adjusted based on the operating range of the instrument.

NOTE 8: Example data on dissolved standard measurement for several instruments is provided in Related Information 1.

8.4 Step 3: Real-World Demonstration with Mixed Bed Ion Exchange Resin Extract

8.4.1 Select semiconductor grade virgin MB IX resin, preferably with a multi-year shelf life and consistent availability from supplier. Refer to manufacturer's recommendations for storage conditions.

8.4.2 Prepare aqueous extract per SEMI C93 grab sample analysis procedure.

8.4.3 Document the following parameters and variables:

- Resin brand or model,
- Resin batch,
- Resin age from manufacturing date, and
- Solution storage conditions (temperature, light exposure, container).

8.4.4 Prepare and measure three replicates each at three different concentrations: 100%, 30%, and 10%. If the concentration of the undiluted extract (100% concentration) is higher than the maximum analytical limit, then the dilutions should be prepared at approximately 80%, 24%, and 8% of the maximum analytical limit of the instrument (nine total samples).

8.5 Report the measurement performance information that is shown in the template provided in § 9.