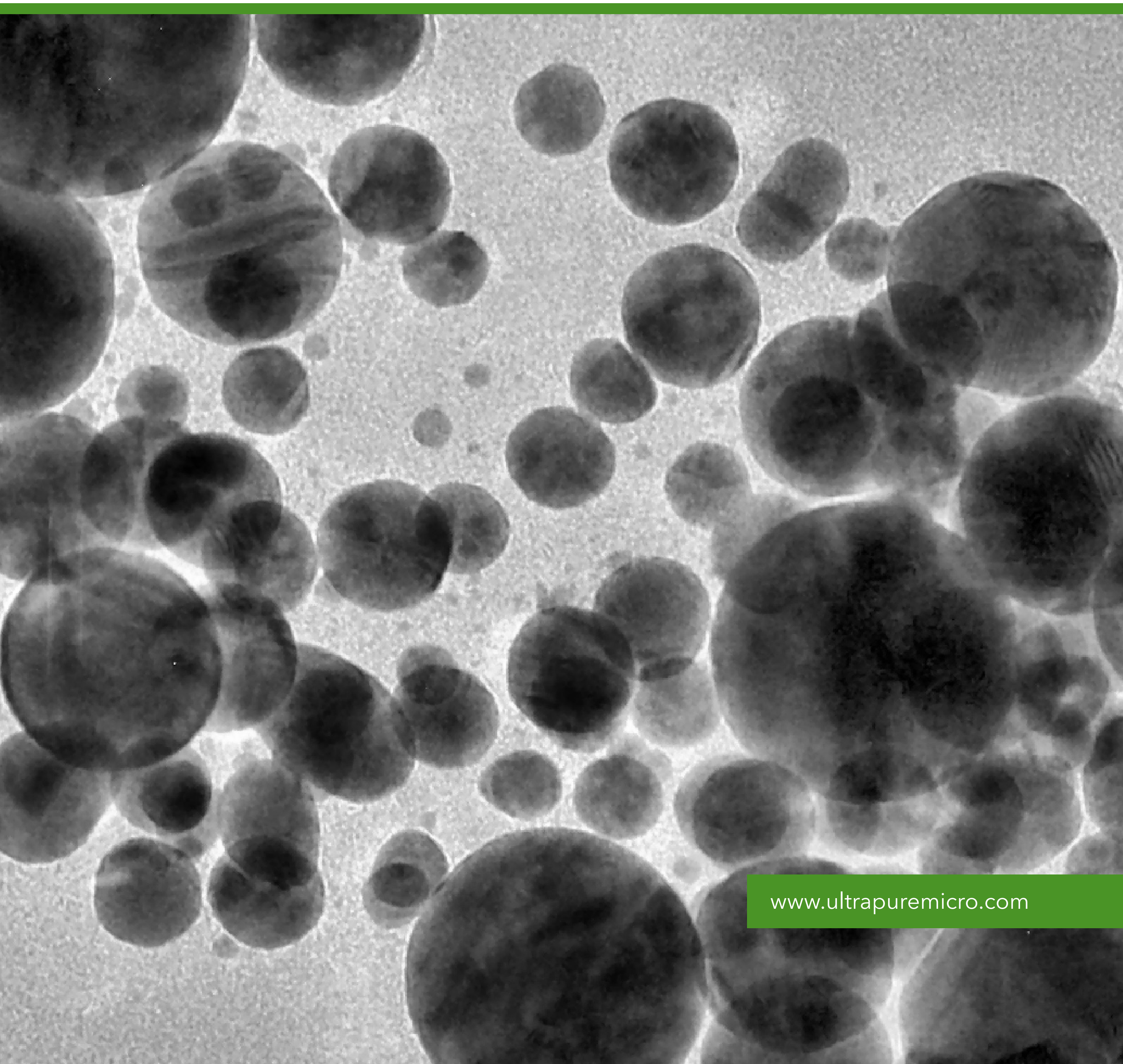
ULTRA PURE MICRO

PARTICLES

VOL 1 NO 1



www.ultrapuremicro.com

ULTRAPURE
MICRO

Characterizing the retention of UPW filters using enhanced SEMI C79 testing

Gary Van Schooneveld[1], Mark Litchy[1], Don Grant[1], Uwe Beuscher[2], Kevin Cresswell[2]

[1]CT Associates, Inc., 7121 Shady Oak Road, Eden Prairie, MN 55344
[2]WL Gore, 201 Airport Road, Elkton, MD 21921

Particles in ultrapure water (UPW), used during the manufacture of microcircuits on semiconductor wafers, can deposit onto the wafer surface thereby causing decreased yield and reliability of the microcircuits. As microcircuit future sizes continue to decrease, understanding the ability of a filter to capture and retain these particles becomes increasingly important and challenging.

In 2013, SEMI C79-0113, "Guide to Evaluate the Efficacy of Sub-15 nm Filters used in Ultrapure Water (UPW) Distribution System" was published. This document provides a SEMI recommended method for evaluating the efficacy of filter elements used to remove particles in UPW fluid streams. Since the release of this guide, the method has been enhanced to allow quantification of particle retention over a broad size range. This was accomplished by adding larger silica particles to the Ludox® SM30 silica specified by SEMI C79 resulting in a poly-dispersed silica challenge. A particle size distribution (PSD) slope of -2 (log-log) was selected so the challenge would more closely mimic a PSD typically found in UPW, yet still have sufficient large particles to measure a log retention value of 2 or 99% retention. This silica challenge has been designated as an "area-weighted challenge".

The use of this enhanced method has resulted in some interesting observations including indication of a most penetrating particle size similar to what is observed in gas filtration. The presence of a most penetrating particle size would indicate that retention mechanisms other than sieving are active, particularly for particles smaller than 30 nm.

This paper will review the enhancements made to the test method, review the retention data from a number of filter types and manufacturers, and discuss the implications for filters used in UPW.

Keywords: Ultrapure water, semiconductor industry, particles

INTRODUCTION

Particles present in ultrapure water (UPW) can deposit onto wafer surfaces during semiconductor manufacturing processes resulting in decreased yield and reduced circuit reliability. While UPW filters are effective at reducing particle concentrations, the unrelenting path toward smaller feature sizes demands that filters need to be increasingly more efficient at particle removal. Particles with dimensions equal to and smaller than 15 nm are of increasing concern for the most advanced semiconductor products.

In recent years, several test methods have been published that seek to quantify filter removal efficiency for particles smaller than 50 nanometers; SEMI C79 - Guide to Evaluate the Efficacy of Sub-15 nm Filters Used in Ultrapure Water (UPW) Distribution Systems; SEMI C82 - Test Method for Particle Removal Performance of Liquid Filter Rated 20 to 50 nm With Liquid-Borne Particle Counter and SEMI C89 Test Method for Particle Removal Performance of Liquid Filter Rated Below 30 nm with Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS). SEMI C82 and C89 use gold as the test particle while SEMI C79 uses silica. It has been shown in previous work[1], that particle retention can be significantly affected by the type of particle used for the test. In this reference, silica was shown to have the lowest particle to membrane interaction compared to gold and polystyrene latex (PSL). Interest in using silica as a test particle is also enhanced given that colloidal silica is a contaminant found in UPW systems. This paper will expand on the work conducted during the development of SEMI C79 and examines possible enhancements of this test method to measure filter retention of a poly-dispersed particle challenge that more closely mimics "real life" particle size distributions typically found in UPW systems.

SEMI C79-0113

In SEMI C79-0113, the retention of silica particles by microporous (MF) membrane cartridges or ultrafiltration (UF) membrane modules is measured. The silica particles must have a mean size between 5 and 15 nm. The filters are challenged at fixed concentration (5E9 particles/milliliter (mL) is suggested) and face velocity (0.8 cm/min for MF cartridges; 0.6 cm/min for UF modules). The challenge is continued until the filter has been exposed to a minimum of one monolayer of particles, with monolayer coverage based on projected particle cross-sectional areas assuming perfectly spherical particles. The test is typically 4-6 hours in duration. Particle concentrations upstream and downstream of the filter are measured using either or both of the following 2 techniques:

- Samples are collected at defined intervals and concentration is measured off-line via inductively-coupled plasma mass spectrometry (ICP/MS).
- Filtrate particle concentrations are measured continuously using in-situ liquid particle measurement (using an aerosol particle detection technique).

A schematic of a test system used for SEMI C79 testing is shown in **Figure 1**. UPW injected with silica particles is passed through the test filter at a fixed face velocity. The particles are injected using a peristaltic pump. An in-line static mixer is used to ensure a uniform challenge concentration. Valves are included upstream and downstream of the filter to allow grab sample collection. Valves are also included to direct a slip stream of either the filter inlet or outlet liquid to an in-situ instrument. In **Figure 1**, the in-situ instrument shown is a Liquid Nanoparticle Sizer (LNS)[2]. The main components of the LNS are an ultrafine atomizer and a scanning mobility particle sizer (SMPS). Its particle concentration measurement capabilities are described elsewhere[3-5].

There are potential shortcomings associated with SEMI C79. The method uses a challenge containing fairly mono-dispersed particles (typically Ludox® SM30 which has a median size of approximately 12 nm) while particles in UPW are poly-dispersed. Use of mono-dispersed particles only allows retention measurement over a narrow size range while the presence of other sized particles may influence retention of the 5-15nm particles.

In addition, the challenge concentration suggested by SEMI C79 (5E9/mL) is significantly higher than actual concentrations in UPW. The filters must be challenged at an elevated concentration so that retention measurements can be performed and the effects of loading can be determined. The challenge concentration can have a significant effect of filter retention as indicated in **Figure 2** which shows retention as a function of loading for several different challenge concentrations. Retention is shown as log reduction value (LRV) defined as:

LRV = log10 (challenge concentration/filtrate concentration)

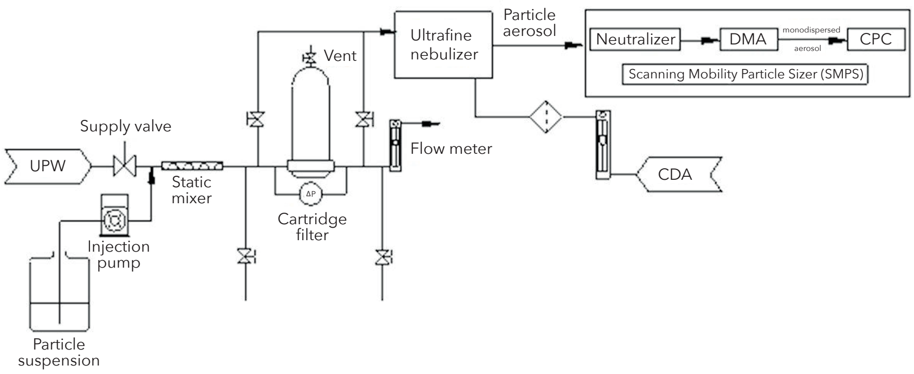


Figure 1: Schematic of a system capable of SEMI C79 testing
Source: Grant *et al.*, 2011

Figure 2 indicates that, at least for the type of filter tested, retention increases substantially when concentration is reduced. At 0.1 monolayer coverage retention was ~99% (LRV=2.0) with a challenge concentration of 1.2E7/mL but only 37% (LRV=0.2) when the challenge concentration was increased to 3.2E9/mL.

PARAMETRIC TESTING

Testing was undertaken to investigate the effect of particle size distribution on retention. The test method was similar to SEMI C79 but was performed using reduced concentrations (1.5E9/mL > 10nm) of poly-dispersed particles. Poly-dispersed challenges were simulated using mixtures of three commercially available silica particles: Ludox® SM30, Ludox® HS40, and Snowtex® OL. Their size distributions and the size distribution of a mixture of the three are shown in **Figure 3**. The modes in the distributions occur at 12, 28 and 48 nm.

The filter's particle retention was measured using four different mixtures of the three silica solutions. The mixtures were prepared using different size weightings of the three particles: number-weighted, diameter-weighted, area-weighted and volume-weighted. The number-weighted distribution contained equal number concentrations of the three particles. The diameter-weighted distributed was prepared such that the concentrations of the sums of the diameters of the three particles were the same. Similarly, the area-weighted and volume-weighted distributions contained equal area concentrations and volume concentrations of the three particles; respectively.

Testing was performed using a commercially available 30nm filter with a challenge concentration of 1.5E9/mL > 10nm and a filter face velocity of 0.8 cm/min. Two or three filters were tested with each size weighting.

Figure 4 presents retention of particles by three filters tested with the area weighted challenge. Retention is shown as LRV for particles >10 nm as a function of loading. Retention is seen to decrease with loading. The three filters tested had very similar retention. Similar repeatability was seen in tests with the other weightings.

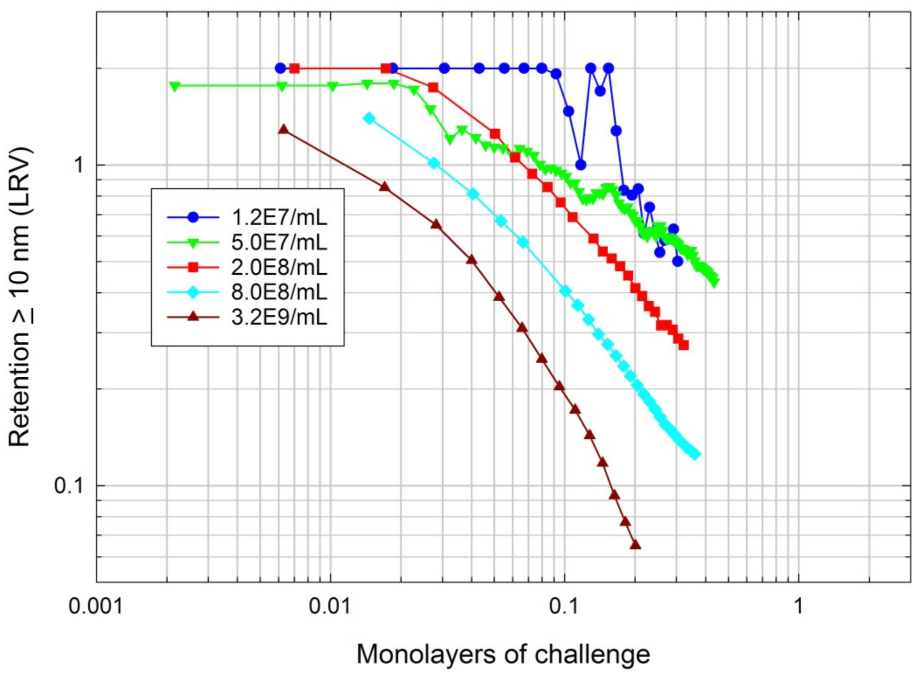


Figure 2: The effect of challenge concentration on retention of 12nm silica particles by a commercially-available UPW filter challenged at 0.95 cm/min

Source: Grant *et al.*, 2013

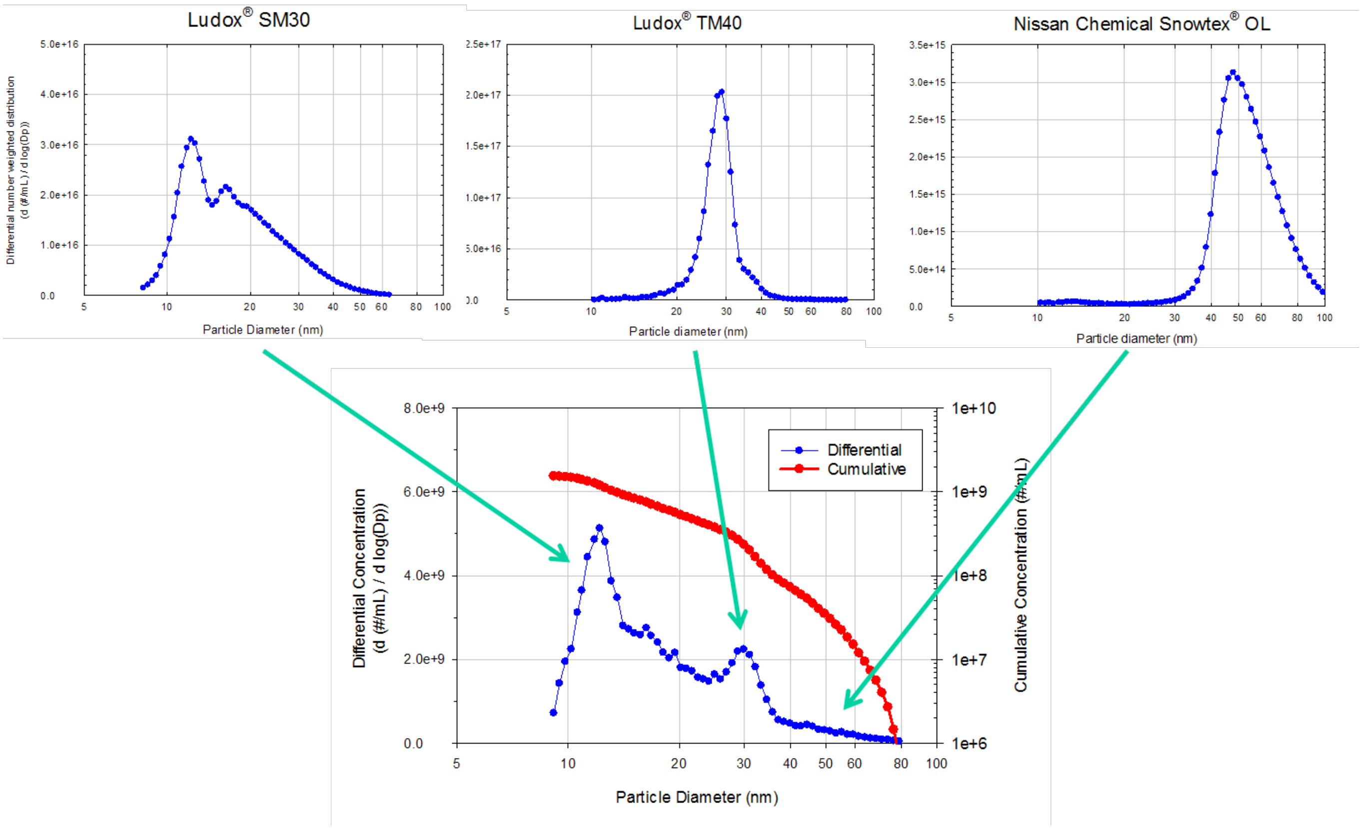


Figure 3: Size distributions of individual silica particles, and all three combined, using an area-weighted distribution

Source: Author, 2017

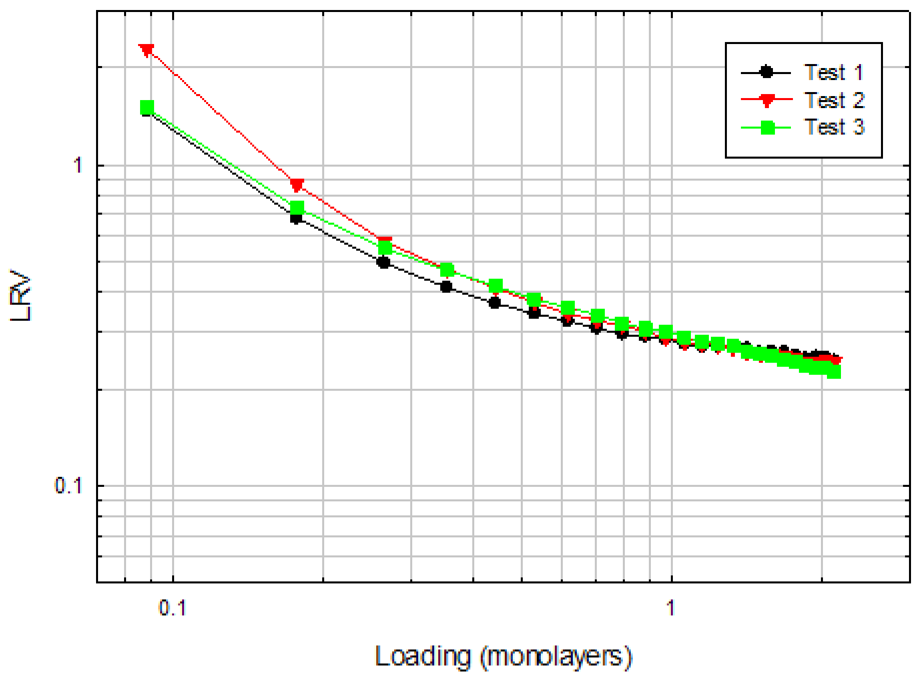


Figure 4: Repeatability of 30 nm filter retention with an area weighted challenge

Source: Author, 2017

Figure 5 compares filter particle retention for the four different weightings. The average retention by the multiple filters tested with each size-weighting is shown. Weighting had a substantial effect on retention, with retention decreasing as the weighting factor increased from number to diameter to area to volume. Retention with a number-weighted challenge was approximately 90% (LRV=1.0), while with a volume-weighted challenge it was about 20% (LRV=0.1) at a loading of one monolayer.

Since the particle size distribution in the challenge can have a significant effect on retention it seems logical that the challenge size distribution should mimic "real-world" size distributions. The ITRS roadmap (now IRDS), for many years, has published that a typical particle size distribution (number concentration as a function of particle diameter) found in UPW has a log-log slope of -2 to -4. The area-weighted and volume-weighted size distributions fall within this range. Therefore, one of these weightings would be a preferred filter challenge. Since the area-weighted challenge allows for better measurement of retention of the larger particles in the distribution compared to the volume-weighted distribution (because there are higher concentrations of larger particles present in the challenge) the area-weighted distribution was chosen for further testing.

FILTER TESTING USING ENHANCED SEMI C79 TESTING

Testing, using the enhanced SEMI C79, was undertaken to compare the retention of 10" microporous membrane cartridges containing 3 types of filter media with retention ratings between 20 nm and 100 nm. The enhancements being lower challenge concentration and the use of an area-weighted poly-dispersed particle challenge. The test parameters were:

Particle type: Area-weighted mixture of Ludox® SM30, Ludox® HS40 and Snowtex®-OL
Particle concentration: 1.5E9/mL > 10 nm
Particle size distribution: Shown in **Figure 3**
Face Velocity: 0.8 cm/min
Loading: 1.25 monolayers standard; up to 10 monolayers in extended tests

With these test conditions LRVs up to two (99% retention) can be measured for particles ranging in size from 10 to 70 nm using a 95% confidence limit based on the background concentration for the largest particle measured.

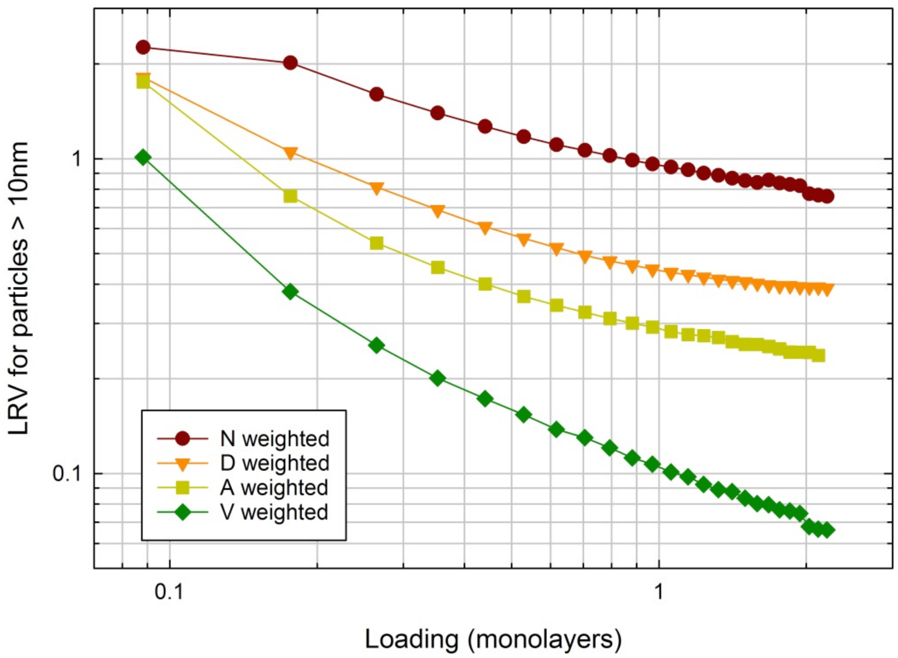


Figure 5: The effect of particle size distribution weighting on retention of silica particles by a 30 nm Type A filter (1.5E9 particles/mL > 10 nm; 0.8 cm/min)
Source: Author, 2017

The three types of filter media tested were:

- Polyarylsulfone (PAS)
- Surface modified polytetrafluoroethylene (PTFE)
- Charge modified nylon 6,6

All of the filter media tested were hydrophilic. They were randomly designated Types A, B and C for the following discussion. Two or three filters of each type were tested.

Figure 6 presents retention by filter Type A (30 nm retention rating) as a function of particle size at selected loadings. The average retention by three filters tested is shown. The results show that retention was non-monotonic with respect to particle size and retention decreased with increased particle loading.

Figure 7 shows the variation in retention by the filter Type A (30 nm retention rating) when loaded to 0.5 monolayers. The error bars shown represent ± 1 standard deviation and indicate that the three filters tested had similar retentions. Similar repeatability was seen in all tests.

Prior to performing this testing, it was thought that filters of this type captured silica particles mainly by sieving[7]. Sieving theory predicts that capture increases with increasing particle size and decreases with loading[7-9]. The observed decrease in retention with loading is consistent with sieving theory. However, the observation of intermediate-sized particles that penetrate the filter more readily than both smaller and larger particles, a most penetrating particle size (MPPS), is not. Hence, it can be concluded that capture mechanisms other than sieving are active.

Observation of a MPPS is common in aerosol filtration where particle capture can be described using a combination of interception and diffusion[7,10-12]. Particle capture by interception is low for small particles and increases with increasing particle size. Particle capture by diffusion is effective for small particles by decreases as particle size increases. Hence, the combination of these two capture mechanisms results in a MPPS.

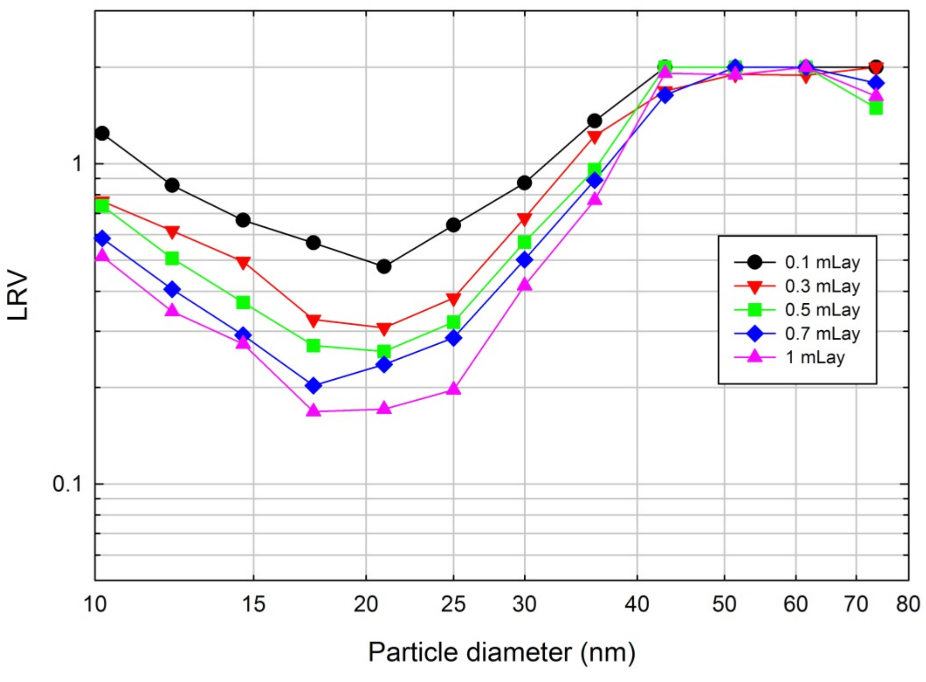


Figure 6: Retention of area-weighted silica particles by a 30 nm Type A filter (1.5E9 particles/mL > 10 nm; 0.8 cm/min)
Source: Author, 2017

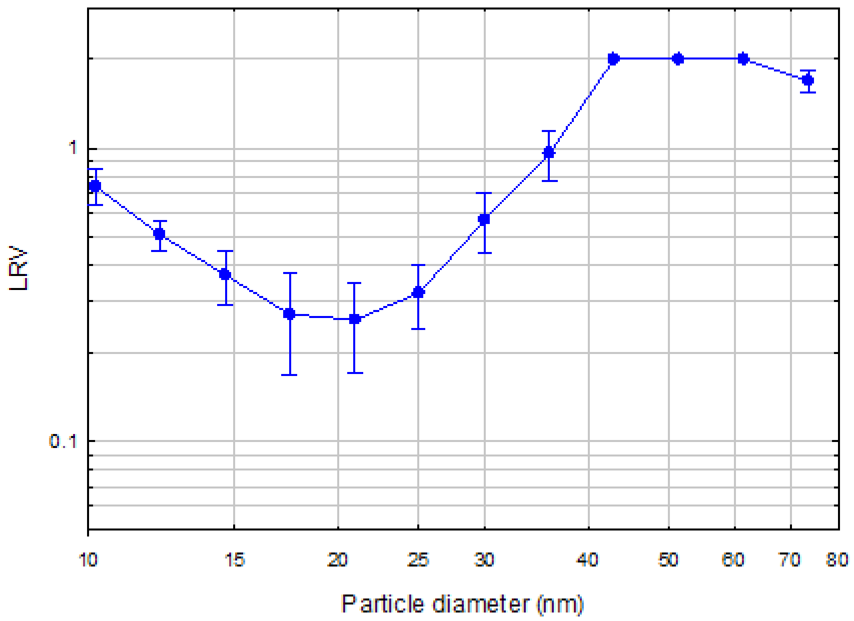


Figure 7: Repeatability of 30 nm Type A filter retention at 0.5 monolayers of loading with the area-weighted challenge
Source: Author, 2017

It has been shown that when interception and diffusion are active with membrane filters having a liquid retention rating of 200 nm or smaller, aerosol LRV's greater than nine are typical[7]. While it appears that these mechanisms may be active in some of the filters tested, the influence on retention appears to be much lower in UPW, when compared to aerosol filtration.

Retention of Type A filters with four different retention ratings (20 nm, 30 nm, 50 nm, and 100 nm) is shown in **Figure 8**. Several observations were made:

- Retention decreased with loading for all four filter ratings.
- The smaller the retention rating, the more retentive the filter.
- A most penetrating particles size was observed for all four filter ratings.
- The most penetrating particle size decreased as the retention rating of the filter decreased.
- Loading had little influence on the size of the most penetrating particle size.

The most penetrating particle size varied from about 15 nm in the case of the 20 nm rated filter to about 30 nm in the case of the 100 nm filter. Retention at the most penetrating particle size and a loading of 0.1 monolayers varied from 95% (20 nm rating) to 20% (100 nm rating).

Figure 9 presents particle retention for a 30 nm rated Type B filter and a 40 nm rated Type C filter. Retention as a function of particle size at different loadings is shown. Retention by the filter Type B increased with particle size as would be expected if sieving is the dominant capture mechanism. Retention by filter Type C indicated the presence of a most penetrating particle size similar to that of the Type A filters.

The filter retention examples shown in Figures 8 and 9 indicate that sometimes filter retention increases with increasing particle size. In other cases, is does not, and a most penetrating particle size exists. If a most penetrating particle size exists, filter retention measured with a single sized particle can be misleading. For example, when the 50 nm filter shown in **Figure 8** is loaded to 0.5 monolayers it has an LRV of 0.5 (70% retention) for 10 nm particles, but only 0.07 (15% retention) for 20 nm particles. It could be mistakenly assumed that if a filter retains 70% of 10 nm particles it would retain >90% of 20 nm particles; not 15% as was measured.

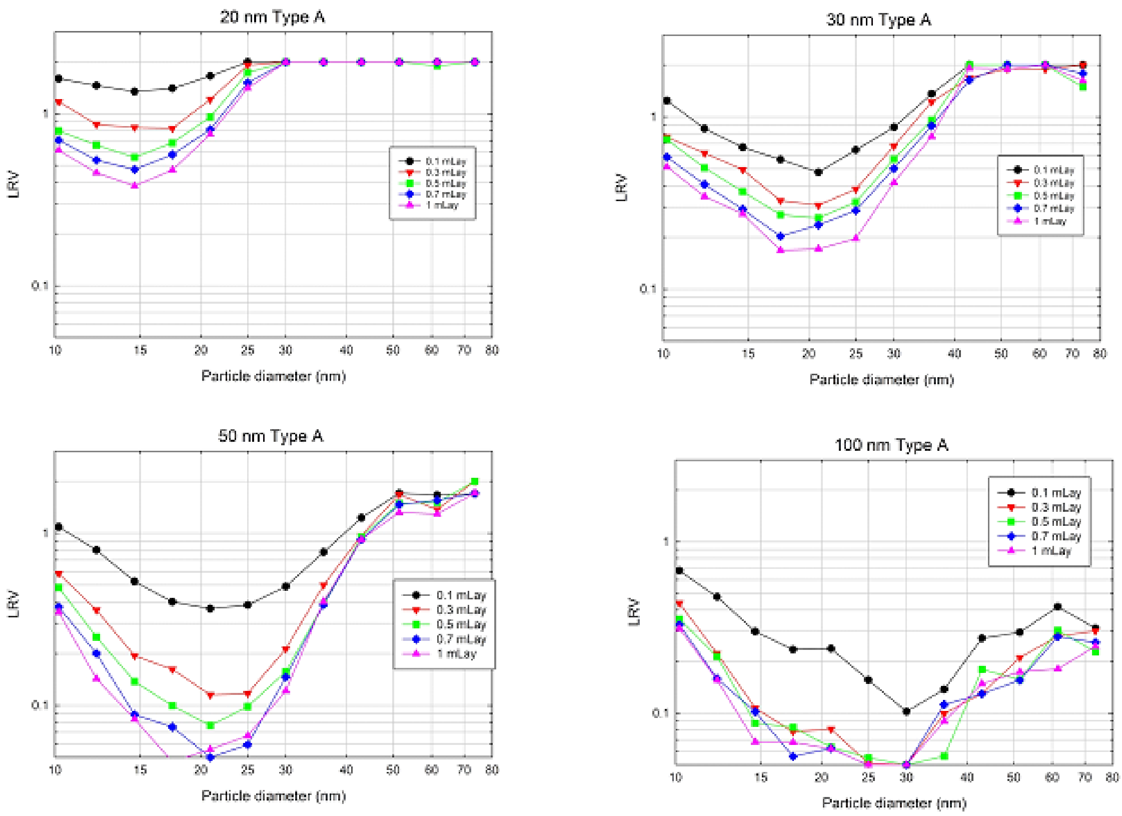


Figure 8: The influence of retention rating on capture of area-weighted silica particles by Type A filters (1.5E9 particles/mL > 10 nm; 0.8 cm/min)
Source: Author, 2017

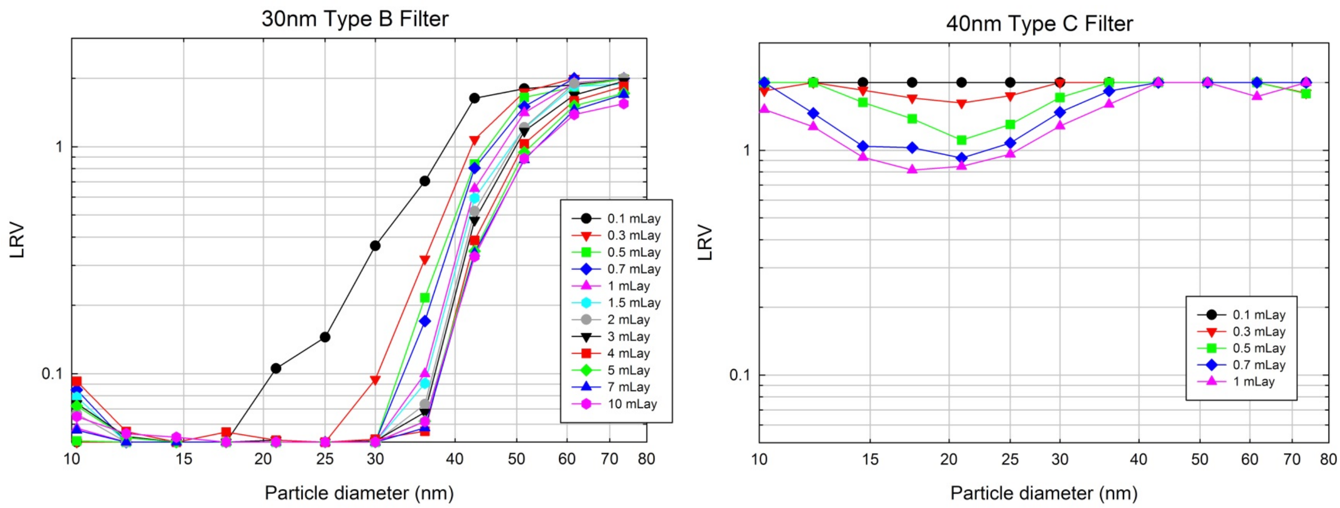


Figure 9: Retention of area-weighted silica particles by 30 nm Type B and 40 nm Type C filters (1.5E9 particles/mL >10 nm; 0.8 cm/min)
Source: Author, 2017

SUMMARY AND RECOMMENDATIONS

It has been shown that:

- Filter retention can be influenced by particle concentration and may lead to higher retentions at lower concentrations.
- The size distribution of particles in UPW can have a significant effect on retention with the presence of larger particles resulting in decreased retention of smaller particles.
- Retention by some filters shows a most penetrating particle size with greater retention of both larger and smaller particles.
- Evaluating a filter's ability to remove particles using a single particle size can be misleading.

Therefore, it is recommended that considerations be made to modify SEMI C79 testing to:

- Use an area-weighted silica challenge which has a size distribution similar to that typically seen in UPW rather than mono-dispersed particles.
- Use the lowest challenge concentration possible (i.e. ≤ 1.5E9/mL) to more closely approximate particle concentrations in UPW and yet still be able to measure particle retention up to an LRV of 2.

Additional areas for future research:

- A direct, side-by-side comparison of the three SEMI filter retention methods would be useful for better understanding of how the methods will affect filter retention results and provide end users the opportunity to compare data from different methods and sources.
- Additional research is needed to understand what retention mechanism(s) might be operative with sub-15 nm particles. Understanding these mechanisms could assist membrane and filter manufacturers with improving capture efficiency of these particles.
- Continued research toward understanding the nature and composition of sub-15 nm particle contamination is needed to ensure that the retention data generated by SEMI C79, C82 and C89 is relevant in real-world applications.

REFERENCES

1. Grant, D. & Van Schooneveld, G (2011). *Measuring sub-50nm particle retention of UPW filters* presented at the Levitronix 2011 CMP and Ultrapure Micro Conference, 2011, Dallas, Texas, USA.
2. Liquid Nanoparticle Sizer http://www.kanomaxfmt.com/liquid-nanoparticle-sizer.html (Accessed September 2017)
3. Van Schooneveld, G.; Litchy, M.; Grant, D. (2011). *A novel method of measuring sizes and concentrations of 5-500 nm particles in colloidal suspensions, TechConnect World 2011*, Boston, MA, USA.
4. Van Schooneveld, G.; Litchy, M.; Grant, D. (2010). *A new method for determining the size distribution of particles in CMP slurries*, pp. 348-351, Proceedings of the 2010 International Conference on Planarization/CMP Technology, Phoenix, AZ, USA.
5. Jeon, S.; Oberreit, D.; Van Schooneveld, G.; Hogan, C. (2016). Nanomaterial size distribution analysis via liquid nebulization coupled with ion mobility spectrometry (LN-IMS), *Analyst*, Vol. 141, No. 4, pp. 1363-1375.
6. Grant, D.; Van Schooneveld, G.; Beuscher, U. (2013). *The effect of particle concentration and face velocity on the removal of sub 100 nm particles from ultrapure water*, Ultrapure Water Micro 2013, Portland, OR, USA.
7. Grant, D.; Liu, B.; Fisher, W.; Bowling, R. (1989). Particle Capture Mechanisms in Gases and Liquids: An Analysis of Operative Mechanisms, *Journal of Environmental Sciences*, Vol. 42, No. 4, pp. 43-51.
8. Grant, D.; Liu, B. (1991). Sieving Capture of particles by Microporous Membrane Filtration Media, Part. Syst. Char., Vol. 8, pp. 142-150.
9. Grant, D.; Zahka, J. (1990). Sieving Capture of Particles by Microporous Membrane Filters from Clean Liquids," Swiss Contamination Control, Vol. 3, No. 4a, pp. 160-164.
10. Rubow, K. (1991). *Submicron Aerosol Filtration Characteristics of Membrane Filters*, PhD thesis, University of Minnesota, Minneapolis, MN, USA.
11. Liu, B.; Robow, K.; Pui, D. (1985). Performance of HEPA and ULPA Filters, *Proceedings of the Annual meeting of the Institute of Environmental Sciences*, pp. 25-28.
12. Rubow, K.; Liu B.; Grant, D. (1988). Characteristics of Ultra-High Efficiency Membrane Filters, Journal of Environmental Sciences, Vol. 31, No. 3, pp. 26-30.