NEW DEVICE FOR THE COLLECTION, AND ELEMENTAL IDENTIFICATION OF SUB-50-NM PARTICLES IN UPW

To successfully manufacture semiconductor devices, particles contaminating high-purity water (UPW*) must be controlled and the elements within the particles identified. Current guidelines suggest that these particles should be smaller than one half of the line-width of the device geometry, yet the available optical particle counters (OPC) can only measure particles >40 nanometers (nm). At one half of line width, the 65-nm semiconductor devices now in production would need to be able to detect particles <32.5 nm, a size below the current detection limit of OPCs. In addition, the ability to identify elements within a particle <100 nm is impossible with current technology.

Semiconductor manufacturers therefore do not have critical measurement tools to control of waterborne particles. This article will introduce a new metrology device intended to identify contaminant elements in particles <50 nm. The device uses an agglomeration technique to "create" particles that are large enough for elemental analysis with a commonly used X-ray diffraction technique.

Need for a New Technology

As semiconductor manufacturers move towards 32-nm-and-smaller line width architectures, and towards using 450-millimeter (mm) diameter silicon discs, the metrology required to monitor the manufacturing processes must make significant advances. Of particular concern to the International Technology Roadmap for Semiconductors Ultrapure Water (ITRS UPW) committee is the apparent lack of progress in metrology needed to support the ITRS 2008 Update Front End Processing requirements and beyond (1). Specifically, the lack of speciation (explicit identification of specific contaminant elements) in almost all on-line measurements (particles, total organic carbon [TOC], and dissolved inorganic residue) is no longer acceptable. The on-line monitoring of particles using OPCs poses a particular problem. While OPCs rapidly detect undesirable increases in particle concentration, they cannot provide information on the elemental nature of the particles detected. Without some indication of the chemical nature of the particles detected by the OPC, the UPW engineer is left to guess the source of the potentially contaminating particles.

The current smallest particle size detected by OPCs is 40 nm, and there is little chance of lowering the detection limits any further (due to the fundamental limits of light scattering). Based on the ½ line width rule, this ≥ 80-nm geometry solution is inadequate for an industry producing mainly 65-nm, and smaller devices.

The traditional way of capturing particles for elemental analysis has been to collect them on a scanning electron microscopy (SEM) filter where a typical filter pore size is approximately 100 nm. However, the SEM filter must remain on-line for several weeks in order to collect enough particles for X-ray diffraction (EDS) analysis. Further, it will not reliably collect many particles of interest for 90 nm and smaller device producers. A metrology time period of several weeks is unacceptable to the semiconductor industry, as is the 100 nm minimum particle size limitation of SEM EDS analysis.

To address these deficiencies in particle metrology, the authors have developed a new UPW metrology tool called the nano-Particle Collection Device (nPCD). The nPCD can agglomerate sub-50 nm particles in 24 hours or less and release the agglomerates for collection, using a standard SEM filter, in just a few minutes. The nPCD therefore significantly shortens particle collection time, and because the particles are agglomerated to larger sizes, the established EDS technique can then be used to identify the particle agglomerates rather than individual particles. While traditional SEM analysis measures particle size distribution and attempts to analyze some of the particles, the nPCD sacrifices the size distribution data in favor of agglomerating sub-50-nm particles for elemental analysis.

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TABLE A
Elements Forming >5% of Agglomerated Particles Found in Final Filtration UPW at 2009 ITRS Round Robin Fabs

Aluminum
Antimony
Bromine
Calcium
Carbon
Chlorine
Chromium
Fluorine
Iron
Magnesium
Nickel
Nitrogen
Oxygen
Phosphorus
Potassium
Silica
Sodium
Sulfur
Titanium
Vanadium
Zinc

Figure 1. Carbon particle—biological material.

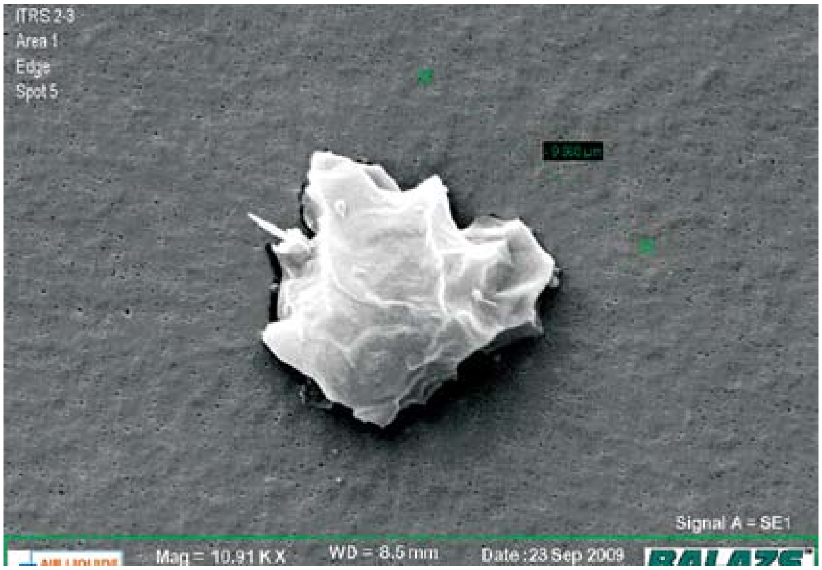

Figure 2. Silica/oxygen particle.

Figure 3. Silica/aluminum/potassium/oxygen particle.

Theory of Operation

The nPCD is an analytical adaptation of patented Microfier Technology that has been, developed and laboratory tested during the previous 2 years (2). The nPCD captures, concentrates, and presents nanoparticle agglomerates for analysis using a traditional technique.

Most UPW particles carry a surface charge. Bacteria carry a negative surface charge as a result of carboxyl and phosphate groups (3). The negative charge is stable over a wide pH range between 2 and 11. The negative charge has been verified by electrophoretic, isoelectric, and colloid titration methods (3), and by the preferential absorption of anionic stains (observed in optical microscopic counting). In buffered aqueous solutions, the magnitude of the negative charge can be reduced by the development of a positive ion counter-layer. However, since high-purity water is deionized, charged particles have a poorly developed counter-ion layer, thus enhancing the negative zeta potential.

Non-biological particles in high-purity water usually originate from system liners, resin beds (resin fragments), pipes, and gaskets. A resin fragment exhibits a strong anionic or cationic charge characterized by its functional group. In the electronics industry, the piping and gasket materials are usually composed of chlorinated and fluorinated hydrocarbons, and/or stainless steel. Because of the natural hydrophobicity of negative charges in water, these generally non-polar materials collect negative charges from the surrounding water. Negative ions tend to be excluded from the bulk of the liquid and accumulate at interfaces. As a result, even particles without active functional groups develop a net negative charge (4). Zeta-potential evaluation of deionized water and wafer-cleaning experiments support that nanoparticles found with high-purity water have a strong negative zeta-potential (5).

Charged biological and non-biological particles can be mobilized within a non-conductive dielectric, such as high-purity water, by an electrical field (E-field) force on the particles. The E-field can produce a force on the charged particles by the familiar Equation 1 (6).

$$F = qE \qquad \text{Eq. 1}$$

Where:
F is the vector quantity of force in mks units
E is the vector quantity of E-field strength
q is the net charge on the charged particle seen by the E-field.

This relationship states that the magnitude of the force acting on any charged object, including a nanoparticle, is a product of its net charge and the applied E-field strength. The nPCD technology uses this relationship to move nanoparticles perpendicularly to process chamber flow, thus separating and removing them from the high-purity flow stream.

The force described above acts on many nanoparticles in the water at the same time, driving them toward the electrodes. There the coulombic force captures and holds them. In addition, there is evidence that neighboring nanoparticles agglomerate into much larger particles (either on their way to the electrode or after landing on the electrode). It is quite common to collect multiple particle agglomerates in a 24-hour monitoring period where individual agglomerates are greater than several thousand nanometers. (See Figures 1-6.)

While the agglomeration phenomenon is not yet completely understood, the results are clear. Particle size distributions conducted in the water downstream of the nPCD process chamber show the presence of much larger particles than in the water upstream of the chamber. These larger particles are often composed of elements not found in the chamber's materials of construction, indicating that they were present upstream, but were too small to be detected.

nPCD Design

The nPCD process chamber is a conductive cylinder, containing a conductive rod (with a diameter smaller than that of the outer chamber) positioned inside the cylinder. UPW enters the chamber through a manifold designed to distribute water uniformly across the cross sectional area of the cylinder. The water flows through the chamber with a laminar flow while a direct current (DC) potential produces an E-field force that moves charged particles radially toward the cylinder and rod (electrodes). Positively charged nanoparticles move toward the cathode (- potential) and negatively charged nanoparticles move toward the anode (+ potential).

For high-purity water containing primarily negative nanoparticles, the optimal operation of the nPCD requires a positive rod and a negative cylinder. Operating with a positive rod forces negatively-charged nanoparticles in the high-purity water to move toward, and concentrate near the rod. Eventually the nanoparticles adhere to the rod. Nanoparticles that adhere to the rod or cylinder wall can be dislodged by reversing the polarity of the electrodes, driving them back into the water and flushing them out of the chamber for collection.

The particle agglomerates frequently exceed 1.0 micron (1,000 nm), and can therefore be collected for analysis with a traditional 100-nm-pore SEM analytical filter membrane. Field testing has demonstrated that a high number of particle agglomerates are collected, making it straightforward to use the EDS technique for elemental analysis.

The functionality of the nPCD allows for nanoparticle capture and collection using very little power (<10 watts). Therefore, several nPCDs could easily be powered from a standard 120-volt AC service outlet, or even from alternative power sources such as batteries.

The cylindrical chamber optimizes the removal of negative nanoparticles because of an increasing E-field, and a decreasing cross-sectional area encountered as negative nanoparticles move away from the chamber wall and toward the rod. The E-field strength increases radially at an increasing rate from the cylinder wall to the rod (6). This is the effect of the field lines or vectors being focused closer together at the rod, which has smaller surface area than the cylinder (Figure 7). As a result, the acceleration of charged nanoparticles increases as they move toward the rod.

For a given group of nanoparticles, the concentration (number/unit volume) increases almost exponentially as the nanoparticles move from a homogeneous distribution in the chamber to a small volume near the center of the chamber. For each linear movement (X) of nanoparticles toward the rod, the volume of the contaminated water decreases by the square function of the distance traveled (Figure 8).

Because the normal operation of the process chamber is to first capture, and then intentionally release contamination into the stream, the nPCD can be operated for up to several months without the need to perform cleaning or other maintenance procedures. For example, the chamber remained intact during 4 months of round-robin testing by the ITRS UPW committee.

The relatively short capture time (typically <24 hours for current UPW) makes it possible to take a "snapshot" of nanoparticles and use SEM/EDS analysis to quickly identify the elements of contamination. The nPCD operates at a flowrate of nearly 400 mL/min, 10 times the flowrate of conventional SEM filter sampling, allowing hundreds of liters to be sampled in 24 hours.

Because the process chamber can be operated in a neutral (non-capture, non-release) mode, it is possible to have the nPCD standing by for the beginning of a process upset. An existing monitoring system can then trigger nanoparticle capture when it detects an upset in progress. After a capture cycle, the operating personnel can install an SEM membrane and collect the released particle agglomerates for analysis.

Analytical Results

The nPCD captures and agglomerates sub-50-nm particles from UPW, and releases these particles for collection onto an SEM membrane, thus enabling SEM/EDS analysis to rapidly determine particle morphology and elemental composition.

In order to operate effectively as an UPW analytical tool, the nPCD wetted parts (PVDF, PFA, and electropolished stainless steel) must not contribute background contamination. The nPCD supply tubing is fabricated using Flaretek fittings (with no valves) upstream of the process chamber. The process chamber is specially designed for UPW service with no dead-legs or elastomeric surfaces.

To validate the capture, agglomeration, and release of nanoparticles, the nPCD was subjected to controlled testing using an optical particle counter and SEM particle analysis. Figure 9 shows a sche-

Figure 4. Iron/chrome/nickel/oxygen particle—Type 1.

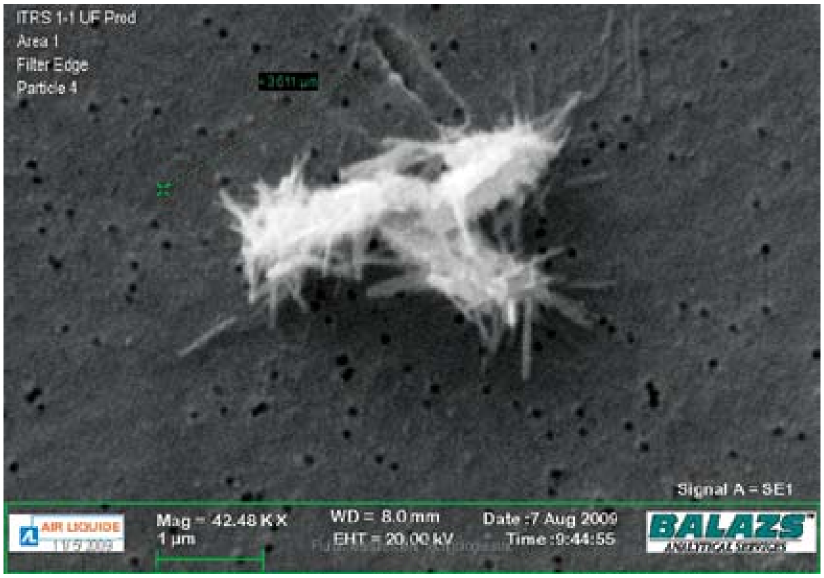

Figure 5. Iron/chrome/oxygen particle—Type 2.

Figure 6. Fluorine/carbon/oxygen particle.

matic diagram of the test setup.

Optical particle test. A PMS SO2 laser-based optical particle counter, which can discriminate 15 particle sizes (ranging from 200 to 2,000 nm), was used to monitor the supply water quality to the nPCD during a 51-hour capture cycle. The same instrument was used to document the water quality during a 9-minute release cycle. Figure 10 documents the concentration of particles within the 15 SO2 size categories. The UPW or baseline water quality had an average of 2 particles/mL distributed within the 10 lowest particle size categories, compared to the release water quality with 9 particles/mL and significant increases in all 15 particle size categories. The SO2 data demonstrates that the nPCD captures and agglomerates particles (as seen by the increase in particle sizes and counts).

SEM particle test. A similar test was done with SEM particle analysis. An SEM 100-nm pore size membrane filtered UPW from the supply to the nPCD during a 44.3-hour capture cycle. A separate SEM membrane filtered the water from a 9-minute nPCD release cycle that followed this capture cycle. The feedwater showed 1.9 particles/mL (ranging in size from 100 to 500 nm). In contrast, the release water contained 109 particles/mL, and a significant concentration of particles ranging in size from 100 to >1,000 nm. The SEM samples confirm that the nPCD is capturing, agglomerating, and releasing particles found in UPW.

Both the optical particle counter and SEM tests showed that the nPCD captures and agglomerates particles in 2 days and is able to release a small volume of water, containing a high concentration of agglomerates of particles of interest.

During the SEM testing, particles were captured on SEM membranes and elementally evaluated with EDS. Of the 10 particles randomly selected by an independent laboratory, 50% contained silica/oxygen, 40% contained carbon/oxygen (likely biological), and 10% contained iron/oxygen. The presence of elements not used in the nPCD chamber materials indicates that the nPCD is not contributing background contamination.

Following extensive UPW laboratory testing, the nPCD was tested at 5 fabs (in an ITRS "round-robin" test) from June through October 2009. The purpose of the testing was to validate the ability of the nPCD to capture, release, and collect particles on an SEM filter membrane, and then to evaluate the elemental constituents. The nPCD sampled the supply and product sides of the UPW final filtration systems. The systems tested included both ultrafilter-based, and cartridge-filter-based final filtration systems. Capture times ranged from 9 to 12 hours for supply water, and from 10.5 to 24 hours for product water.

The SEM sampling process documented the concentration of particles on the membrane and randomly evaluated approximately 20 particles per fab by SEM/EDS for elemental composition. All samples were evaluated by Balazs NanoAnalysis, utilizing the same analyst in each case. The individual results from all the round-robin sites are not included in this article but will be described in a future paper.

There was a significant variation in elemental constituents between sites and between final filtration supply and product water within sites. The particles evaluated by SEM/EDS detected the following elements at least once. They are listed in Table A.

Particles containing significant elemental combinations listed in Table B were found at all sites. Typical SEM micrographs of the particles found in the ITRS round-robin testing that relate to the four Table B categories are shown. (See Figures 1-6 as described below.)

The frequency of specific particle morphology and elemental composition varied dramatically between, and within, supply and product sites. When compared by elemental composition, several morphologies appeared quite similar (e.g., silicon [Si], and iron [Fe]-based agglomerated particles).

The Iron/chrome/nickel/oxygen in Figures 4 and 5 clearly suggests stainless steel. The nPCD electrodes are manufactured form electropolished stainless steel, and could be the source of the stainless steel detected on the SEM filters. However, stainless steel was only detected in 2 of the 5 ITRS round-robin sites. This observation, together with the fact that the nPCD is a low power (<10-W) device, strongly indicates that the nPCD is not the source of stainless steel detected on the SEM filters.

Conclusions

The semiconductor manufacturing industry wants to rapidly analyze the amount and composition of sub-50-nm particles in UPW to identify contamination sources as quickly as possible. Until now, identifying elements in sub-50-nm particles has not been possible. However, a new device, the nPCD, is now available to satisfy that need. Extensive field testing has shown that the new technology contained in the nPCD shows great promise to capture, release, and collect sub-50-nm particles for elemental identification. When the source of contamination has been identified, it can be eliminated, and the semiconductor manufacturing yield increased. Industry leaders are currently conducting further tests with the nPCD to monitor their UPW and identify sources of contamination.❑

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Endnote

*In the text, the term UPW refers to semiconductor-grade water produced in microelectronics facilities. Its quality parameters are defined under the International Technology Roadmap for Semiconductors (ITRS).

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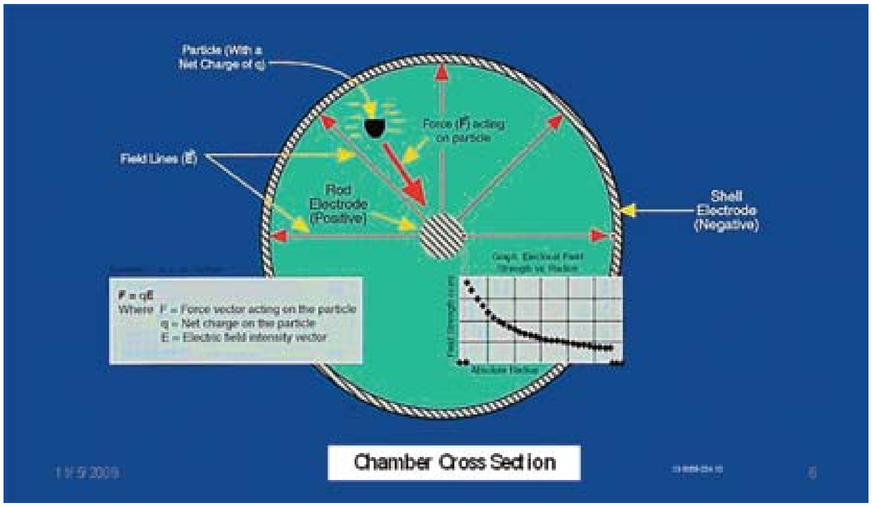
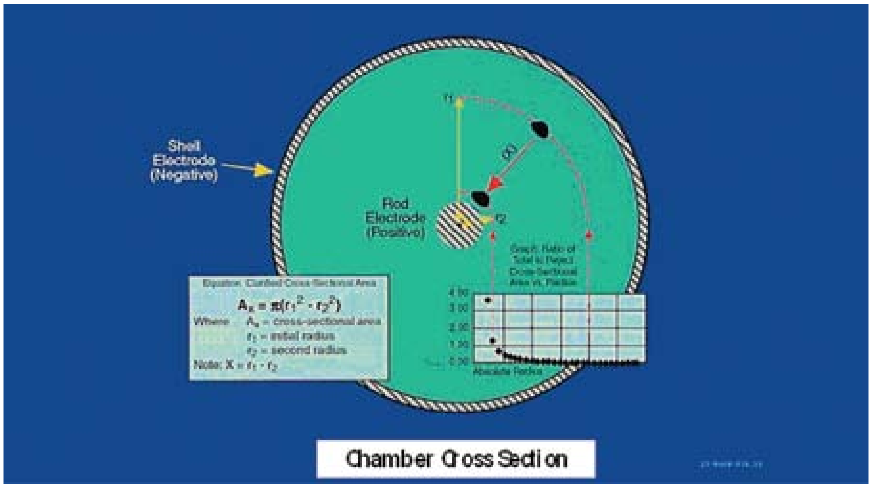
Key words: INSTRUMENTS, MEASUREMENT, MONITORING, PARTICLES, SEMICONDUCTORS, STANDARDS



$F = qE$
Where F = Force vector acting on the particle
q = Net charge on the particle
E = Electric field intensity vector

Figure 7. Electrical design of the nPCD. The electromagnetic field moves charged particles through the UPW.



Equation: Clarified Cross-Sectional Area
$A_x = \pi(r_1^2 - r_2^2)$
Where A_x = cross-sectional area
r_1 = initial radius
r_2 = second radius
Note: $X = r_1 - r_2$

Figure 8. Hydraulic design of the nPCD. The unit uses laminar flow and radial separation to capture particles.

TABLE B
Elements Forming >5% of Agglomerated Particles Found in Final Filtration UPW at all 2009 ITRS Round Robin Fabs

Particle Contaminant	*Illustrated*
Carbon/oxygen	Figure 1
Silica/oxygen/aluminum	Figures 2, 3
Iron/chrome/nickel/oxygen	Figures 4, 5
Fluorine/carbon/oxygen	Figure 6

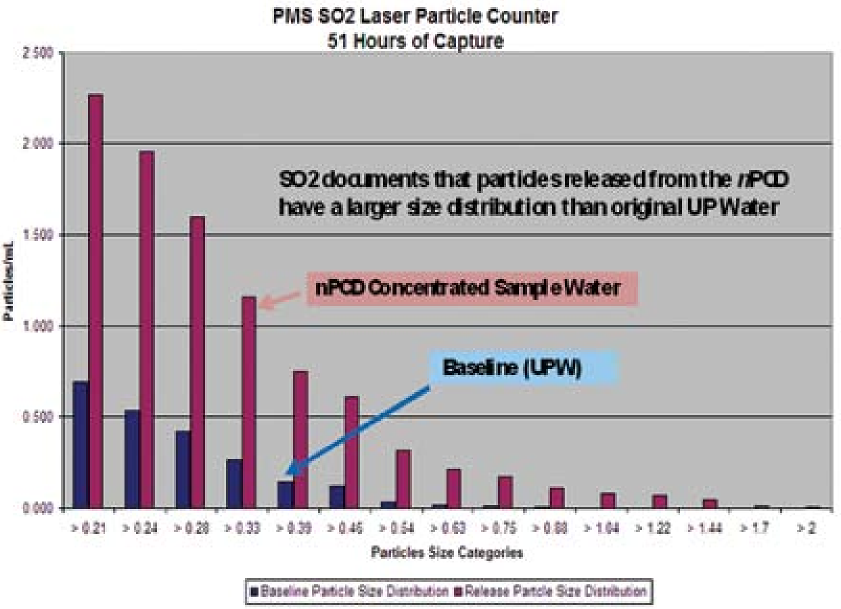


Figure 10. Capture data for PMS SO2 Particle Counter.

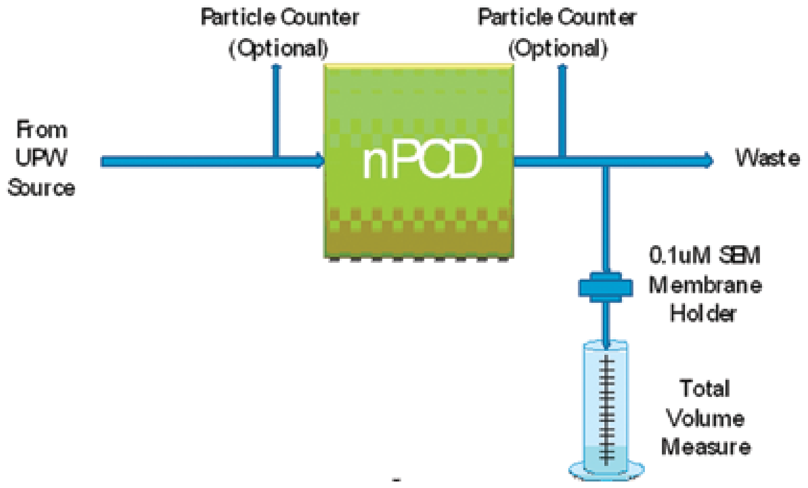


Figure 9. Equipment set up used for round robin testing.