
Understanding Nanoparticle Contamination in Ultrapure Water Systems

Abstract

Monitoring ultrapure water (UPW) systems using the legacy standard of 50 nm sensitivity has been effective and efficient for the last ten years. Assessing particle counts at 50 nm is commonly used for benchmarking UPW cleanliness. UPW is used in critical applications, primarily for washing and removing particulates from the surfaces of products and as dilution for chemicals used for different processes in many electronics industries. The cleanliness of the UPW is critical to achieving optimal particulate removal. The enhancement of ultra-filter performance down to sub-nano filtration capability routinely produce zero or very close to zero particle counts at 50 nm for most of the advanced UPW in use today. In recent years, the emphasis on particle reduction at smaller sizes (less than 50 nm) evolved due to technology advancement with tightening of semiconductor product quality requirements and shrinking design dimensions to pack more transistors into a single chip. Monitoring UPW at 50 nm can no longer provide sufficient differentiation in particle performance between the best and good water systems. Semiconductor industry experts are currently investigating if the performance of sub-nano filtration can be accurately determined using a 50 nm particle counter, or if reducing the sensitivity of the measurement will provide better evidence of the filtration's capability to remove nanoparticles.

Introduction

Semiconductor industry leaders have emphasized the importance of understanding nanoparticle contamination in ultrapure water (UPW) production and distribution. They have explored the advantage of monitoring particle baseline at 20 nm over the existing 50 nm particle performance of the state-of-art UPW system. Many interesting investigations on this space pivot around the motivations to study the value of monitoring particle size down to 20 nm at the UPW system. The objective of looking into this aspect opens various opportunities for better enhancement in particle monitoring and practical use. This application note illustrates various case studies of monitoring methods used in advanced UPW systems. It investigates whether detecting down to 20 nm could add value to the legacy monitoring standard at 50 nm.

Typical Liquid Particle Size Distributions

The particle size distribution in filtered liquids can be estimated using a theoretical calculation based on a power-law distribution. The number of particles is inversely proportional to the particle size (x^{-y} , formatted in **Figure 1** below as x-y), where y is often close to 3. For a theoretical calculation using power-law distribution:

- Assume the particle concentration of a UPW system at 100 nm is 0.1 counts/ml.
- Using a power-law distribution, we can extrapolate the value of y for various exponents to predict the particle counts at 20 nm.

- Calculated particle size distribution as shown in **Figure 1**.

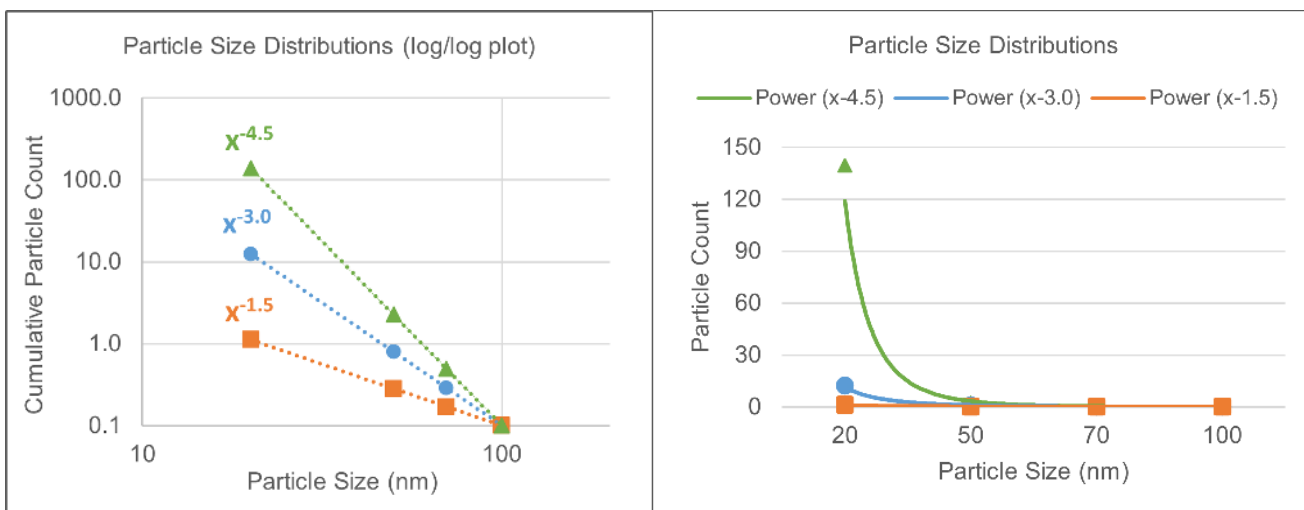


FIGURE 1 PARTICLE SIZE DISTRIBUTIONS

TABLE 1 Particle size (nm) distribution using power law (extrapolated at 100 nm using 0.1 counts/ml)				
EXPONENT	20	50	70	100
$X^{-4.5}$	139.7	2.3	0.5	0.1
$X^{-3.0}$	12.5	0.8	0.3	0.1
$X^{-1.5}$	1.1	0.3	0.2	0.1

Table 1 illustrates the potential misunderstanding that can occur regarding UPW particle performance when comparing two different UPW systems using a 50 nm particle counter. The difference between UPW systems particle performance becomes pronounced when comparing them at 20 nm. Understanding the Particle Size Distribution (PSD) allows better anticipation of the performance of UPW systems at 20 nm and clues for quality improvement.

In general, for 20 nm UPW monitoring, exponent values of 'y' span between 1.5 to 4.5 [1]. This exponent value of y depends on the overall control of UPW systems, e.g., filter efficiency relative to particle counter sensitivity.

- Filter rated << 20 nm, y often approximates to 3 or smaller; filter rated >> 20nm, y is greater than 3.

Sampling Interval with Statistically Significant Particle Data

One of the most important concepts to understand when using particle counters to monitor UPW systems is how to determine the shortest sample interval for an instrument to provide statistically significant particle data to align with best practices across the industry. Essentially, two pieces of information are needed before deriving a suitable sampling interval:

- The first piece of information is the actual sampled flow rate of the instrument. Using UDI-20 as an example, the total flowrate through the instrument is 75 ml/min. As the UDI-20 is a monitor type instrument (as opposed to volumetric), the actual sampled flow rate is 0.45 ml/min. Therefore, the actual volume of ultrapure water sampled in a one minute sample would be 0.45 ml.
- The second piece of information is the cleanliness of the ultrapure water sample. Typical high purity UPW

system contains between 1-5 particles/ml > 20 nm. As illustrated in **Figure 2**, such a clean ultrapure water supply would show fewer than three particles in one minute.

In most cases, when working with extremely clean UPW systems, a one minute sample interval will not represent enough sample to obtain statistically significant data. This results in highly variable data that is difficult to analyze and make decisions with.

Sample Cleanliness* (particles/ml)	TABLE 2 UDI-20 counts per Interval				
	1 min	10 min	30 min	60 min	90 min
0.5	0.23	2.3	6.8	13.5	20.3
1	0.45	4.5	13.5	27	40.5
5	2.25	22.5	67.5	135	202.5
25	11.25	112.5	337.5	675	1012.5

*Particle level (the number of particles per milliliter in the 20 nm size channel)

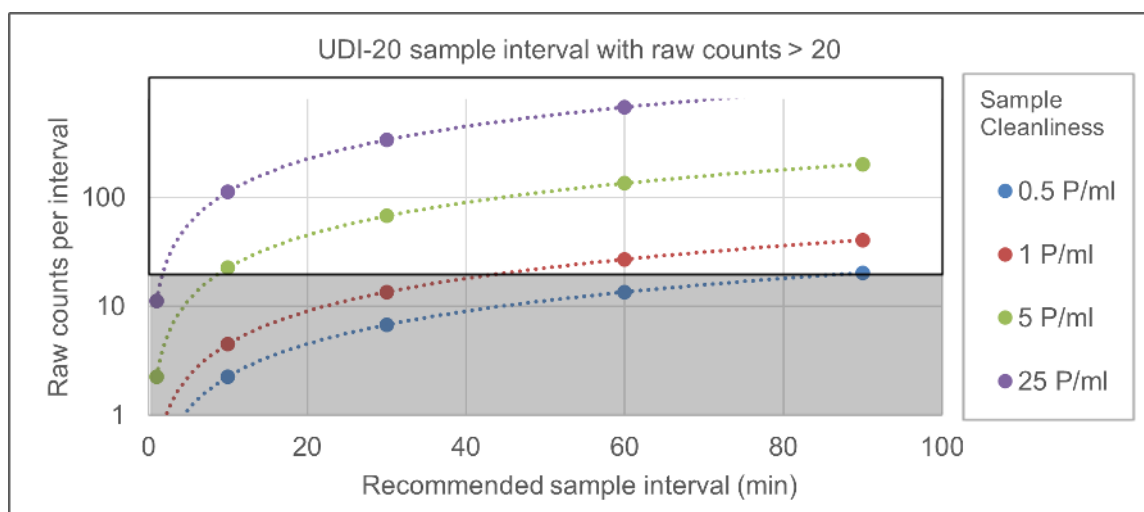


FIGURE 2 UDI-20 SAMPLE INTERVAL VERSUS RAW COUNTS

A general rule-of-thumb for a statistically valid number of particles per sample is when the raw counts are greater than 20. This represents the point where a normal distribution is approximately the same as a Poisson distribution [2]. For a very clean UPW supply with fewer than 5 particles/ml > 20 nm, we would need to sample for at least 10 minutes to obtain sufficient counts to claim some statistical validity. For less clean UPW (example, > 25 particles/ml > 20nm), we would need to sample for at least two minutes to get meaningful data.

Ultrapure Water System Applications

Case Study A: Particle Levels at O₃ (ozone) Water Generator

This case study used a single UDI-20 to measure 20 nm particle levels at three different O₃ water generators at different times. The objective was to use particle data with a smaller channel (20 nm) that helps optimize system performance and troubleshooting.

- Sample monitoring was done on both O₃ water Generators 1 and 2 with low particle counts at 50 nm. As illustrated in **Figure 3**, the 20 nm particle level of Generator 2 showed relatively lower counts than Generator 1. However, the differences between both generators were not obvious when compared to the data of the 50 nm channel. This indicates that Generator 1 may have some contamination sources needing further investigation. Computing the particle size distributions, Generator 2 was observed with a relatively lower exponent value (2.276) as compared to Generator 1 with the exponent value of (2.792).
- A troubleshooting case was conducted on O₃ water Generator 3 with high particle counts at the 50 nm channel. As shown in **Figure 4**, obvious particle spikes at the 20 nm channel are found without noticeable spikes at the 50 nm channel. The findings indicate particle detection of higher sensitivity (50 nm reduced to 20 nm) is required to identify the abnormalities in the system.

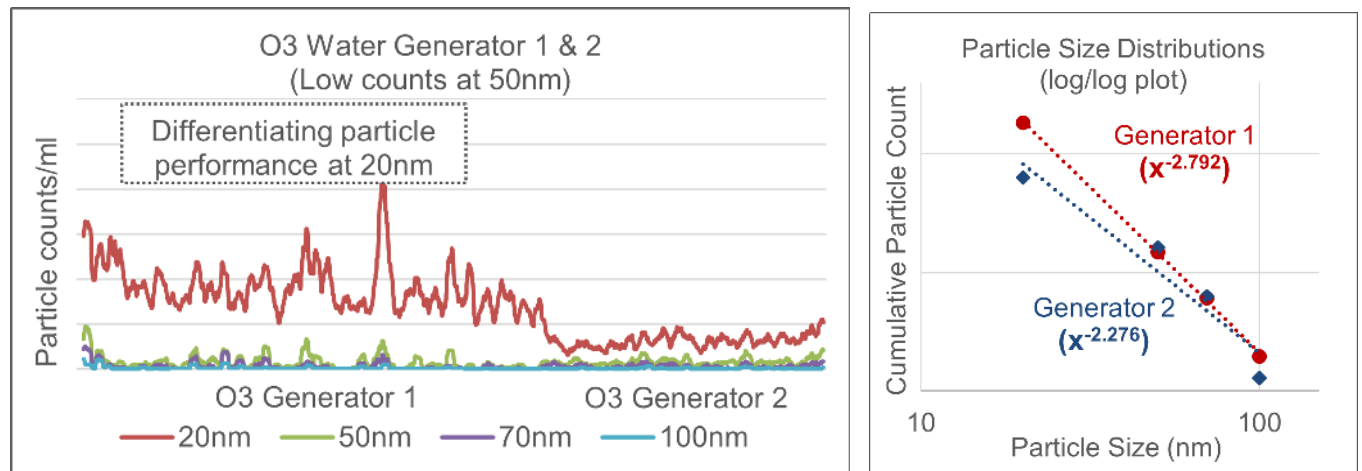


FIGURE 3 O3 WATER GENERATORS PARTICLE LEVELS AT DIFFERENT CHANNELS

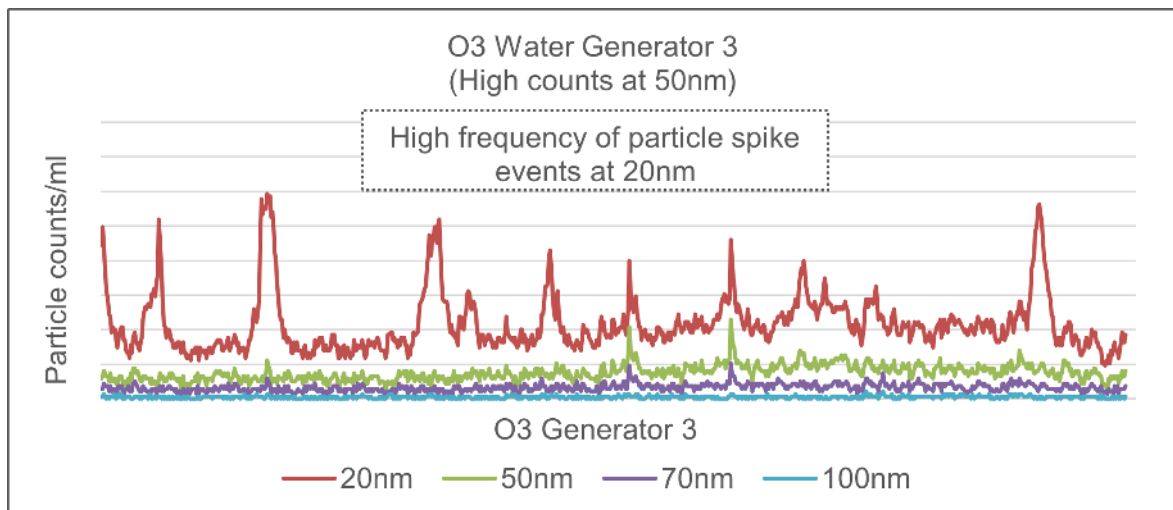


FIGURE 4 MONITOR O3 WATER GENERATOR WITH PARTICLE SPIKES

Case Study B: Particle Levels at Mixed Bed Polisher

In a foundry fab, the particle issues found on the product wafers post-cleaning have led to the investigation of the UPW system. After the partitions to identify the possible causes, the particle source was found to correlate with a change in quality to the UPW system at the mixed bed polishers before ultra-filtration and supply of water to the Point-of-Use for fab processes. Monitoring using UDI-50 revealed some particle level differences between the mixed bed polishers at the 50 nm channel. An interesting question to consider is if a 20 nm channel would tell us more about the problematic source.

- As shown in **Figure 5**, two polishers need to be mixed-run due to fab constraints. The different configurations impact the particle level at the Point-of-Use per previous experiences with the UDI-50.
- An investigation was carried out using the UDI-20 to understand the particle levels of the different configurations (Config 1: mixed bed 1 & 2, Config 2: only mixed bed 1, Config 3: only mixed bed 2).



FIGURE 5 MONITOR SCHEME OF MIXED BED POLISHERS & PARTICLE COUNTER

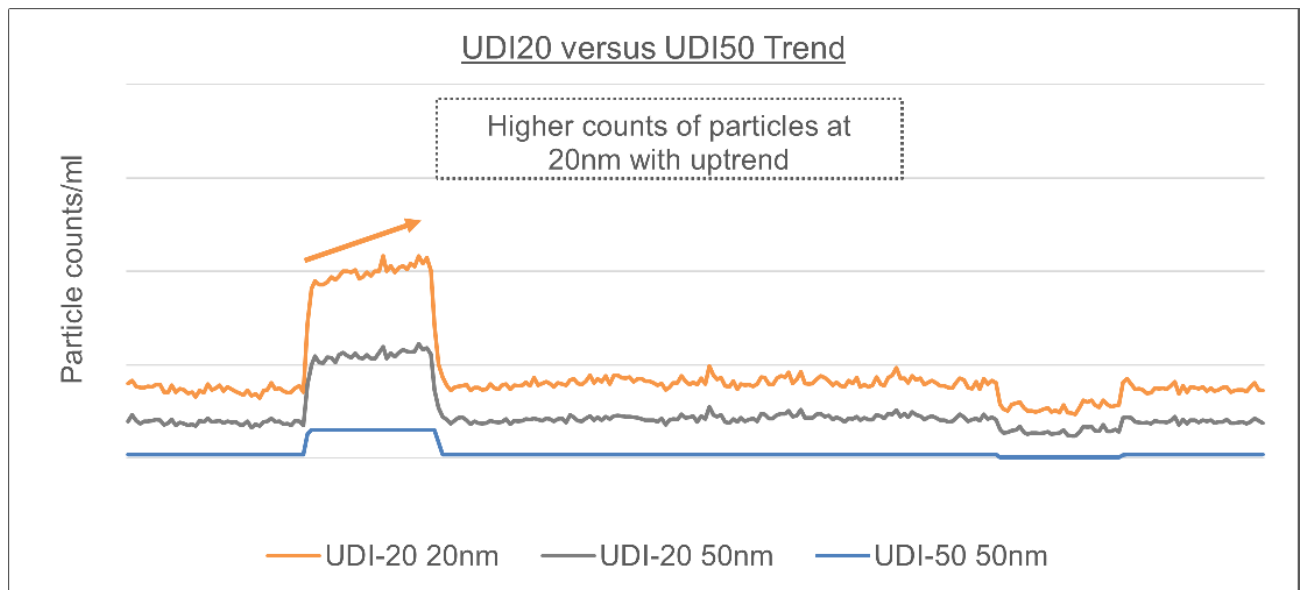


FIGURE 6 PARTICLE LEVELS OF DIFFERENT MIXED BED CONFIGURATIONS (UDI-20 VS. UDI-50)

From the test results illustrated in **Figure 6**, the data from UDI-20 could easily differentiate the particle levels between three mixed bed polisher configurations. Interestingly, with higher sensitivity at 20 nm, a particle uptrend at mixed bed polisher 1 was observed that UDI-50 could not identify. Seeing the uptrend at 20 nm during real-time monitoring allows better control to prevent generating too many nanoparticles in the downstream processes.

Case Study C: Particle Levels at Final Filtration for Filter Comparisons

The UDI-20 was deployed to measure final ultra-filtration and study the performance of two different types of filters. Each new filter type was installed at a different time to characterize the particle levels at 20 nm as illustrated in Figure 7.

- As illustrated in Figure 8, at 20 nm particle counts performance, Filter B was at least twice the particle level compared to Filter A. In addition, Filter B took more than three days to reach a steady-state particle level at 20 nm, whereas Filter A required half that duration.
- When comparing filters at sub-10 nm pore sizes, monitoring the particle size down to the 20 nm channel becomes more critical, and provides a better resolution to differentiate particle levels.

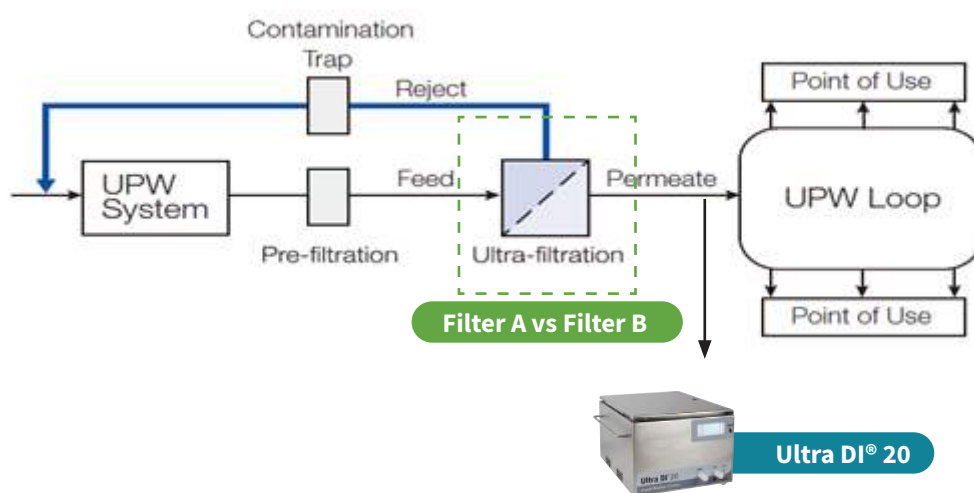


FIGURE 7 LOCATION OF FILTERS A AND B IN SYSTEM

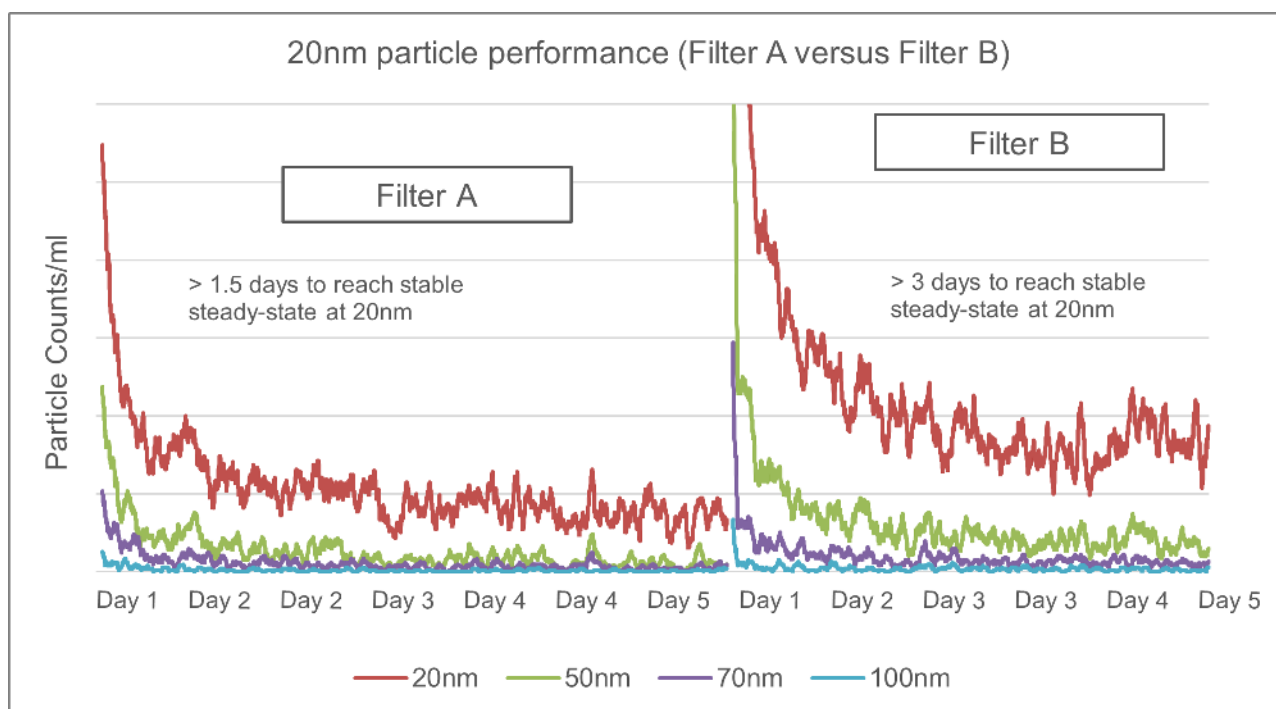


FIGURE 8 20 NM PARTICLE LEVELS OF FILTER A VERSUS FILTER B

Case Study D: Particle Level at Final Filtration for Sensitivity Comparisons (UDI-20 vs. UDI-50)

This study is similar to Case Study C. Both UDI-50 and UDI-20 were used to measure the final filtration (sub-10 nm pore size) to understand the differences of particle levels in an extremely clean UPW system. As illustrated in **Figure 10**, the 20 nm spike event is not visible at the 50 nm channel because most of the particles greater than 50 nm are removed. Excursions of particle size < 50 nm may escape the detection of UDI-50. Achieving reasonable control of UPW systems requires a higher sensitivity of the UDI-20 to enhance detection.

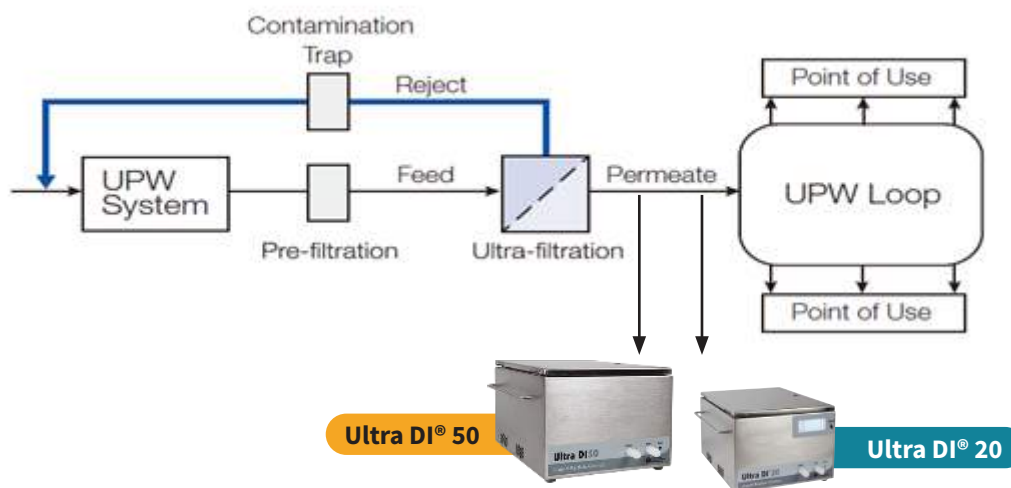


FIGURE 9 LOCATION OF FILTERS IN UPW SYSTEM

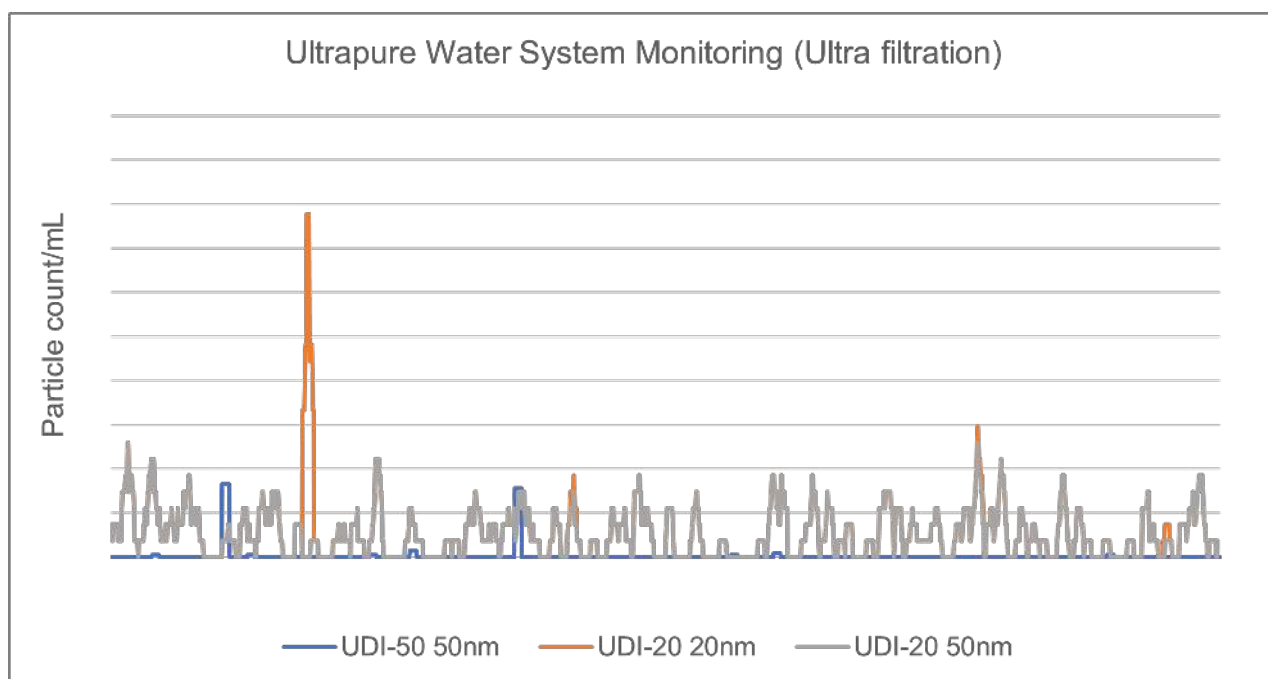


FIGURE 10 MONITORING (UDI-20 VS. UDI-50) AT UPW SYSTEM (ULTRA FILTRATION)

Case Study E: Particle Monitor at Point-of-Use

The UDI-20 was placed at a specific location of the UPW system (aka Point-of-Use) to measure particles for 5 days.

- As shown in **Figure 11**, the particle trend was stable during the first 3 days. On Day 4 and 5, particle events were detected only at 20 nm and with a very stable trend at other channels.
- Further analysis was made to overlay the 5 days' data. Coincidentally, it was observed that 20 nm particle events occurred at a specific time-frame, illustrated in **Figure 12**. These are actionable data, providing clues for further investigations to understand any activities at that specific time frame when the spikes in particles occurred.

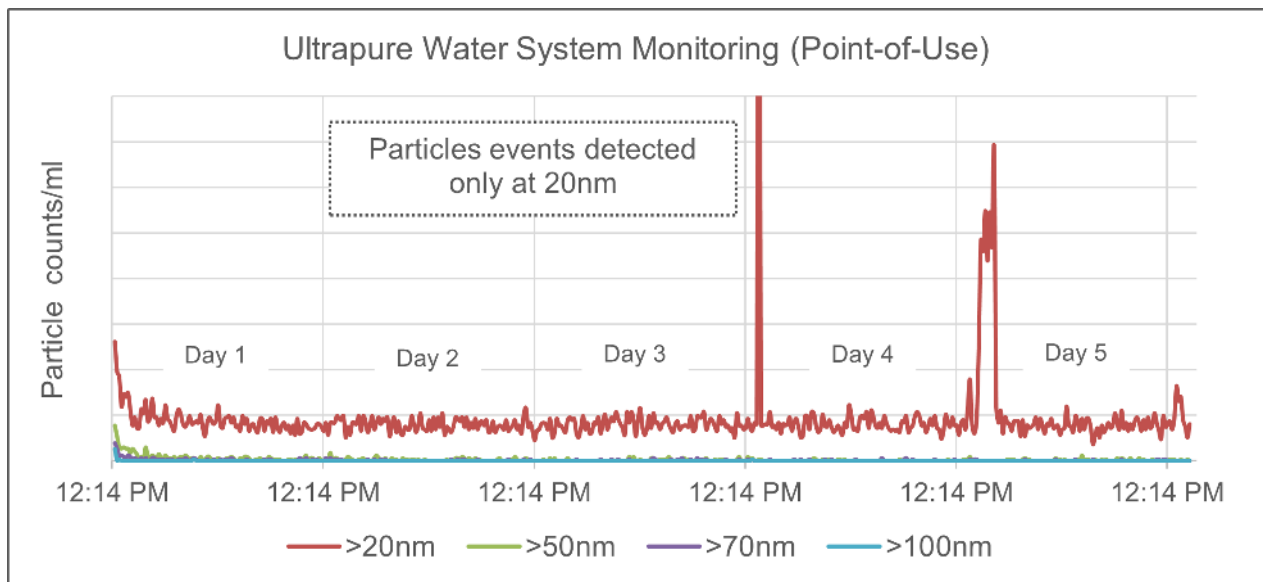


FIGURE 11 MONITORING 20NM PARTICLE PERFORMANCE AT ULTRAPURE WATER SYSTEM (POINT-OF-USE)

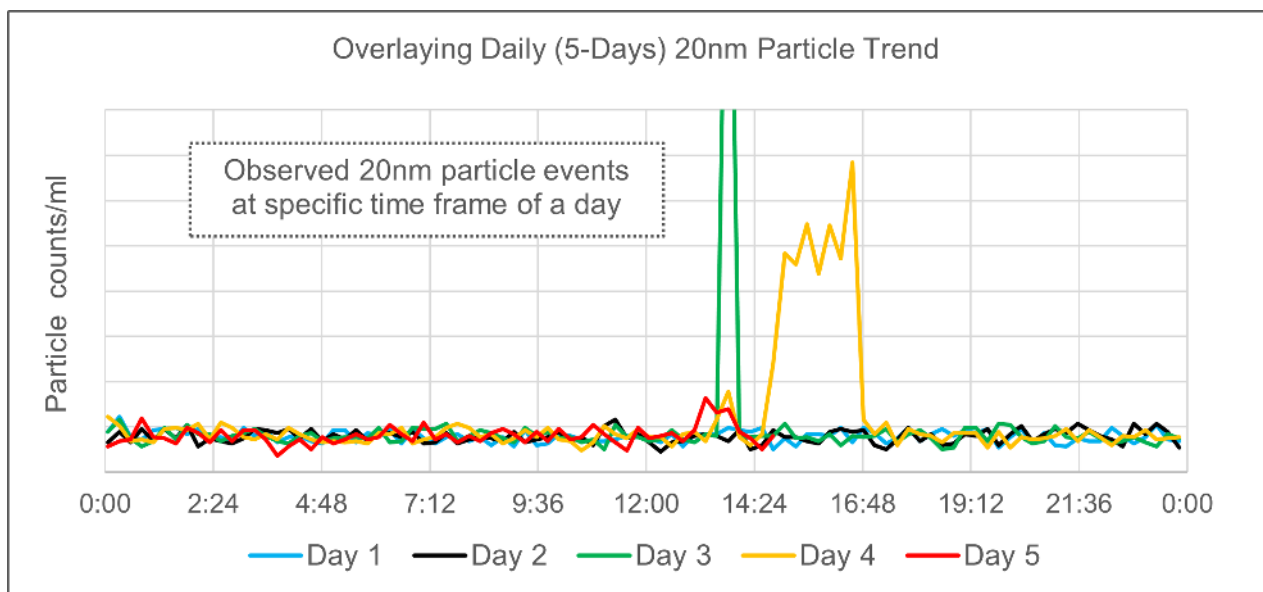


FIGURE 12 OVERLAYING DAILY (5-DAYS) PARTICLE TREND

Cartridge Filter Age Study F:

The particle baseline at each filter housing was measured using a single UDI-20 and UDI-50. The study was done blindly without knowing the filter age. Particles were also measured at the common feed in the system.

- As illustrated in **Figure 14**, re-ordering the particle dataset by filter age indicates a solid correlation to filter life. Multiple cartridge filters were studied at the 4 month and 2 month age, with a high level of consistency.
- The cartridge filters aged one to six months were observed with a twelve-fold increase in the 20 nm channel, whereas the 50 nm channel started to increase at the age of six months. The particle level exceeded the 20 nm baseline in one month.

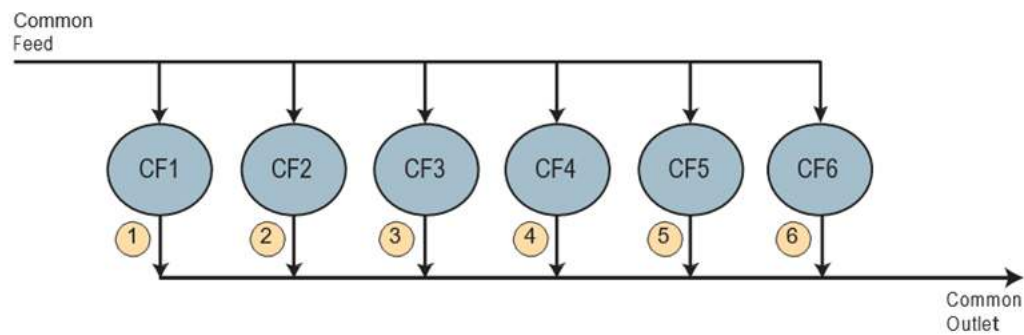


FIGURE 13 SEQUENCE OF CARTRIDGE FILTERS

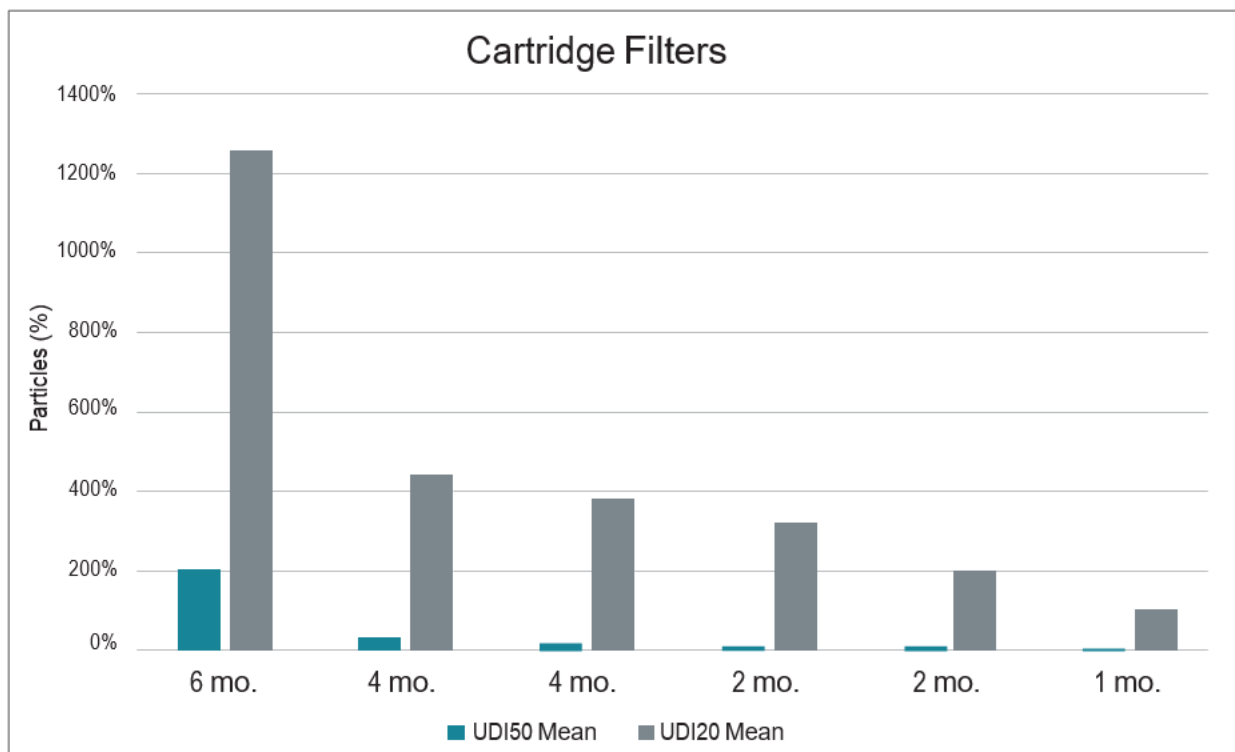


FIGURE 14 CARTRIDGE FILTERS TESTING RESULTS

It is possible to characterize the overall cartridge filtration system efficiency by different bin sizes (20-50 nm; 50-70 nm; 70-100 nm; 100 nm) as illustrated in **Figure 15**. Good filter efficiency (>95%) is found according to UDI-20 results highlighting a lower efficiency of the 20-50 nm bin size (95.63%) compared to other bins (>99%).

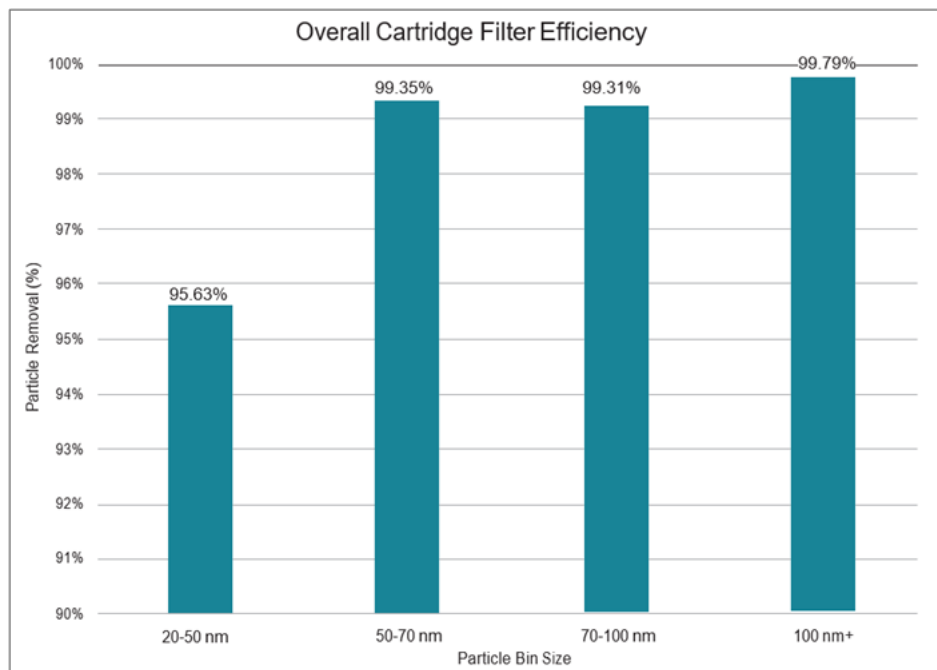


FIGURE 15 OVERALL CARTRIDGE FILTER EFFICIENCY

As the filter ages, filter efficiency degrades sharply with decreasing particle size. The filter efficiency decreases from 94% to just 76% at 20-50 nm between one and six months of use, as illustrated in **Figure 16**. This loss of performance by the six-month housing accounts for the 20-50 nm hit on the overall filtration efficiency, as observed in **Figure 15**.

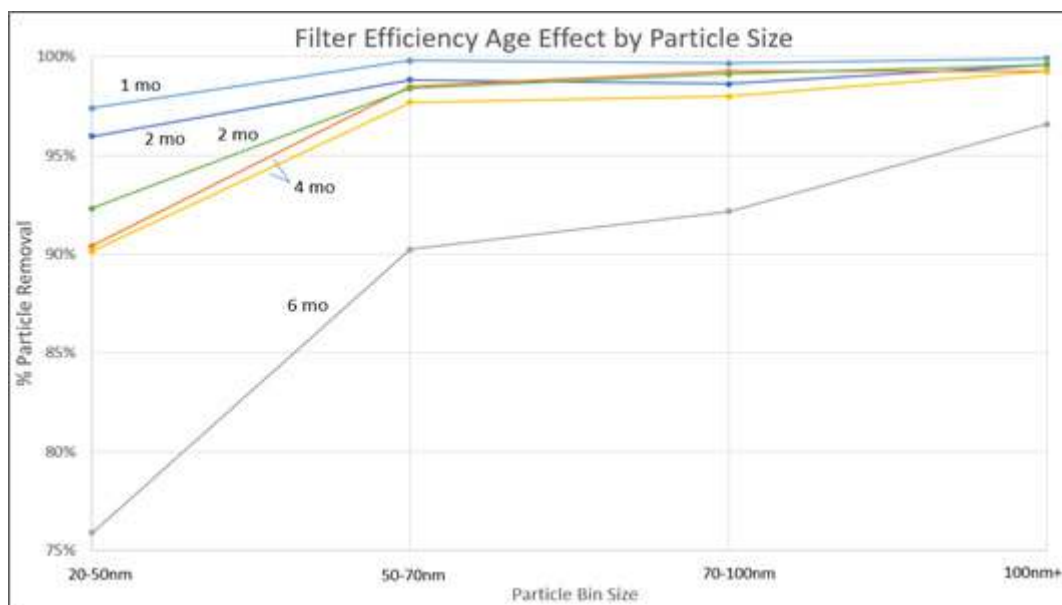


FIGURE 16 FILTER EFFICIENCY AGE EFFECT BY PARTICLE SIZE

Ultra-Filter Age Study G:

The particle baseline was measured blindly using a single UDI-20 at three selected ultra-filter skids representing a full range of filter ages (two years, four years, six years). Re-ordering the baseline results by filter age illustrated a strong correlation to filter life, as shown in **Figure 17**.

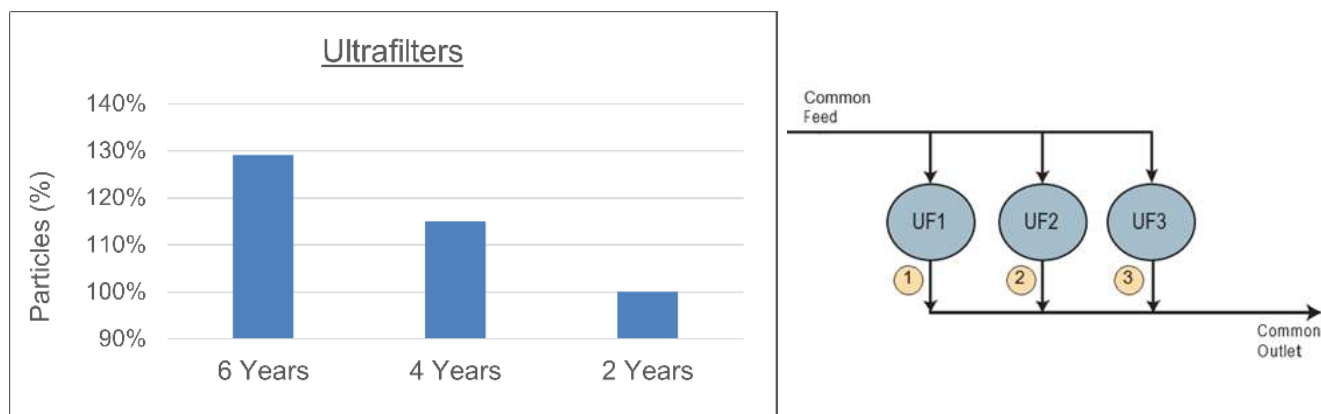


FIGURE 17 ULTRAFILTERS TESTING RESULTS

The above study on Cartridge Filters and Ultra-Filters provides insight into various testing methods to understand particle levels. When monitoring particles at 20 nm, it is easy to detect and track filter performance. The Cartridge Filter performance changes are only visible at 50 nm. After a 1200% increase in 20 nm, contamination was observed following six months of usage.

Summary

In this paper, seven case studies demonstrated the value of monitoring particles at 20 nm versus 50 nm. Due to advances in filtration technology used in UPW systems and the emphasis on driving for lower nanoparticle counts, it is no longer sufficient to keep monitoring at 50 nm. As case studies A through E demonstrate, effective monitoring is essential to ensure proper control, continuous improvement, and troubleshooting in UPW systems. Case studies F & G demonstrate the performance of the polish cartridge, with ultrafilters appearing dependent on their duration of use. This would suggest that the method for filter maintenance could be improved by changing to a quality-based approach versus a time-based approach.

References

1. Knollenberg, R.G., Veal, D.L., *Optical Particle Monitors, Counters, and Spectrometers: Performance Characterization, Comparison and Use*. Proceedings of the 37th Annual Technical meeting of the Institutes of Environmental Sciences, May 1991.
2. Mitchell, J., Bast, B., *Comparing Particle Counter Performance Characteristics for Analyzing High-Purity Water*, Ultrapure Water Journal, February 2000.