UPW technologies
sTPC, nanoSpotLight, NRM, Standards, PDS

by
Gary Anderson
With materials drawn from UPW Conference Proceedings 2017
From Glenn Sundstrom Evoqua
From Daniel Stucky Samsung
And From: Derek Oberreit Ph.D., David Blackford Ph.D, Siqin He Ph.D
Kanomax FMT, Inc.
Gary Van Schooneveld CT Associates, Inc.

The technologies

1) sTPC : particle counting with # > 10nm,15nm and 20nm
2) nanoSpotLight : collects particles from nm to micron for analytical analysis SEM/EDX
3) NRM : does nonVolatile resdiual monitor
4) Standards/PDS : a traceable standard by # and size for calibrating particle counters from 10nm collodial silica

Overcoming Objections
scanning threshold particle counter sTPC

Hurdles that needed to be overcome to have new technology deployed

1) How does the technology work?
2) Why does the sTPC count whereas my OPC does not show anything?
3) How can I use this technology within my fab?
4) Why do I have water in the bottom of the instrument – is there a leak?

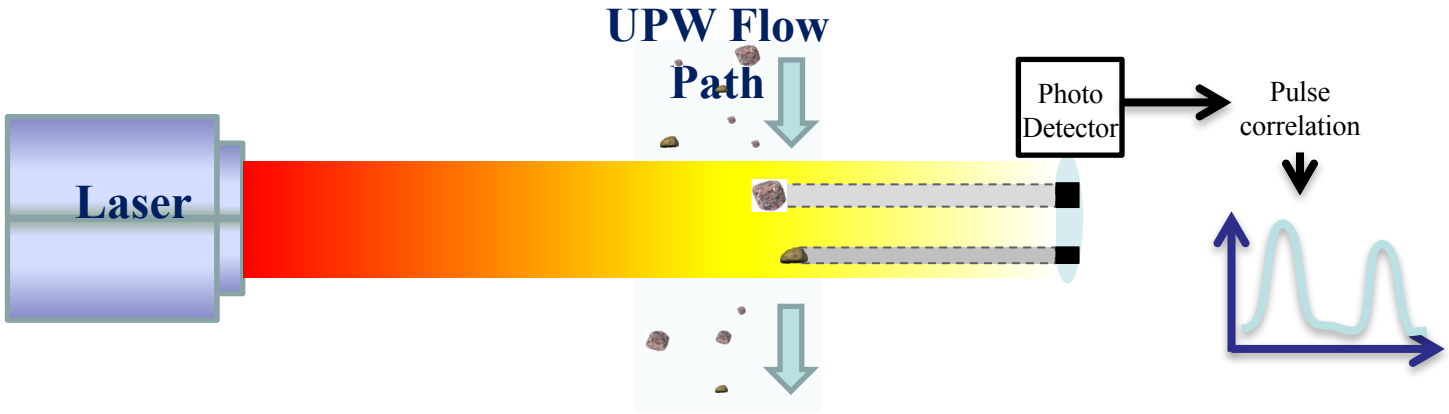
Understanding the technologies (How the technology works)

- OPC optical particle counting
  - Light scattering
- sTPC scanning threshold particle counting
  - Well established aerosol technology extended into the semiconductor applications

Particle Metrology - OPC

- For UPW and Hot UPW supply particle monitoring, the widely accepted technology is liquid Optical Particle Counter (OPC).
- Liquid OPC consists of a calibrated laser emitting light on the sample as it passes through laser path. Particles scatter/reflect light in this path. These events are collected through light sensitive Photo detector. Then, analyzed and correlated to number of particles in sample.
- Liquid OPC has detection challenges for smaller particles and particles with refractive index close to liquid since scattered light is not differentiable from background noise

Simplified Liquid Optical Particle Counter



KANOMAX
The Ultimate Measurements

Particle Measuring Systems founder noted in 1987

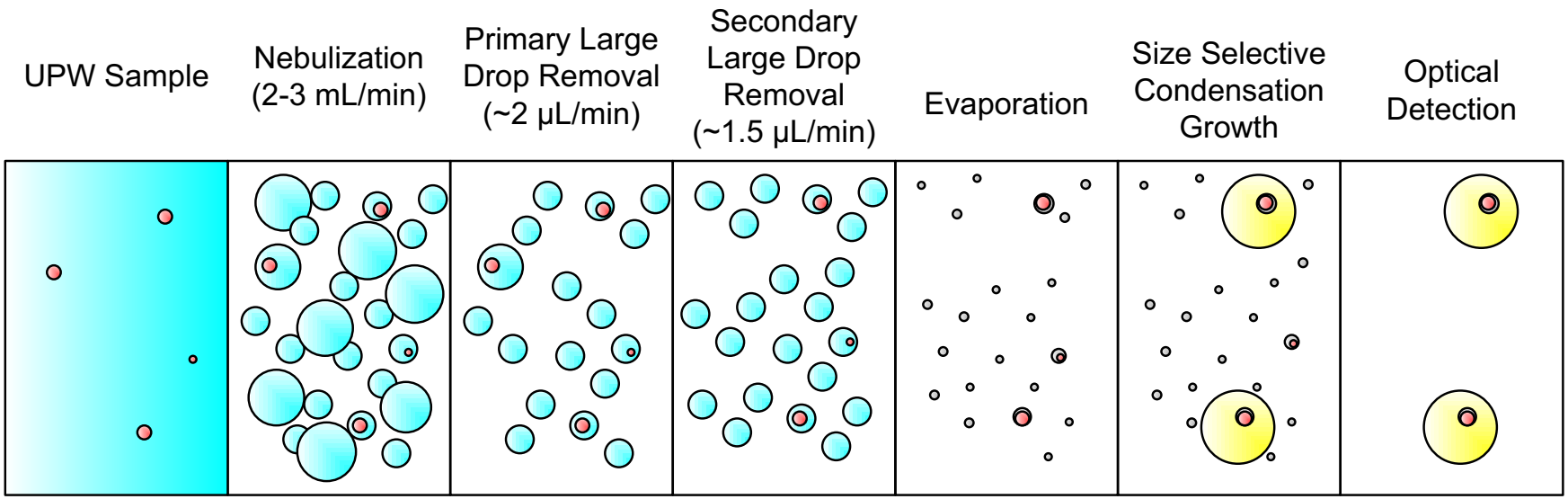
- The Importance of Media Refractive Index in Evaluating Liquid and Surface Microcontamination Measurements
- By: Dr. Robert G. Knollenberg Particle Measuring Systems, Inc. Boulder, Colorado

- Particles scatter by refractive index contrast which is the ratio of particle RI/ media RI (refractive index)
- Water has a RI of 1.33 So particles that have a similar RI do not scatter or scatter much less
- When particles are much smaller than the wave length of the light source, the scattering principle changes from the Mie Regime to the Rayleigh Regime This results in a sixth order effect by particle size and a fourth order effect for wave length. As a practical matter 0.2 micron particle is the transition point from Mie to Rayleigh

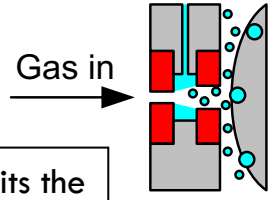
The Measurement of Particle Sizes Below 0.1 Micrometers presented by Knollenberg in 1985 addresses the theoretical limit of the technology

- The NET effect is that OPCs have a theoretical scattering limit AND
- The semiconductor industry needs a new technology to go lower….

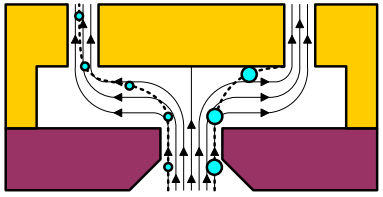
Scanning Threshold Particle Counter



Impactor 1



Impactor 2



Condensation Particle Counter

CPC detects only large liquid borne particles which are larger than a preset threshold diameter

Large Droplet Removal limits the formation of large Precipitated Non-Volatile Residue (PNVR) Particles

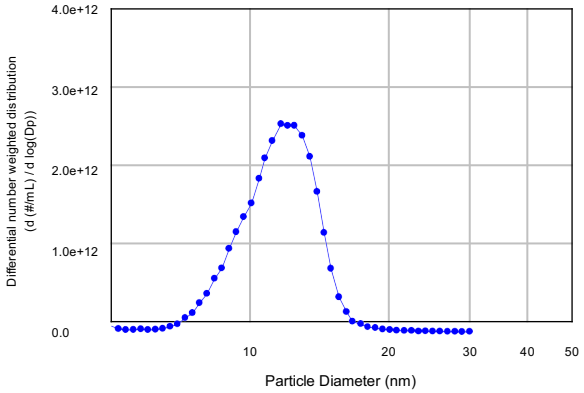
KanomaxFMT introduces particles of known size and number to calibrate

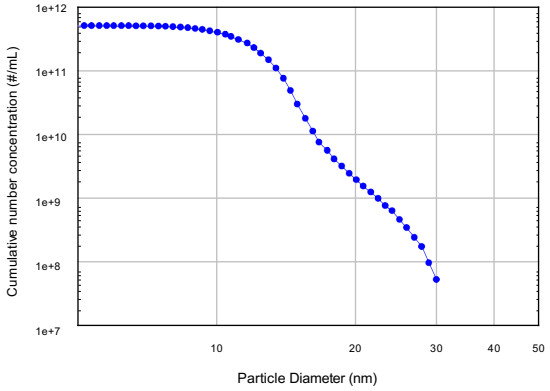
Precision Dilution System Model 9210

KANOMAX
The Ultimate Measurements

10 nm colloidal silica

Kanomax FMT Lot # Particle Size Distribution





Traceable Standards (Uniquely supplied by KanomaxFMT

KANOMAX FMT
A Kanomax Company

Certificate of Analysis

Silica Concentration Standard
(10 nm Colloidal Silica)

DESCRIPTION: This concentration standard is a silica colloid prepared in ultrapure water to ensure low dissolve residue content. Particle size distribution was determined using a Liquid Particle Sizing (LNS) system. Particle size data are NIST and ERM traceable.

Kanomax FMT Lot #
Shelf Life: 6 months

Concentration Data

Number concentration (#/mL ≥ 5 nm)	5×10^{11}
Accuracy	± 10 %
Reference standard	FMT 1006
Reference instrument	LNS #1
Analysis date	01/26/2016

Number-weighted Size Data (nm)

Median	12.2
Mean	12.5
Mode	13.0
Geo. SD	1.25

Physical Data

Particle composition:	Silica
Particle density:	2.2 g/cm3
No surfactant added	

Note: Avoid exposure to direct sunlight

David B. Blackford.

David Blackford (President - KFMT)

Important point to understand

- sTPC is not replacing OPCs

- The sTPC technology is an Extension of particle counting
- The sTPC does number of particles greater than 10 nm 15 nm and 20 nm
  - Or the sTPC could do a continuous sampling at a dedicated size
- The sTPC is proving invaluable in covering processes that the OPC cannot cover, however the OPC can show larger particle failure modes
  - Such as mechanical abrasion
- Our point is that the OPC is beyond its theoretical limit in nm space
- So a recommended particle protocol would be to use OPCs but at a more cost efficient price point (such as micron level) and use the sTPC for the nm analysis

sTPC and OPC counting differentials (Why they count differently)

ScanningTPC reports particle concentrations 4-5 orders of magnitude higher than historical metrology methods would suggest:

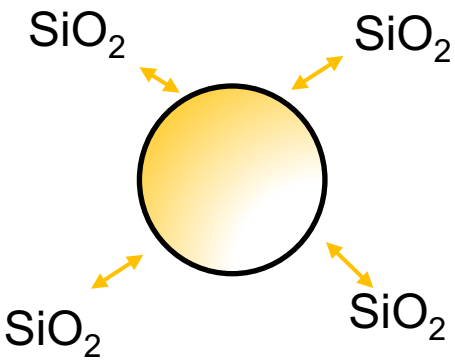
- Differences in detection efficiency definitions, natural particle distribution shape, and refractive index account for ~1000x higher reported concentration
- Particles in the size range detected by the ScanningTPC should intuitively be removed by state of the art filtration

- What is the ScanningTPC counting?
- Why aren't filters removing these particles?
- Why are these particles not detected by other instrumentation?

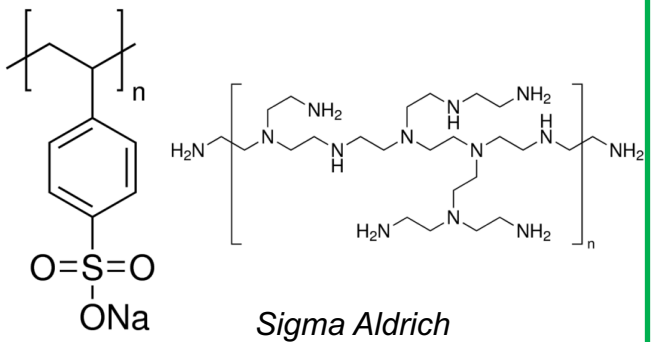
What is the ScanningTPC counting?

Potential Candidates

Colloidal Silica
(primary contaminant in UPW)

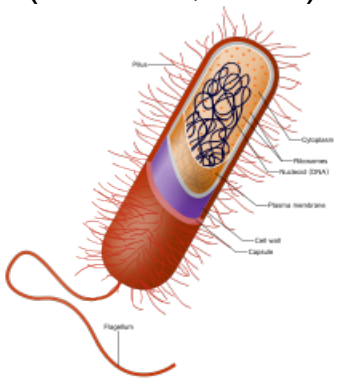


High Mw Polymers
(from IX resin)



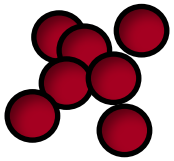
Sigma Aldrich

Organic Material
(bacteria, DNA)



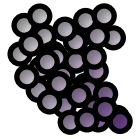
Wikipedia

Loose Aggregates



Focus of this work

Precipitated NVR



Answer: We don't know, yet.

Materials and Methods

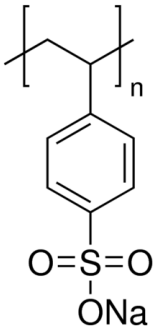
- Select high Mw polymers that may be found in IX resin material
- Inject these polymers into UPW sample stream
- Measure response factor of several measurement methods
- Challenge membrane filter to observe polymer retention

Sucrose

- Represents dissolved organic non-volatile residue
- Show interference by dissolved NVR
- Confirm TOC measurements

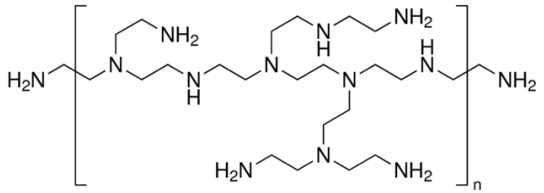
Poly(sodium 4-styrenesulfonate)
PSS

- Represents breakdown product of cation resin
- Refractive index 1.39
- Mw 1M ~ 7.5 nm
- Mw 70k ~ 2.7 nm



Poly(ethyleneimine)
PEI

- Represents breakdown product of anion resin
- Refractive Index 1.52
- Mw 750k ~ 6.5 nm

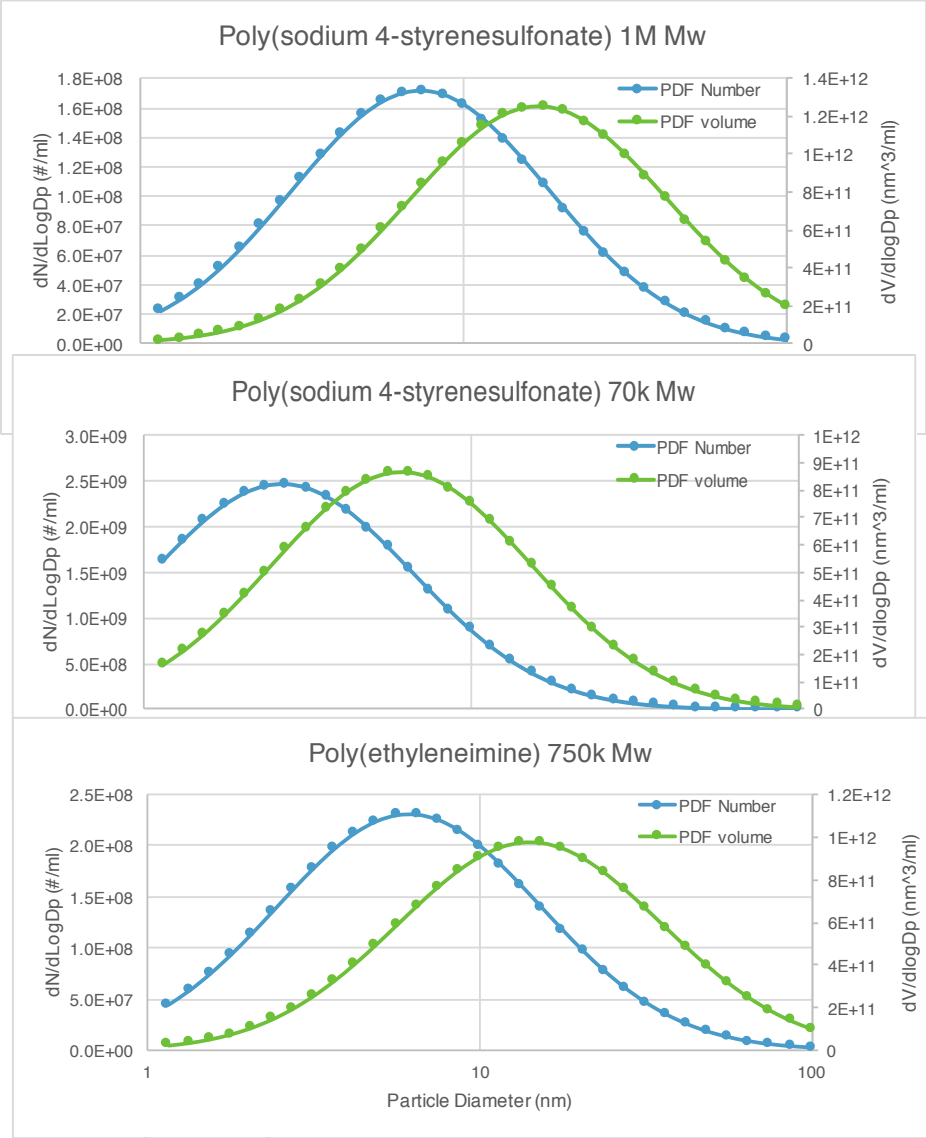


Note: RI for water is 1.33

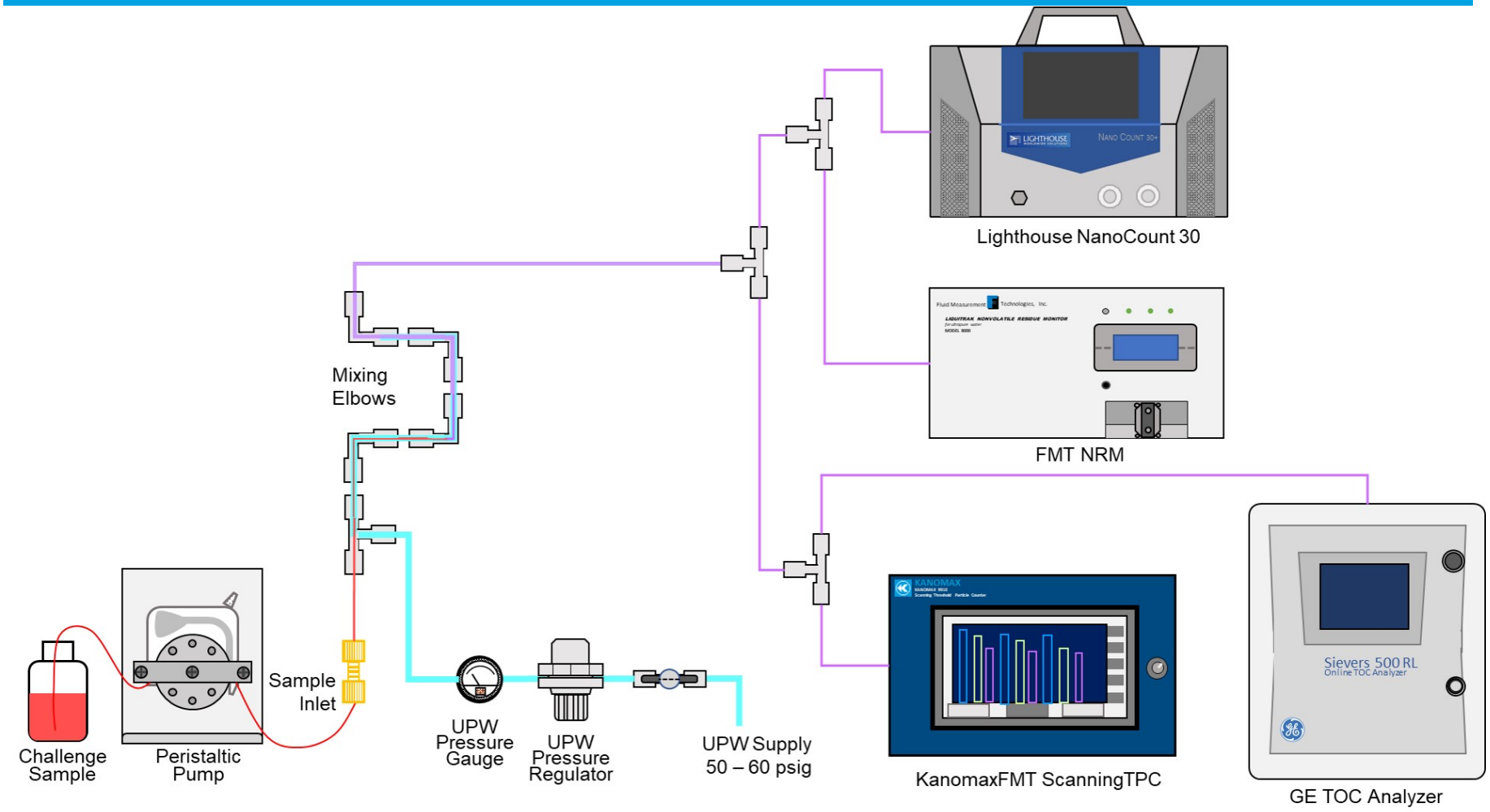
Polymer Challenges

- Assume bulk density spherical particles
- Use a geometric standard deviation of 2.5 (based on fitting the Mw and Mn values given for PEI)

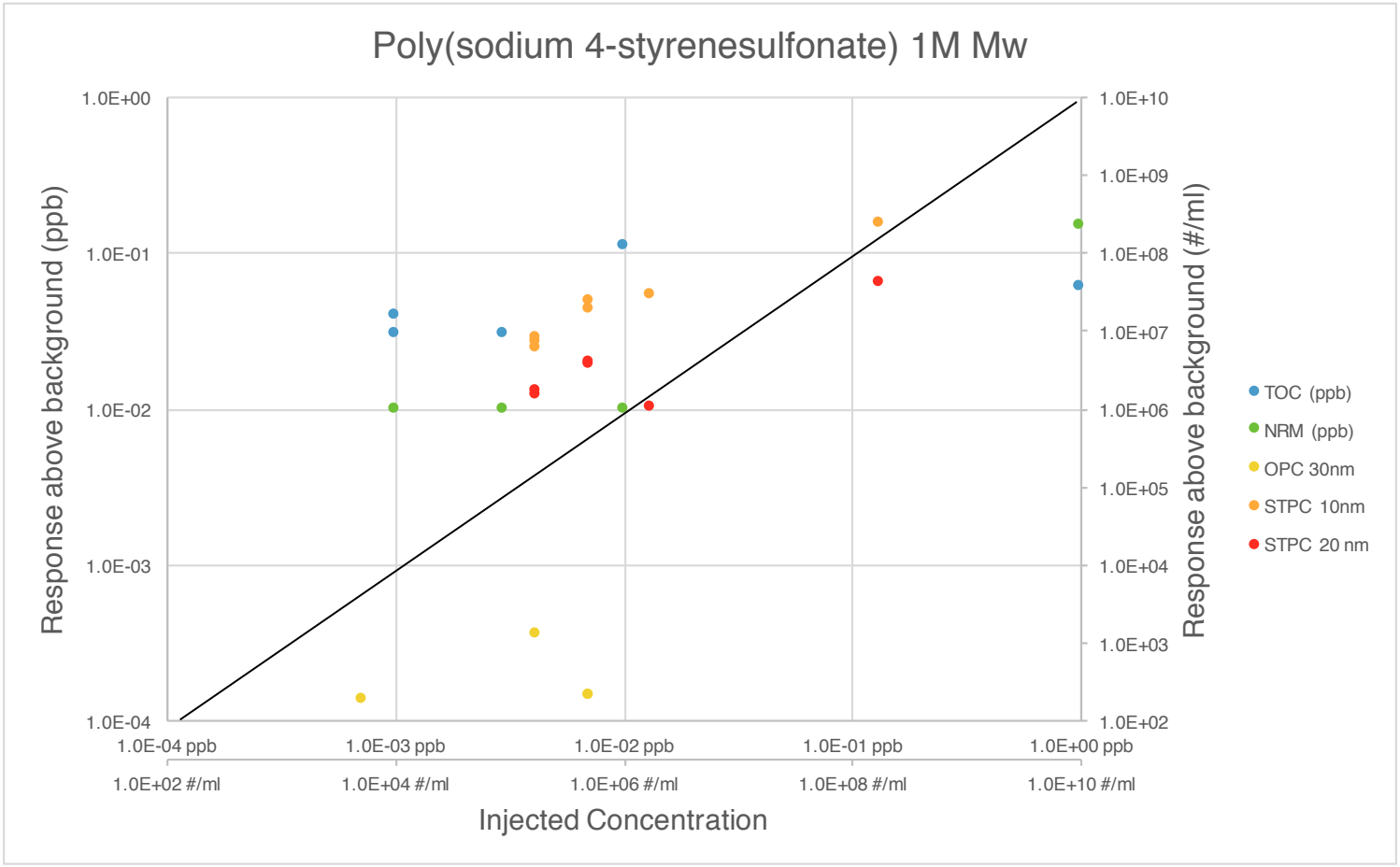
- Prepare 100 ppb stock solution, confirm material fully dissolved
- Dilute stock solution offline to 1 ppb
- Dilute online at dilution ratios ramping from 100-10000x



Test Schematic

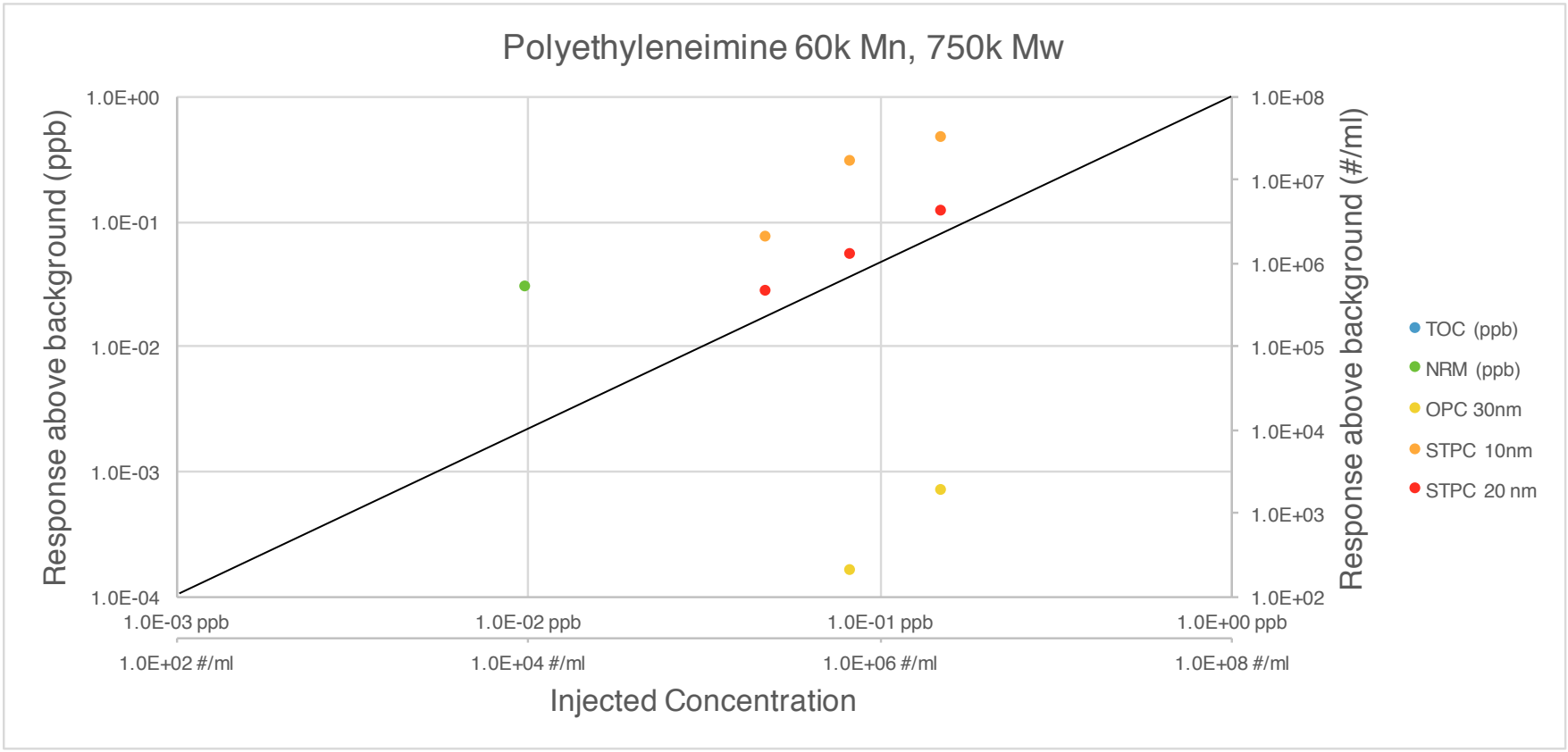


PSS 1M Mw
Relative Response



- ScanningTPC and TOC monitor both show positive response factor near 1:1
- OPC shows low response factor in the measurement range of the device

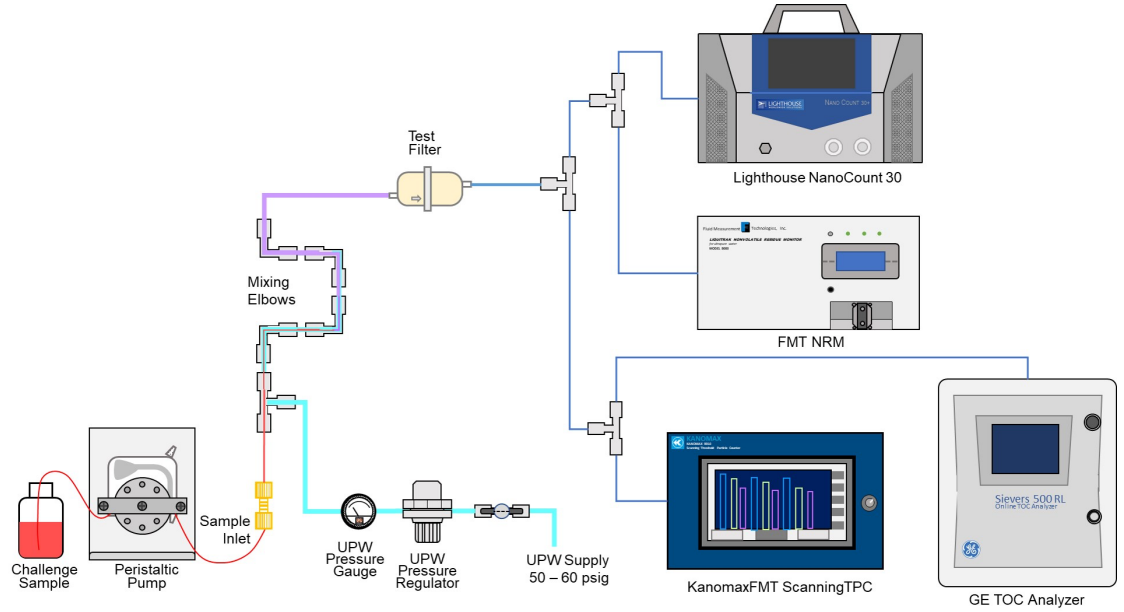
PEI 750K Mw
Relative Response



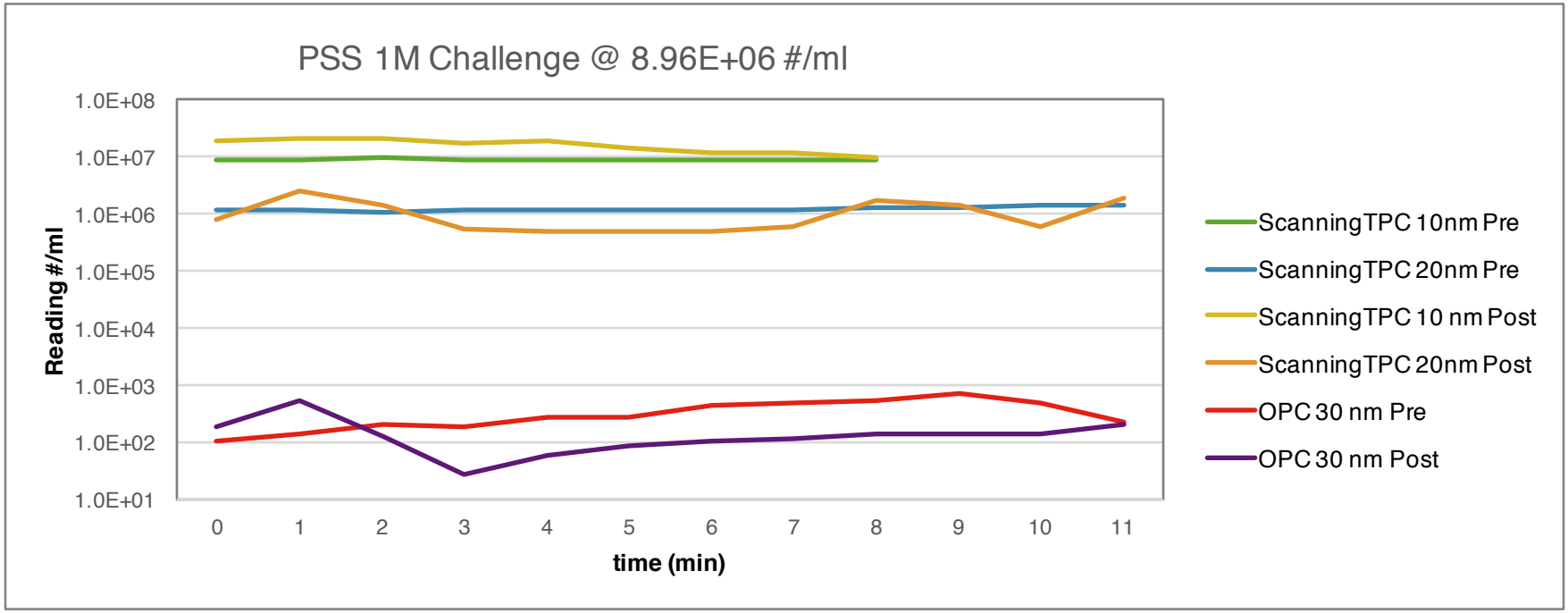
- ScanningTPC shows correlation to the injected concentration
- OPC shows correlation but at a fraction of the injected concentration

Challenge of POU 20nm Filter

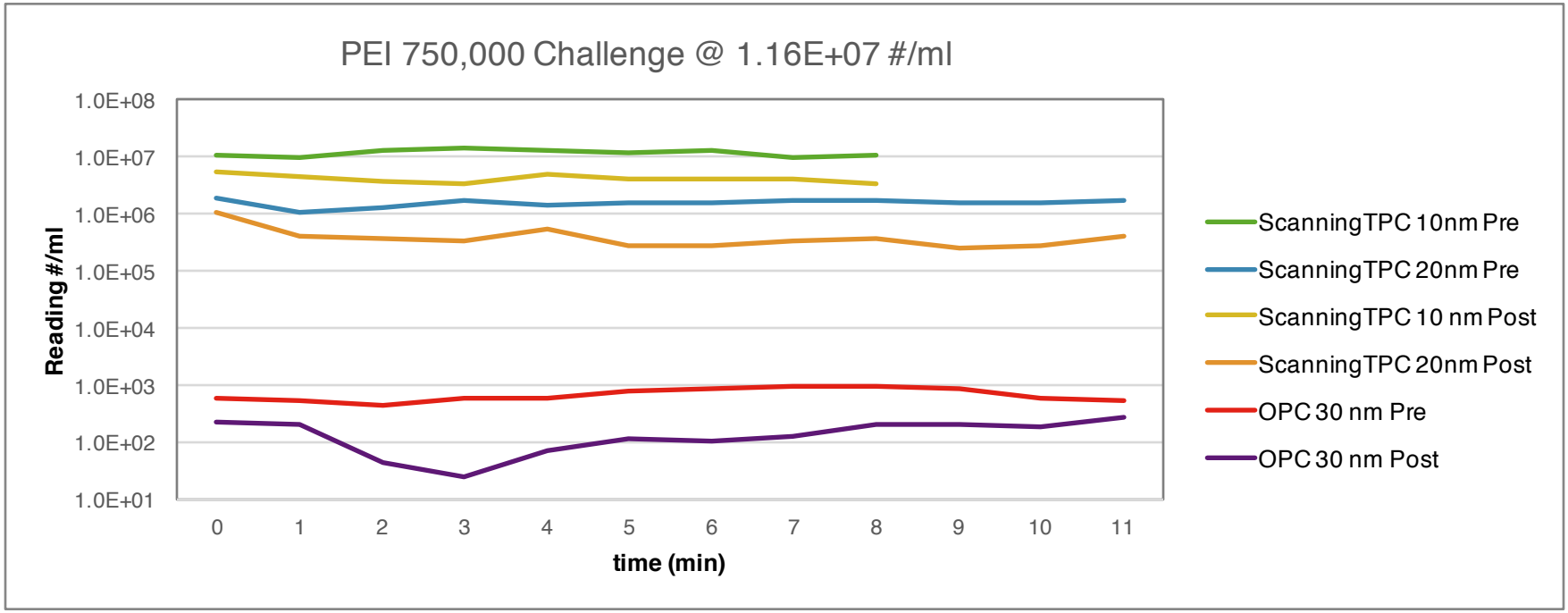
- Rinse and establish background
- Challenge PSS 1,000,000
- Challenge PEI 750,000
- Background UPW



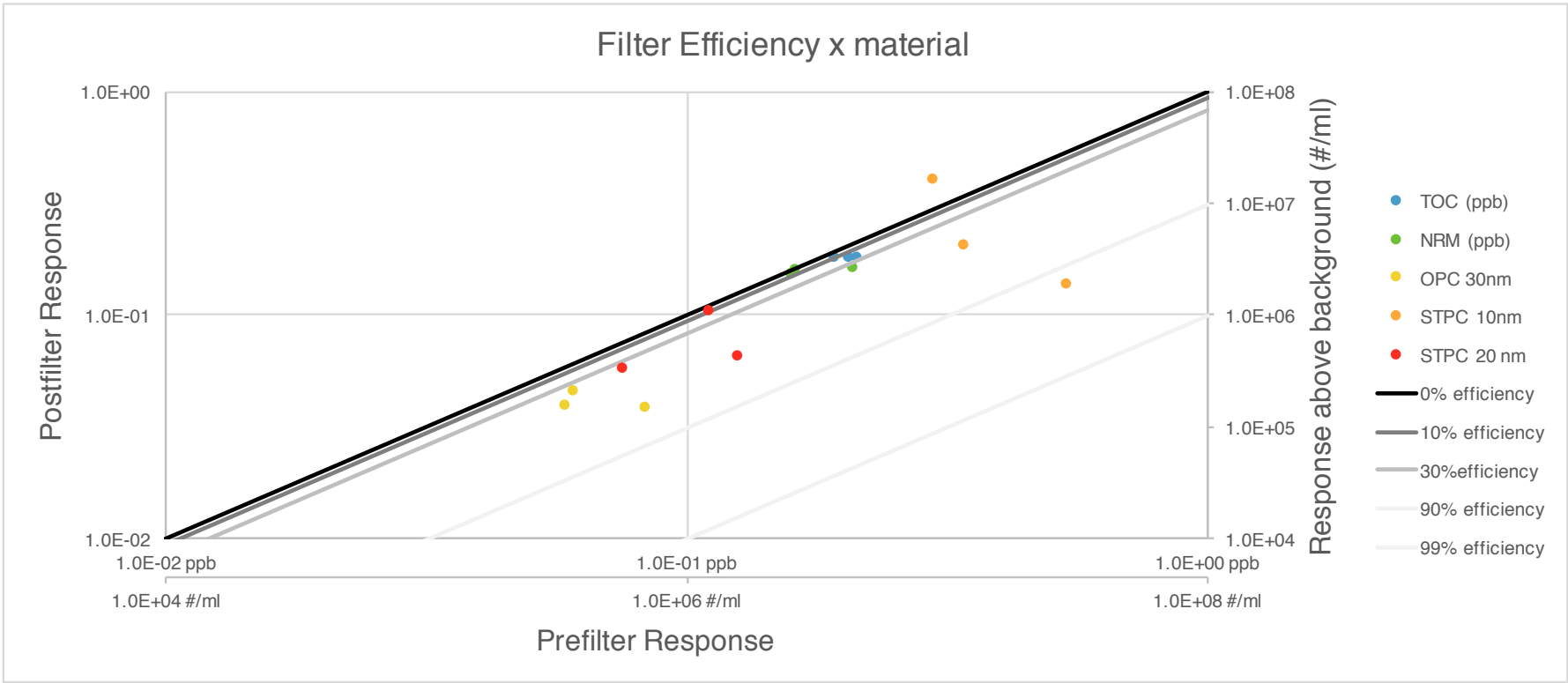
PSS 1M Mw
8.96E+06 Challenge 20nm POU Filter



PEI 750K Mw
1.16E+07 Challenge 20nm POU Filter



20 nm Filter Efficiency with Organic Challenge



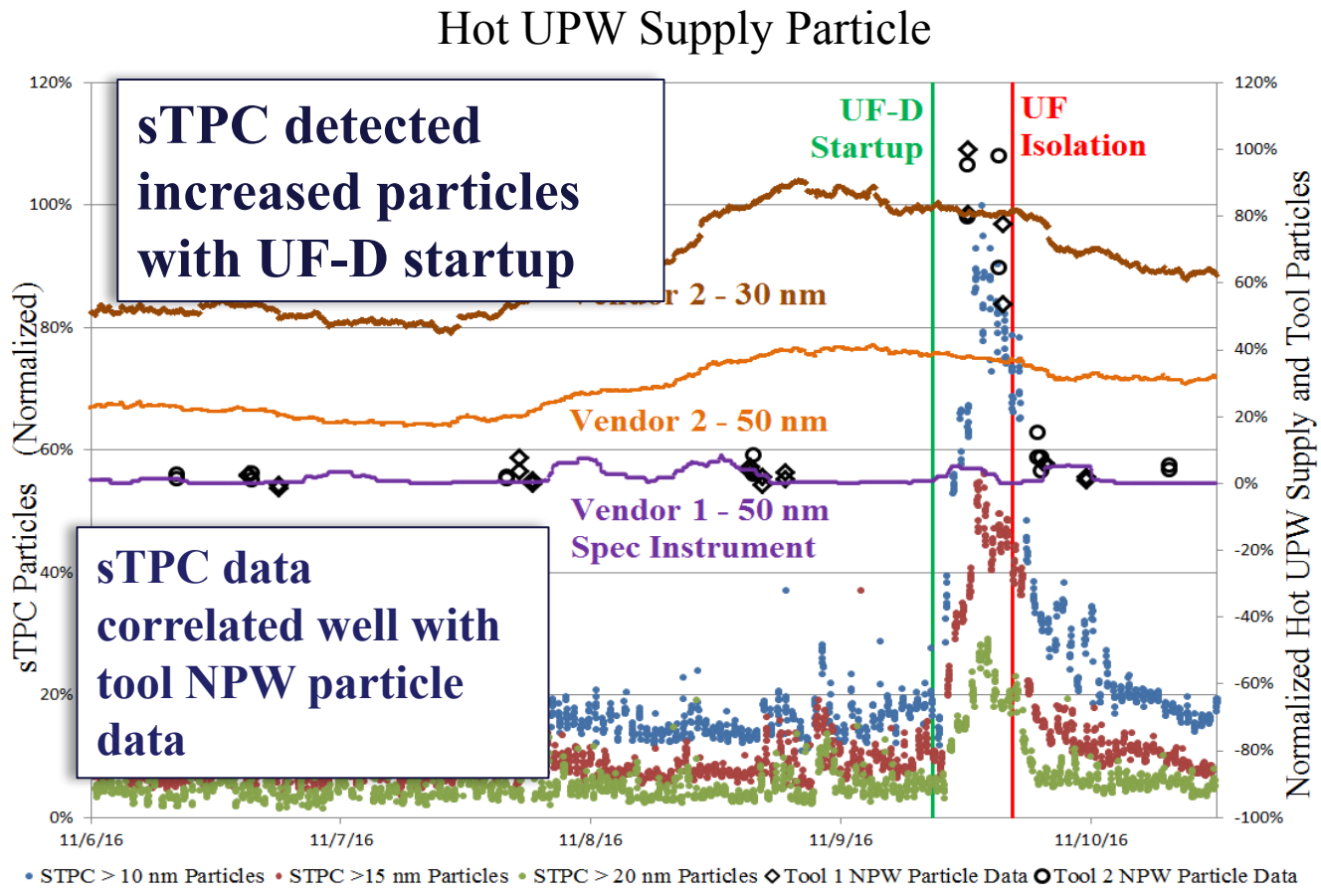
Organic (soft) particles from resins

- Organics are detected by sTPC by 4 – 5 orders of magnitude greater than OPC
- This is due in some measure to the RI (refractive index contrast) PSS for instance has a RI of 1.39 and water is 1.33
- This may not be the only reason but is a good candidate
- The nanoSpotLight technology is aiding in the identification of hard and soft particles

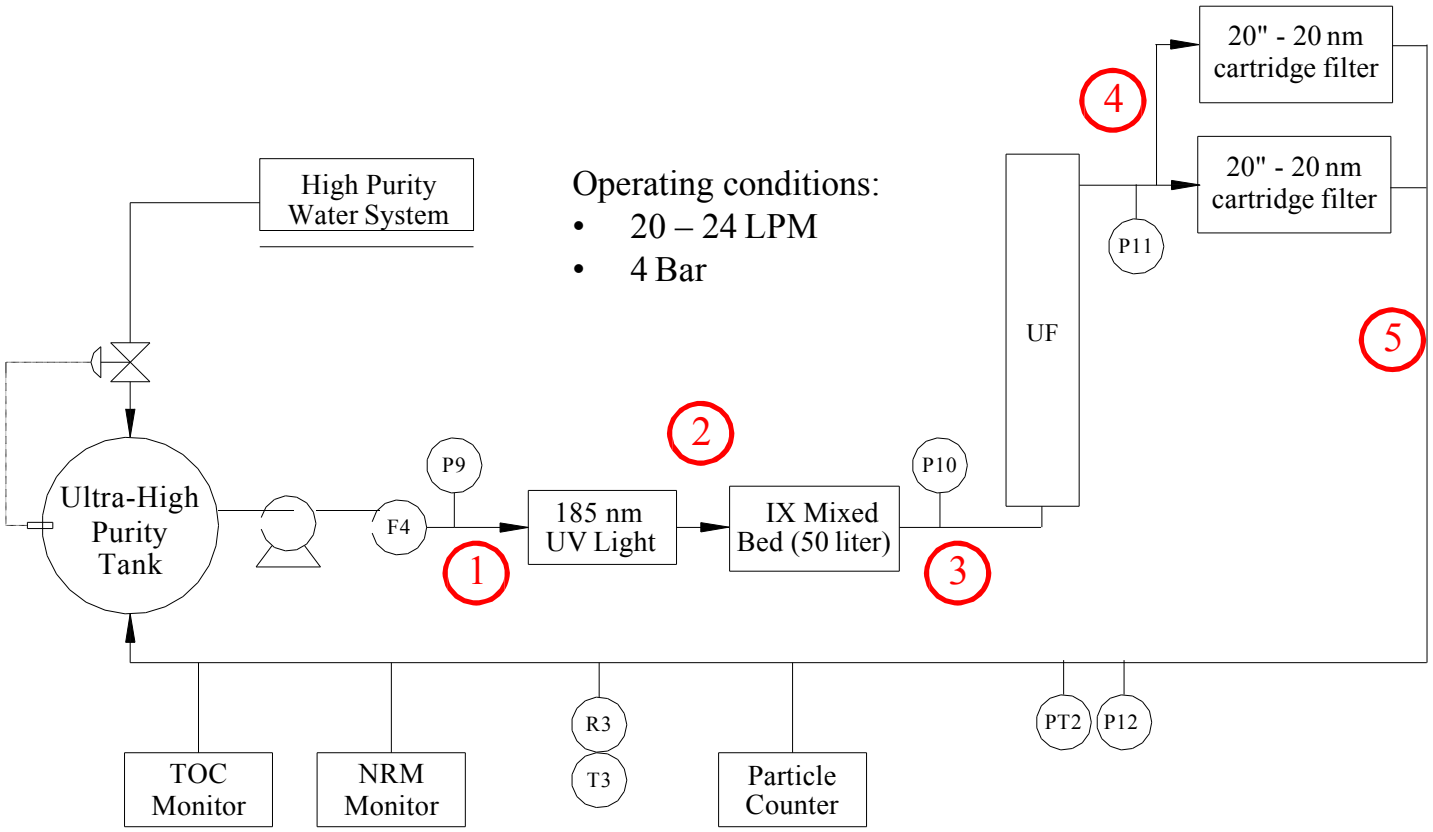
Where can I use this in the fab

- From moving the sTPC around the subfab
  - UF changeout uncovered an episode (excursion) that the sTPC saw but the OPC missed This is a GOLDEN opportunity that directly links Yield loss to a particle problem!!
  - Resin changeouts and monitoring of the resin is accomplished uniquely by the sTPC
  - Hot DIW rinsedown is orders of magnitude faster with the sTPC (as discovered by SAS)
  - UV particle shedding as seen by CT Associates

Actual Fab experience with episode that was detected by sTPC and confirmed at the wafer level and not observed by OPCs

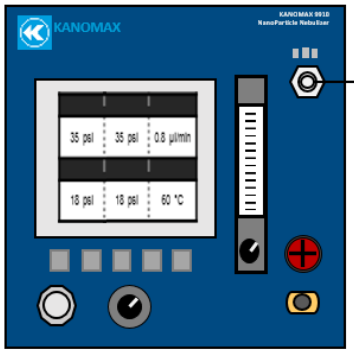


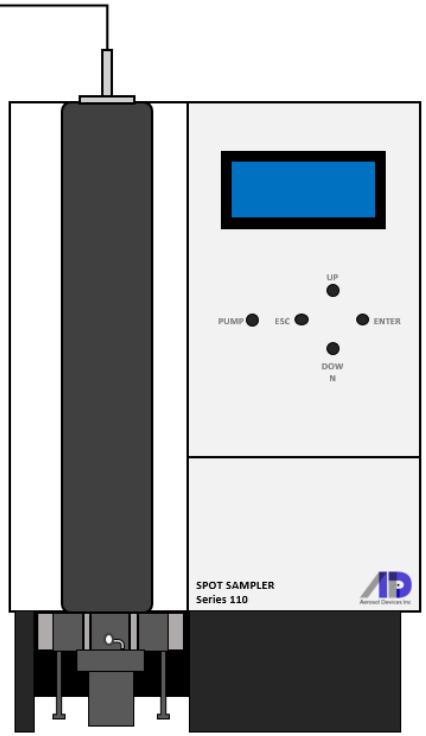
UPW System Sample Points



nanoSpotLight merges 2 patented technologies

NanoParticle Nebulizer
(KANOMAX Model 9110)

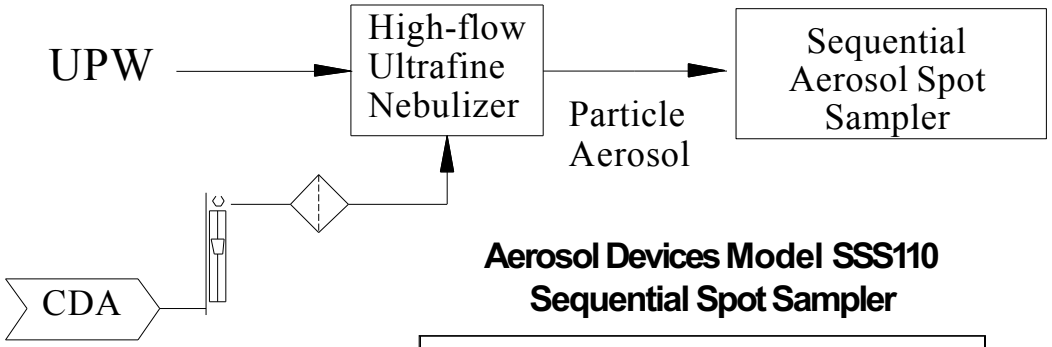




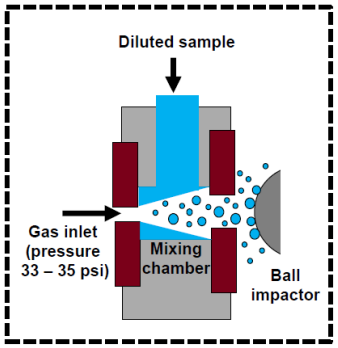
Sequential Spot Sampler
(ADI SSS110)

ULTRAPURE WATER Conference,
Portland, OR, May/June 2017

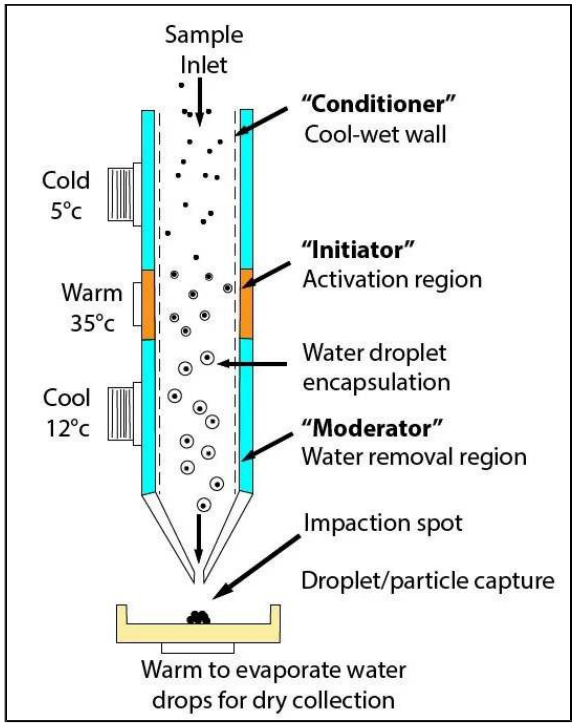
Theory of Operation and Capabilities - Aerosol Solutions
Sequential Spot Sampler

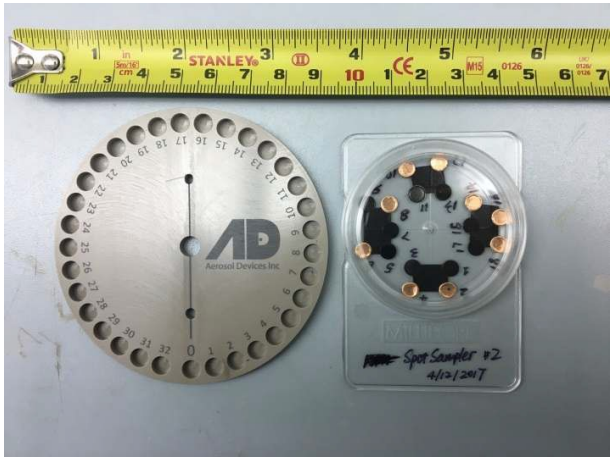


Kanomax FMT NanoParticle Nebulizer Model 9110*



Aerosol Devices Model SSS110 Sequential Spot Sampler

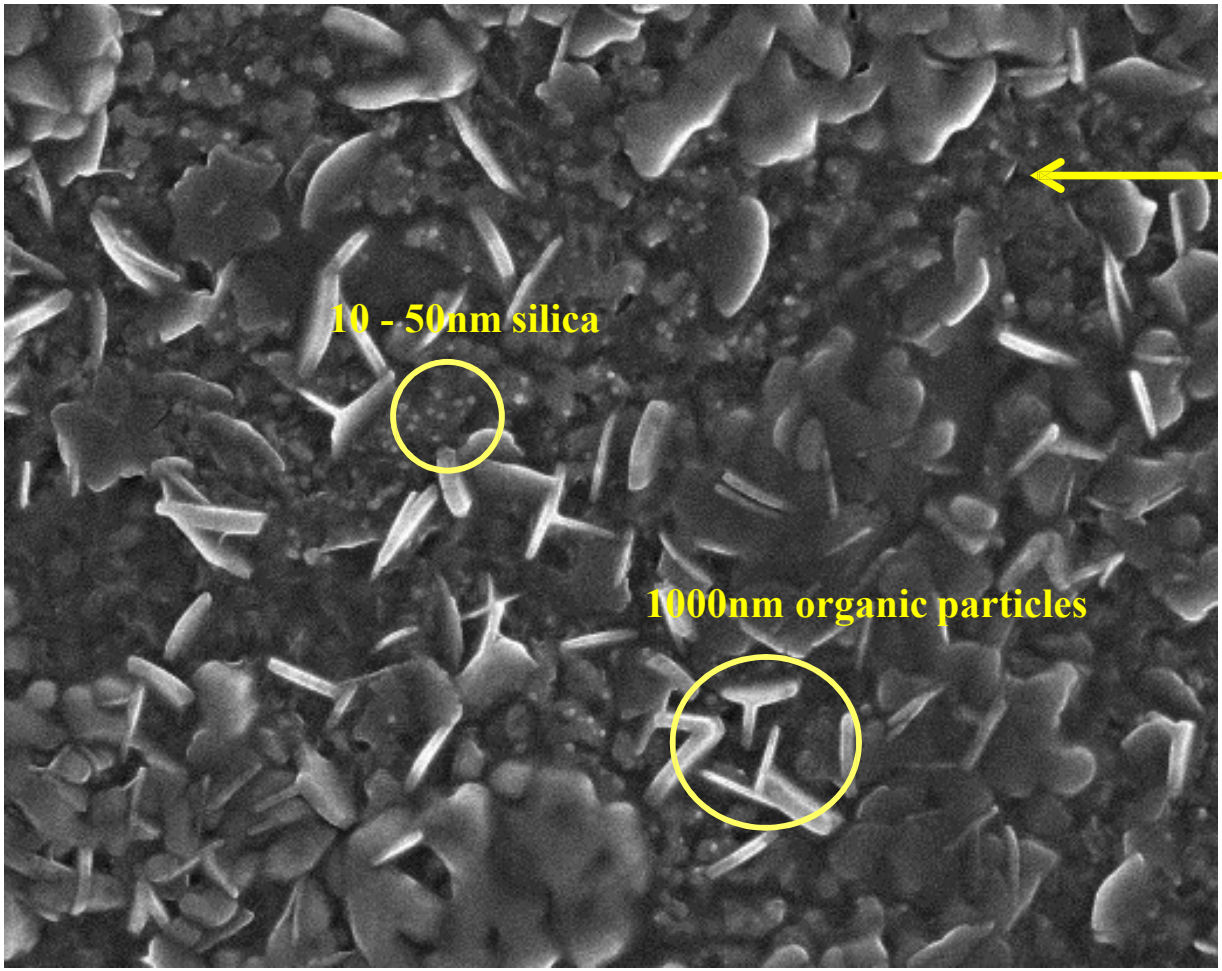


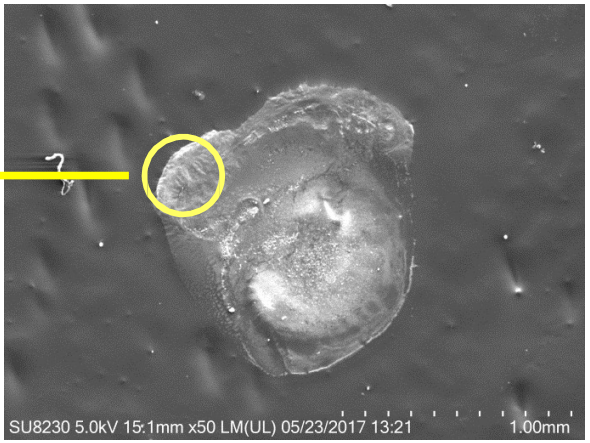


CTAssociatesinc.com

Van Schooneveld, et al., Ultrapure Water Micro 2017 – Portland, Oregon

Spot Sampler SEM/EDS Analysis

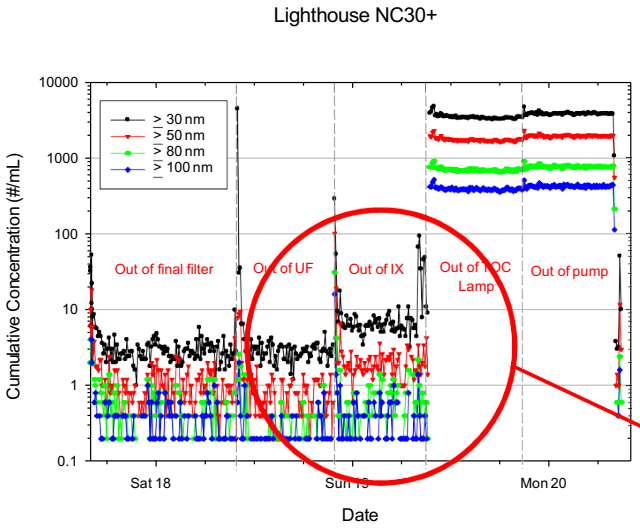


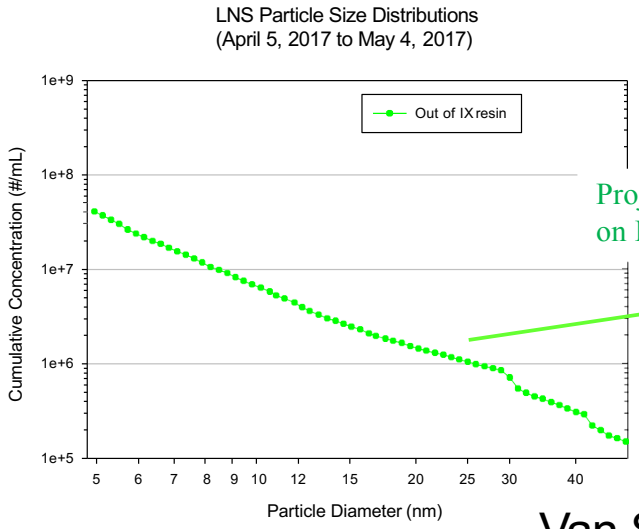


Elements Detected:

- Carbon
- Oxygen
- Silicon
- Sulphur
- Zinc
- Magnesium

Projected Spot Size – OPC to LNS



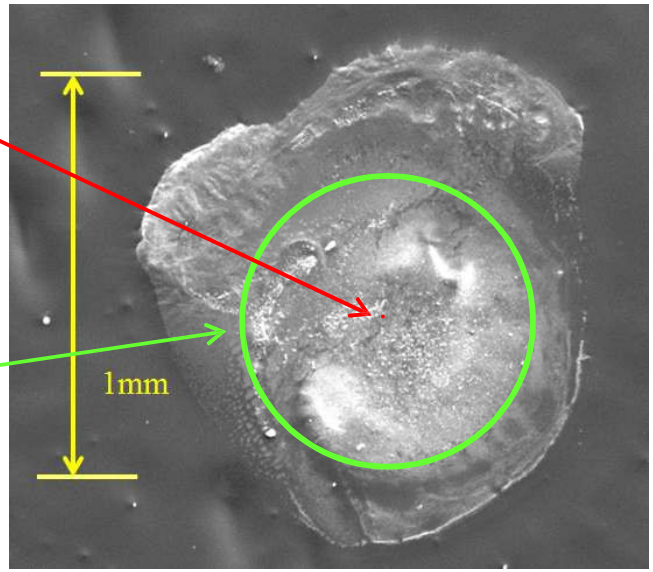


Assumptions:

- Only consider particles > 7 nm
- OPC PSD extrapolated using power law ($f(x) = K * (1/d^n)$ where n=3)
- OPC measurements from February are still valid.
- Nebulization rate 0.5 ∝m/min
- 1% packing efficiency

Projected spot diameter based on OPC data – 0.004 mm

Projected spot diameter based on LNS data – 0.63 mm



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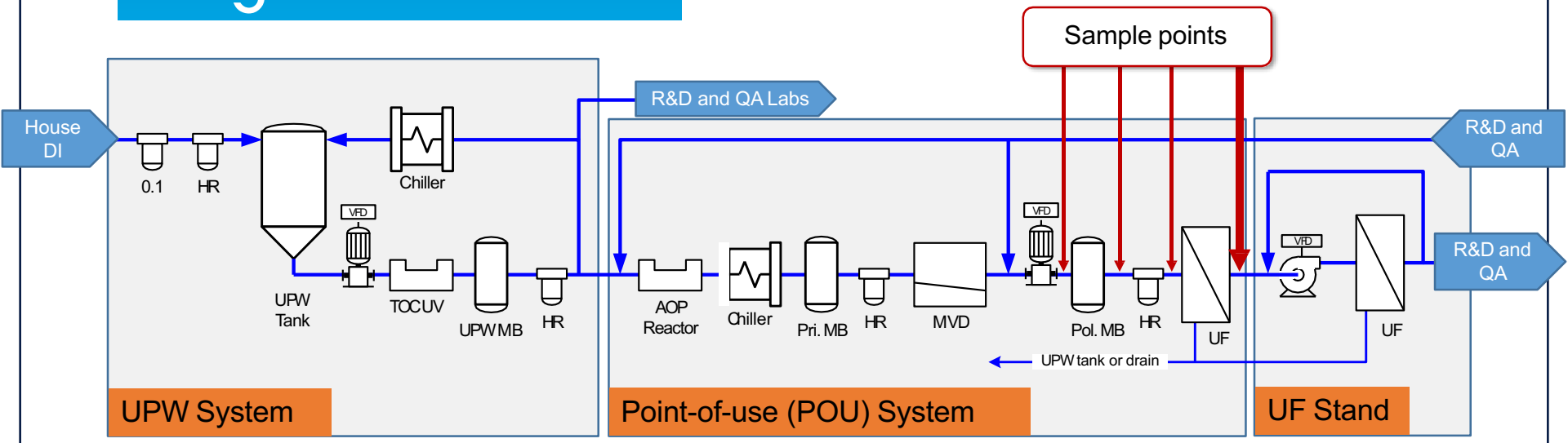
Van Schooneveld, et al., Ultrapure Water Micro 2017 – Portland, Oregon

Process Flow Diagram



UPW Tank levels vary from 70 to 95% daily. Weekends typically as low as 30%. On occasion it will be 0%

Demonstration system designed for immersion lithography tools for reduction of TOC < 1 ppb, reduction in oxygen, metals, silica, particles…

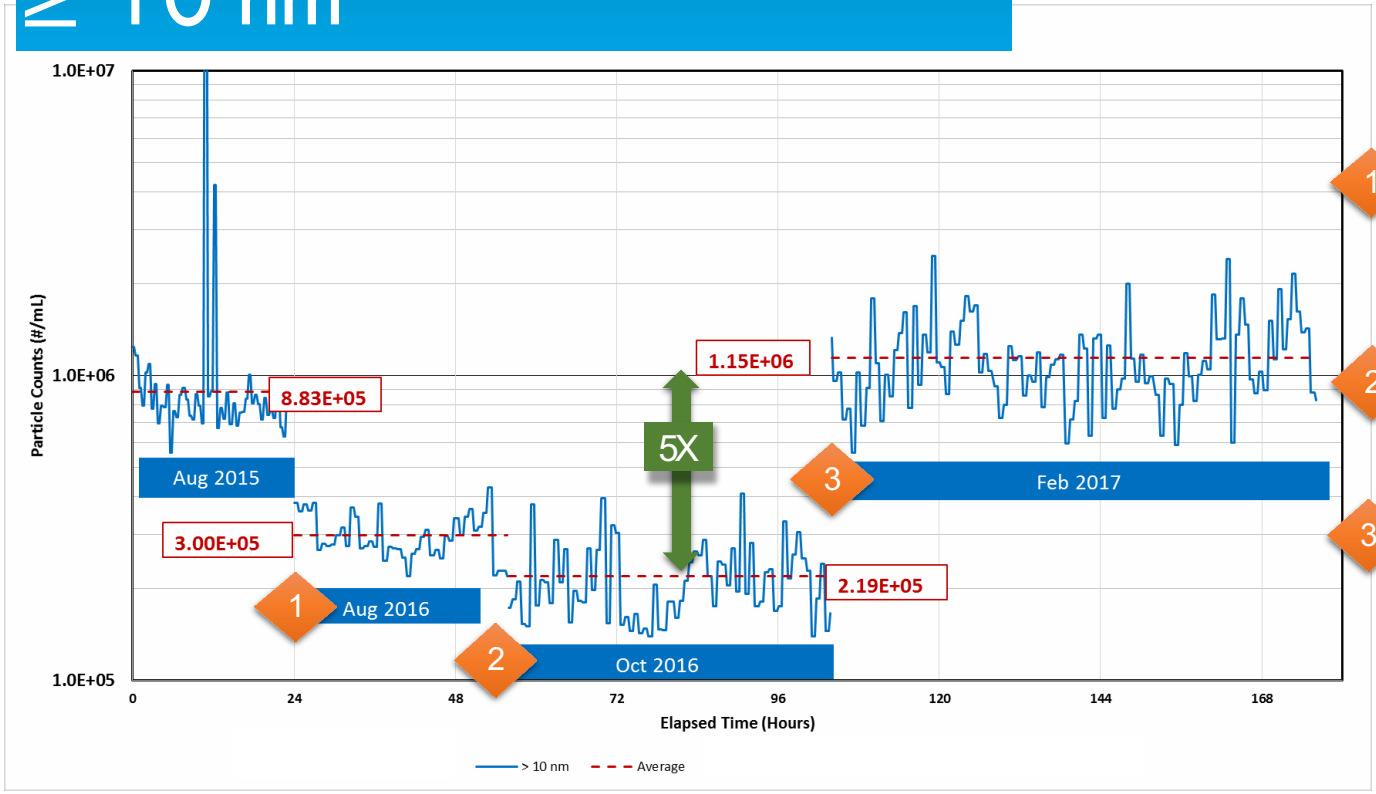
Hot water conditioning of UF modules and point-of-use filtration development.

Most "experiments" were planned, some were result of upset conditions in the equipment or water supply.

Glenn Sundstrom Evoqua

ULTRAPUREWATERMICRO.COM

Operational Experience: ≥ 10 nm

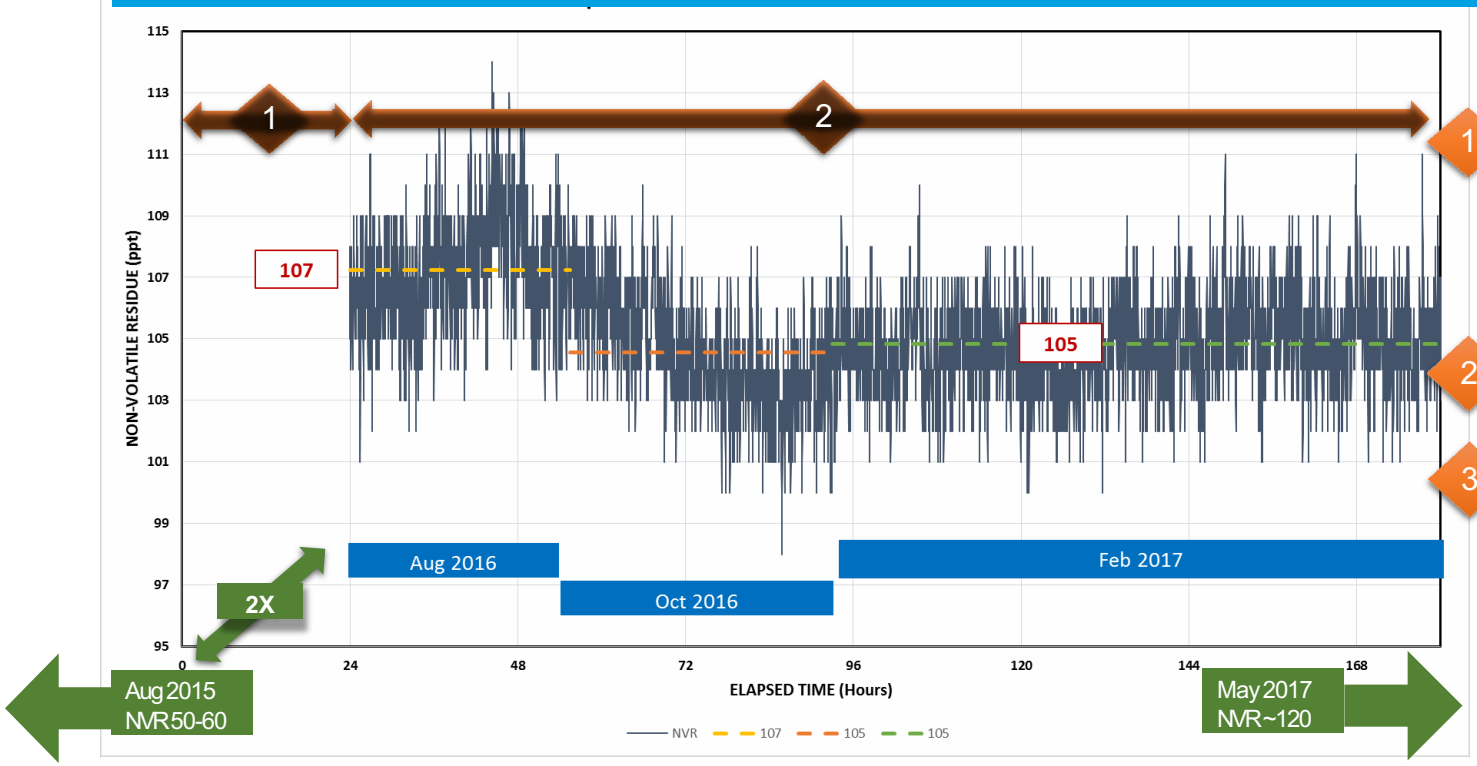


Sample point: POU UF permeate

1. Continued rinsing, UPW mixed beds and HR filter replaced, POU primary mixed bed replaced
2. Modified UPW tank fill. Added 0.1 and HR filters on UPW tank supply
3. POU polishing mixed beds and HR filters need replacement

Constant monitoring and more routine maintenance is required to meet particle specifications.

Operational Experience: Non Volatile Residue



Sample point: POU UF permeate

1. NVR doubled over the course of 1-year.

   POU polishing mixed bed needs replacement.

2. No significant change over 7-months

3. Continued increase => POU polishing mixed bed needs replacement

Constant monitoring and more routine maintenance is required to meet particle specifications.

KanomaxFMT opportunity technologies UPW

- sTPC
- NRM
- nanoSpotLight
- PDS and standards

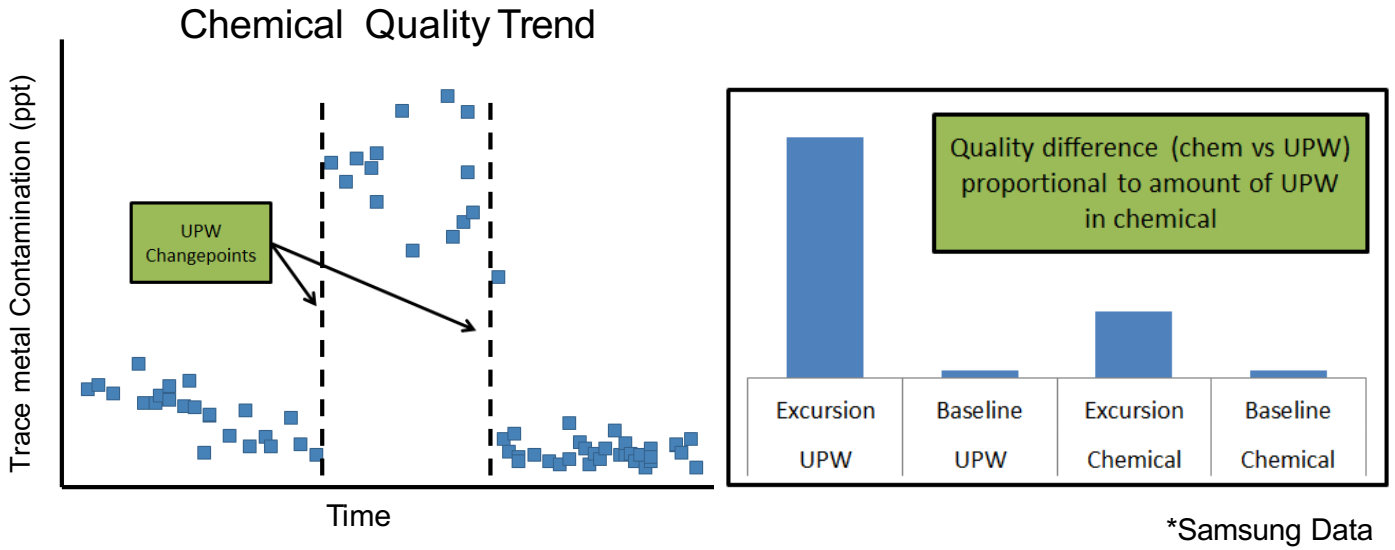
Other opportunities for UPW sTPC monitoring

- Initially the sTPC will be seen as a diagnostic instrument capable of detecting events that other technologies are incapable of seeing
- As customer confidence grows or an episode is detected, the sTPC will be required to sustain process and the sTPC will have a dedicated role requiring multiple units to be deployed
- The nanoSpotLight should replace SEM sampling and will act to confirm sourcing of the contaminants. SEM samples take weeks and are difficult to find on 25mm filters. The nanoSpotLight could be as short as minutes as the protocol continues to be refined
- For instance Daniel Stucky outlined the importance of chemical vendors to monitor their UPW
- For EUV the immersion technology requires UPW to be continuously monitored and controlled

Why Does UPW Matter?

Daniel Stucky Samsung Austin

- **UPW impacts chemical quality**
  - Improvements & Excursions
  - Proportional to amount of UPW in chemical
- Manage UPW like high purity chemical process
  - Inline monitoring
  - Changepoint management
  - Excursion prevention



*Samsung Data

EH&S is our Foremost Principle of Management

Max Production

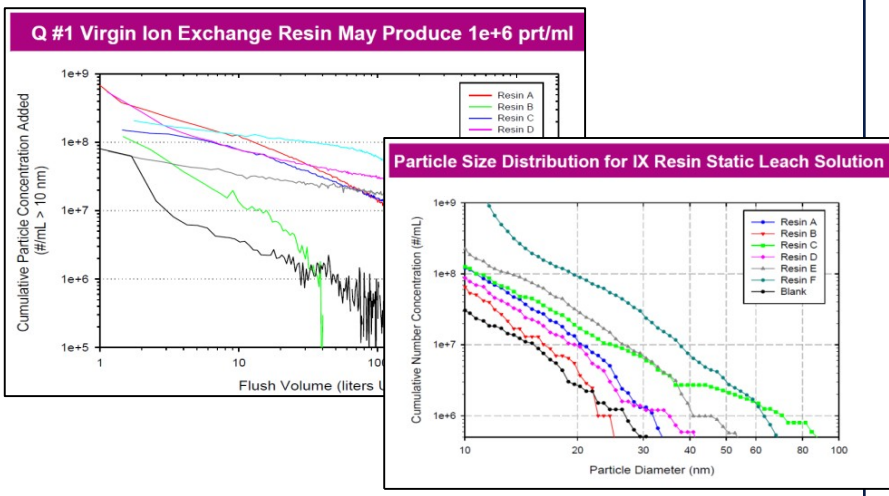
Ultimate Yield

UPW Improvements

Daniel Stucky Samsung Austin

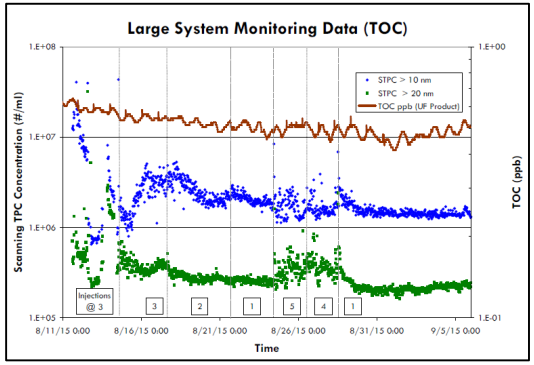
- **UPW & Chemical industries are connected**
  - Very similar challenges
  - Advancements in UPW later transition to chemicals
    - **Chemical suppliers should watch UPW closely!**
  - Examples:
    - ➢ Metrology not keeping up with need
    - ➢ Filtration
    - ➢ Particle analysis: driving to <10nm
    - ➢ Detection limits: ICP-MS ppt ☾ ppq
    - ➢ Purification material management

Not all resins perform the same!



Source: Libman, et al. "ITRS and SEMI Synergy of Enabling Advanced Existing and Future Technologies." UPW Micro 2015, 27 October 2015, Portland, OR.

Advanced 10nm Monitoring



Source: Oberreit, Blackford, Schooneveld. "Application of a 10nm particle counter and non-volatile residue monitor for component diagnostics within a UPW system." UPW Micro 2015, 27 October 2015, Portland, OR.

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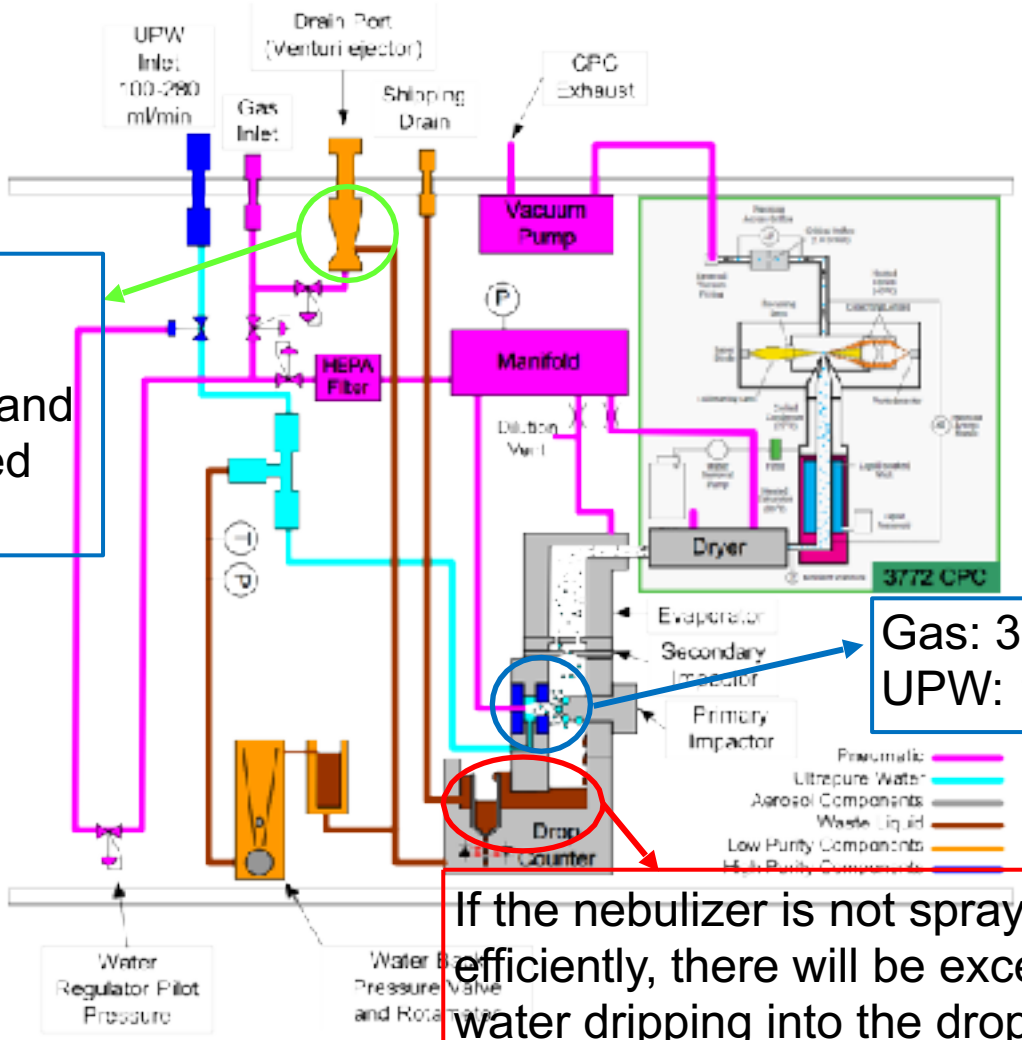
Cause of water in bottom of sTPC

- Improper operation of the nebulizer by virtue of incorrect pressure
- Only a % of the UPW is nebulized the rest is used to determine flow through the nebulizer through a patented and accurate drip counter
- NET result: not a leak but indication of improper operation

Scanning TPC

Flow Diagram

Gas: 5 psi
The back pressure is necessary to pull out and drain the water dripped into the drop counter.



Gas: 35 psi
UPW: 14 psi

If the nebulizer is not spraying liquid efficiently, there will be excess amount of water dripping into the drop counter open area, and quickly flooding the limited holding volume

New Technology

The technology is unique and therefore early adopters will benefit from these tools.

KanomaxFMT is committed to the success of the technology and ultimately to your success.

As Archita Sengupta from Intel says, “Today’s process variations is tomorrow’s process excursions”

With KanomaxFMT tools, the industry is supported in the nm space.

It is being discovered that even mature lines benefit from this information because reliability is being effected by contaminants that do not kill the device but reduce its lifetime.