ULTRAPURE MICRO 2022

Critical Organics Risk Assessment of High-Purity Polymer Piping

Gary Van Schooneveld[1], Larry Zazzera[1], Ali Altun[2], Bob McIntosh[3]

[1]CT Associates, Inc., 7121 Shady Oak Road, Eden Prairie, MN 55344

[2] UNISERS AG Bändliweg 30, 8048 Zürich, Switzerland

[3] Enviro-Energy Solutions, 13023 NE Highway 99, Vancouver, WA 98686

Creative Technology

CT Associates, Inc.

UNISERS UNIVERSAL CONTAMINATION ANALYZER

This type of study can not be done alone!

IRDS Critical Components Task Force

IRDS UPW Task Force

UNISERS

SCREEN

Asahi America

Daiken America

Entegris

Georg Fischer

Saint Gobain

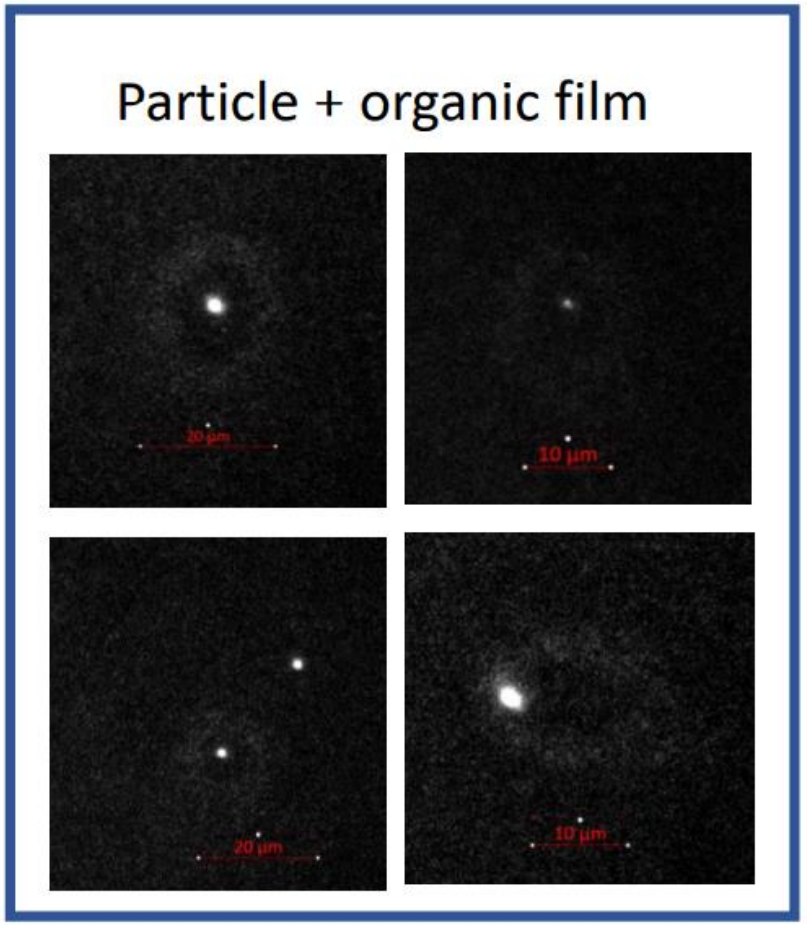
Solvay

Presentation Outline

- Introduction and Problem Statement
- Technical Objectives
- Analytical Metrologies
- Test Results
  - PFA and PVDF Extract Analysis
  - Wafer Surface Analysis
  - Thermal/Vacuum Desorption Analysis
- Summary and Take-aways

Introduction and Problem Statement

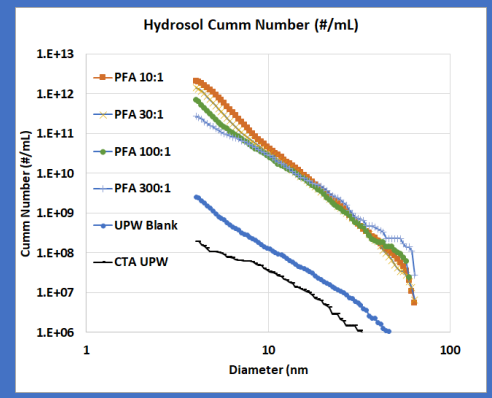
- Organic contamination present in UPW pose a risk of depositing on the wafer surface during processing and cleaning. Of greatest concern are those deposits that are non-volatile **critical organics**.
- Pressure for increased yield, improved performance and long-term reliability combined with the **lack of online metrology** require that critical organic contamination be **proactively managed**.
- **New tools and methods** are needed to better understand these risks and support material improvements and new material development.



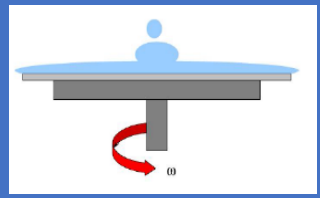
Source: 2021 IRDS UPW Particle Precursor (HMWO) Deposition Study - UNISER

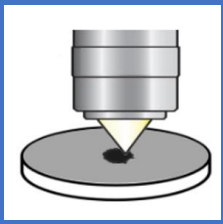
Technical Objectives

1. To quantify critical organic extracted from high-purity piping by hot UPW; specifically, PFA and PVDF.
2. Assess the affinity of the organic contaminants to the wafer surface during spin processing.
3. Determine the relative concentrations of organic contamination remaining on the wafer surface as a function of temperature.

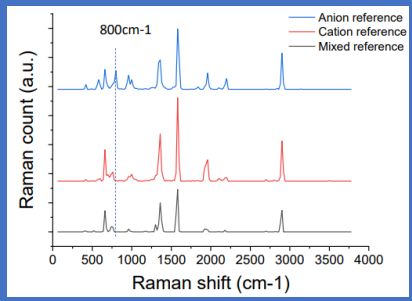


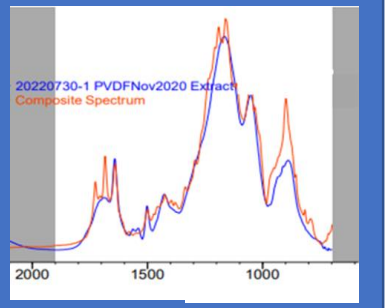
Particle Size Distribution Analysis and TOC





Spin Coat → Surface Analysis





Molecular Finger Printing

Analytical Metrologies

Kanomax FMT Liquid Nanoparticle Sizing (LNS)

Jasco 6600 Fourier-Transform Infrared Spectroscopy (FTIR)

Surface Enhanced Particle Sizing (SEPS)

Surface Enhanced Raman Spectroscopy (SERS)

Sievers 500 RLe Total Organic Carbon (TOC)

Phase 1 Proof of Concept Test Approach

Test Materials

½" PFA Tube
32 mm PVDF Pipe
UPW only

Prepare Extracts

Extended SEMI F40
(85°C, 14 days)

Total Organic Carbon (TOC)

Measure TOC

Liquid Nanoparticle Sizing (LNS)

Prepare Deposition Solutions

Dilute ~ 10:1 and ~100:1 in UPW (target – equivalent particle concentrations of PFA and PVDF)

Spin-coated on 6" wafers cleaned by Screen Japan

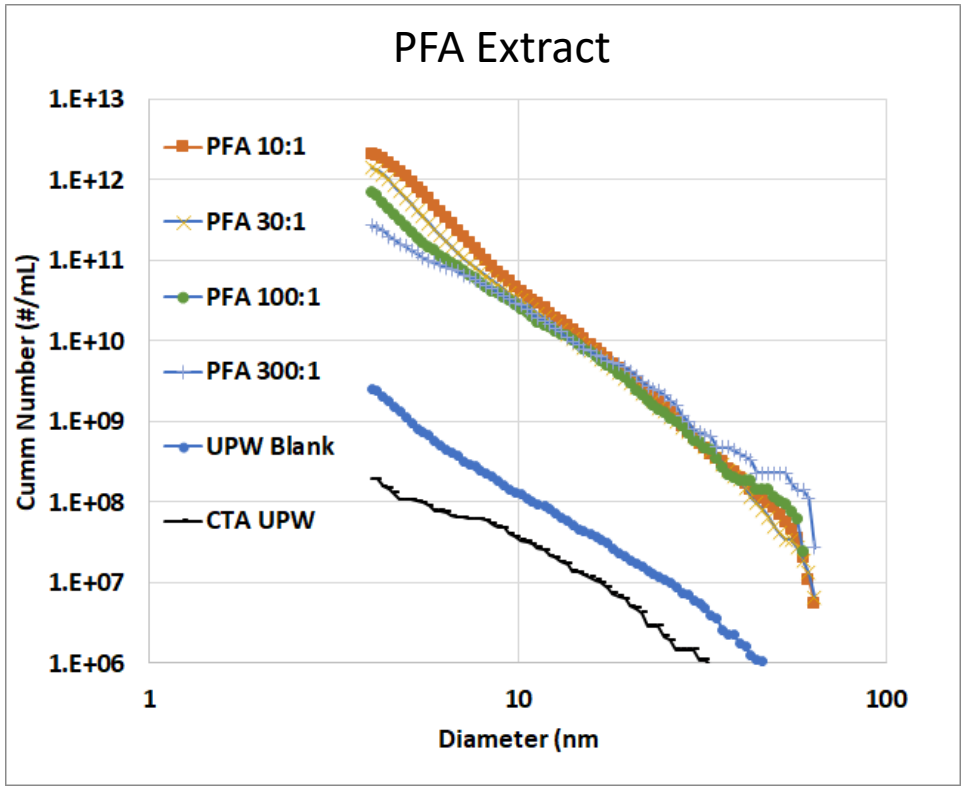
Measure Extract Particle Size Distribution (PSD)

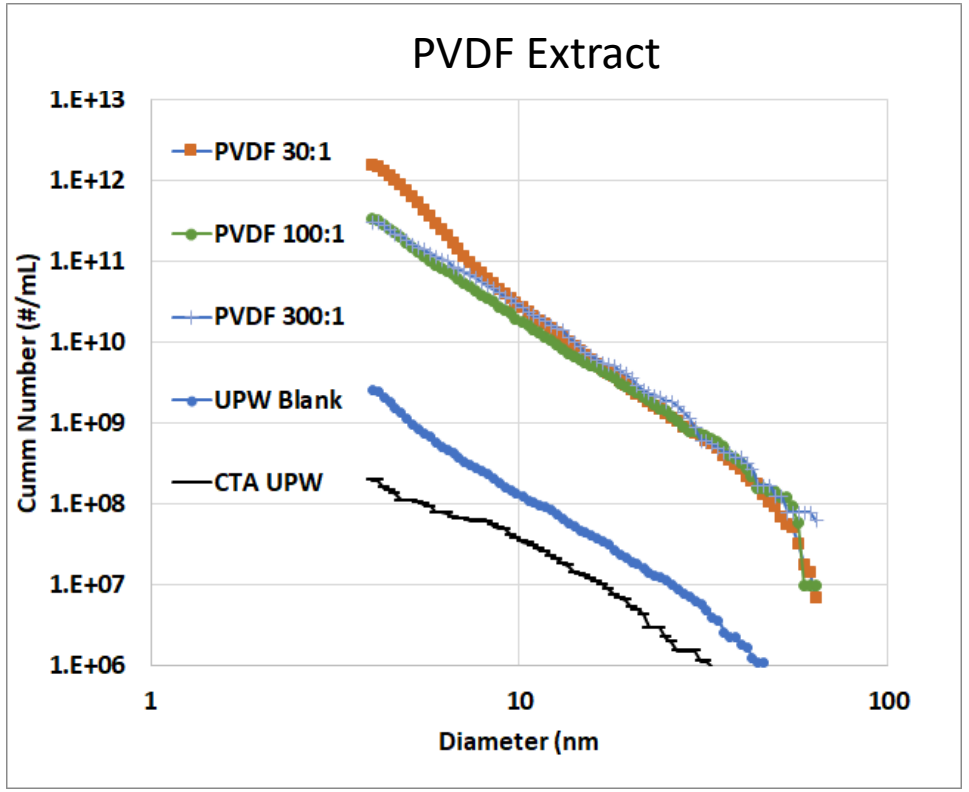
On wafer PSD

Surface Enhanced Particle Sizing to 8 nm (all wafers)

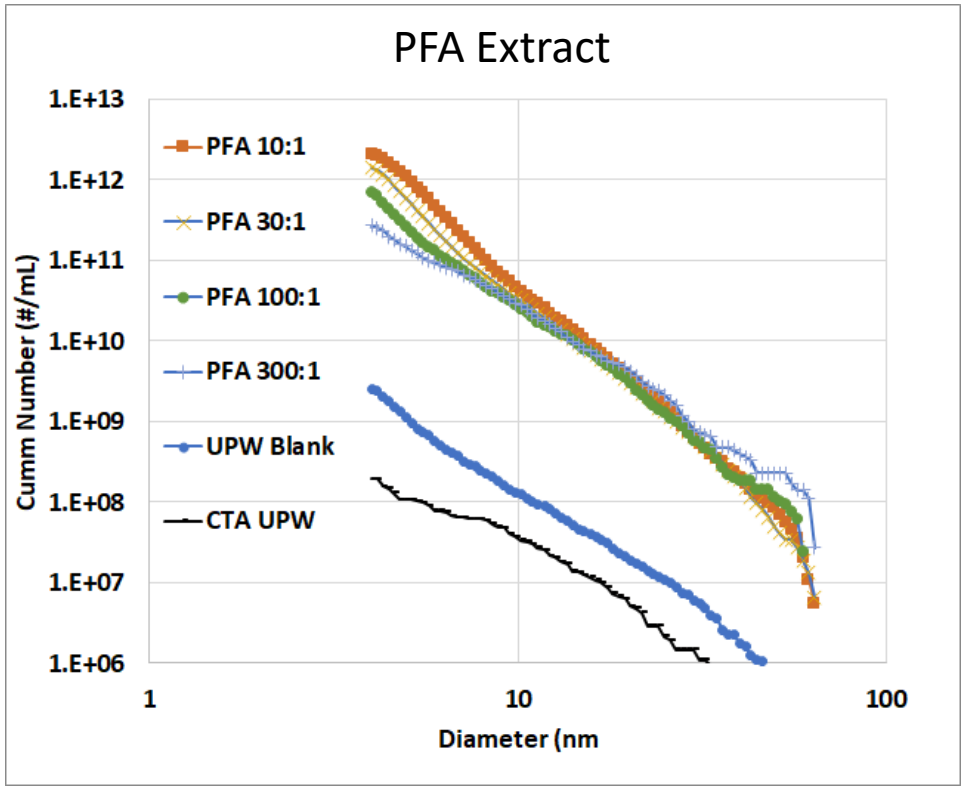
SERS Analysis (wafer subset)

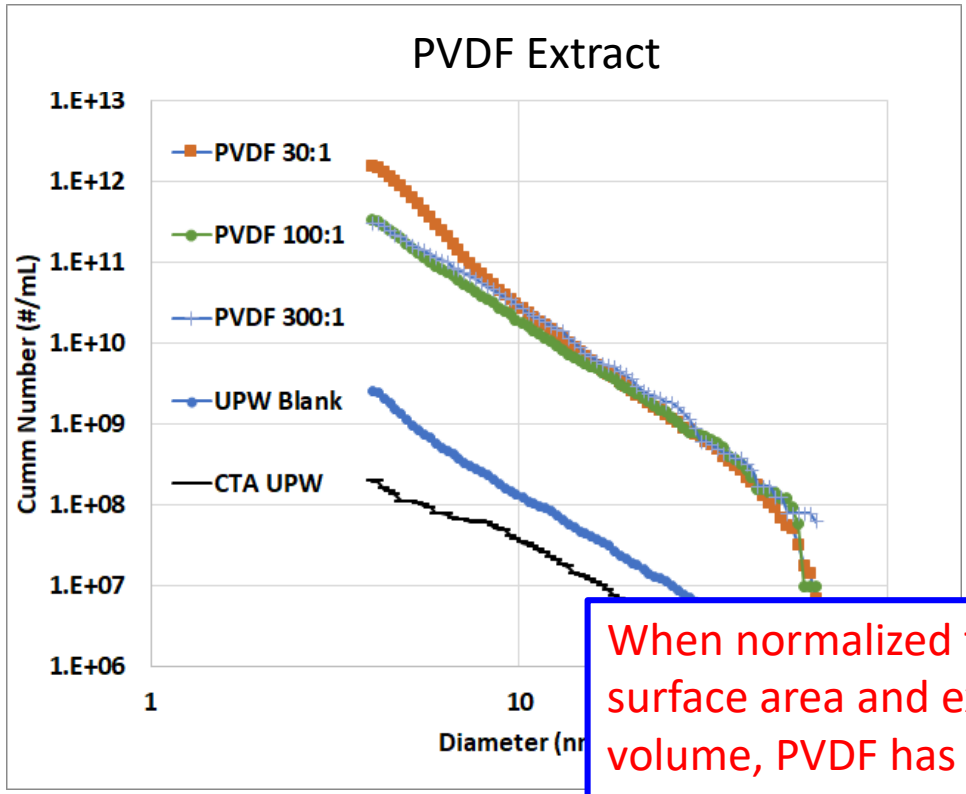
LNS Analysis of PFA and PVDF Extract, 14 Day at 85˚C





LNS Analysis of PFA and PVDF Extract, 14 Day at 85˚C

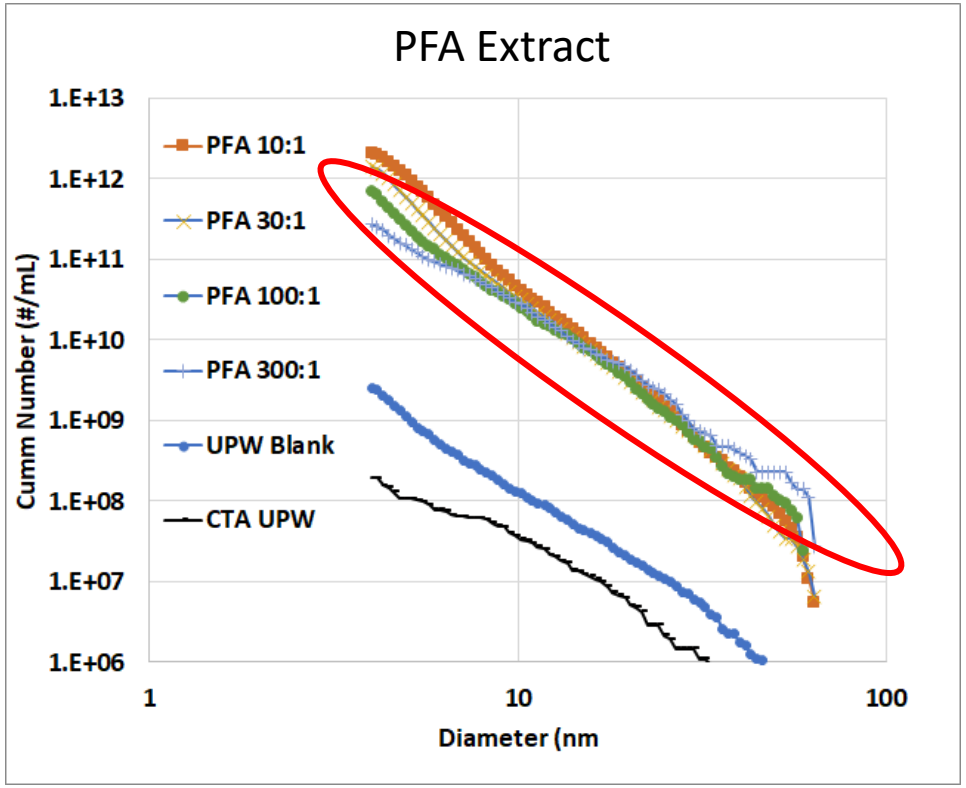


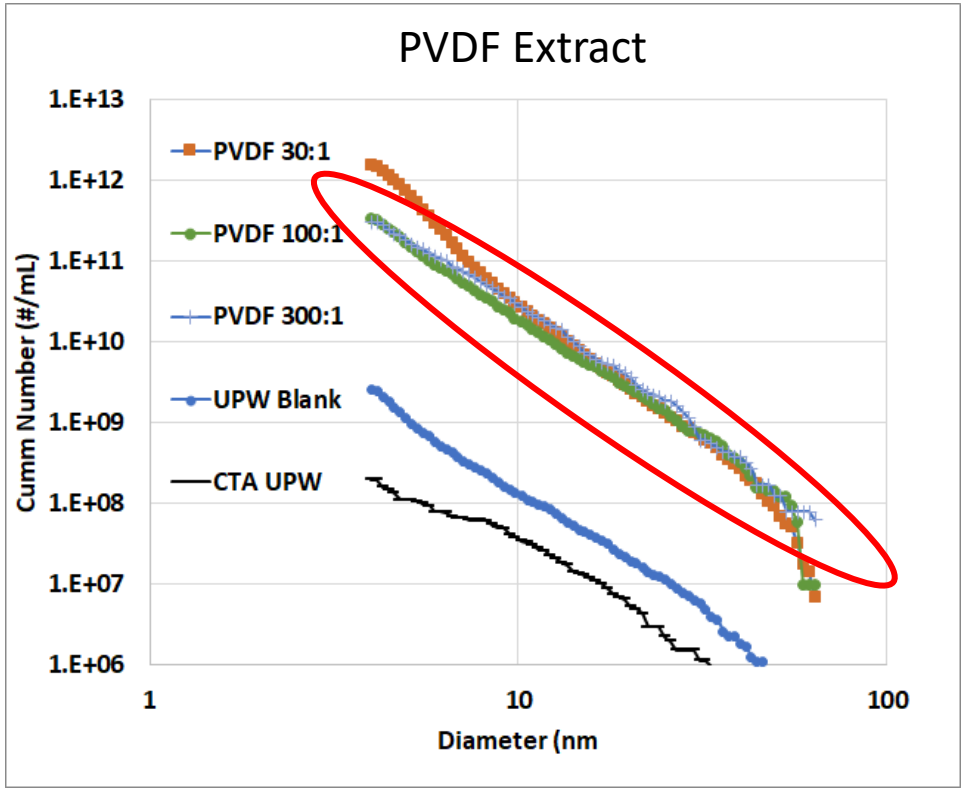


When normalized for surface area and extraction volume, PVDF has > 4 times the particle concentration of PFA.

	PFA Extract	PVDF Extract	PFA/PVDF
Surface Area to Extract volume Ratio (mm^2/mL)	384	92	4.2

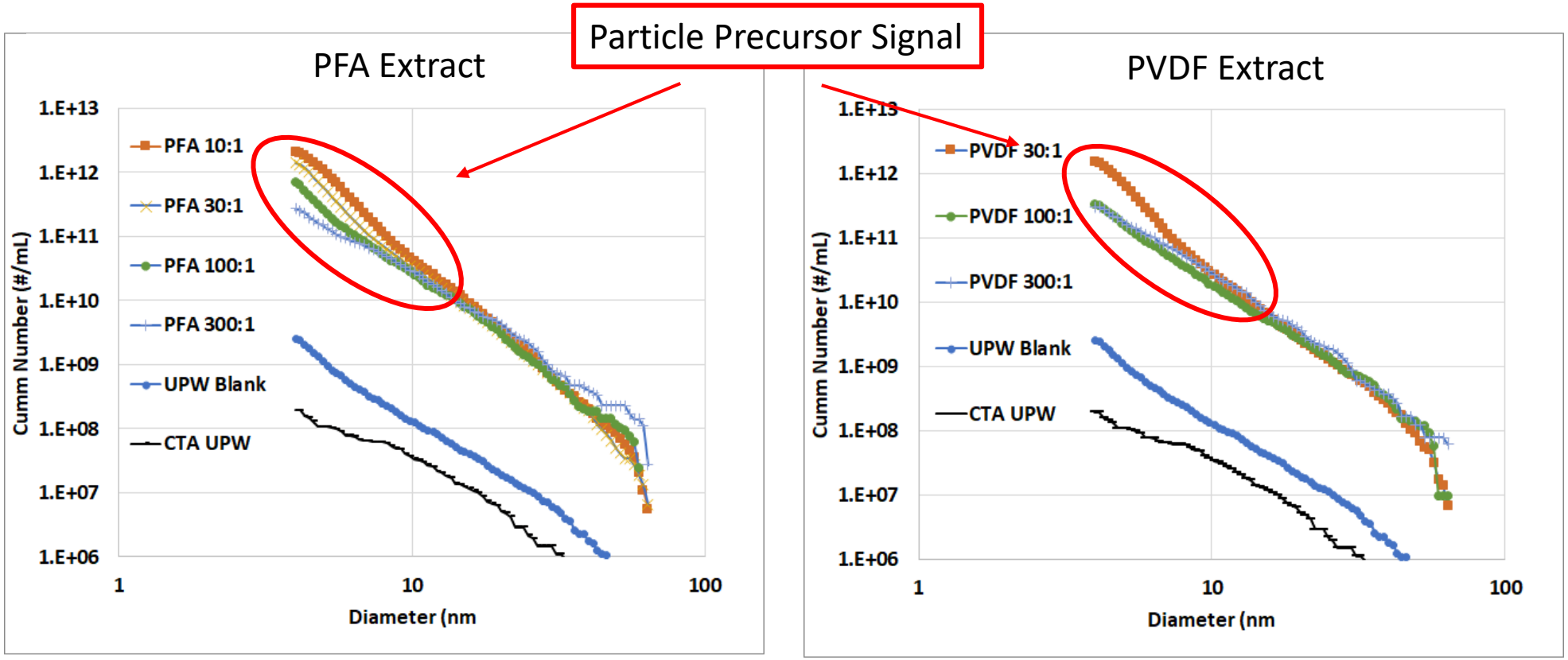
LNS Analysis of PFA and PVDF Extract, 14 Day at 85˚C





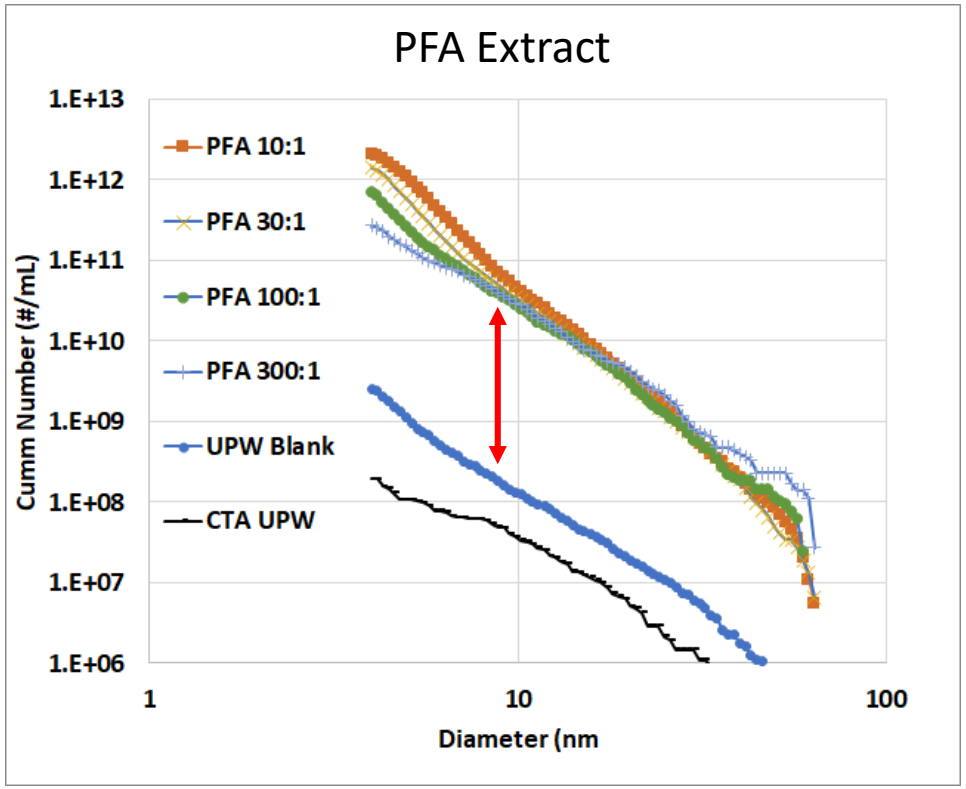
- Similar particle size distribution curves observed for both PFA and PVDF

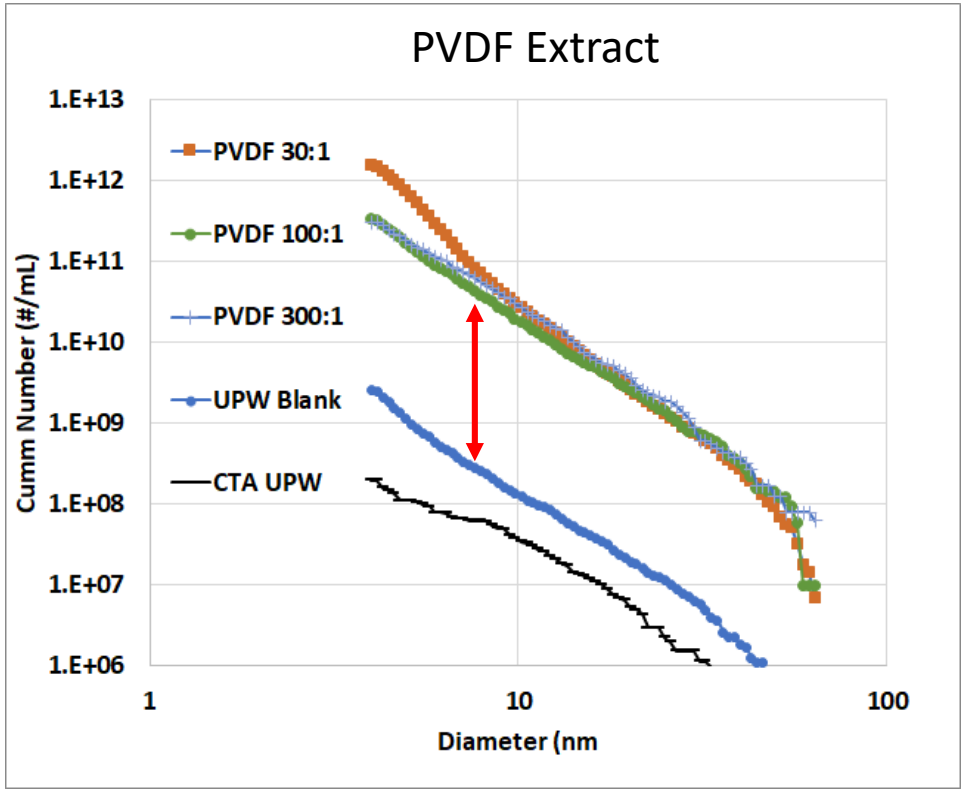
LNS Analysis of PFA and PVDF Extract, 14 Day at 85˚C



- Similar particle size distribution curves observed for both PFA and PVDF
- Particle precursors are evident in both extracts. PVDF may have a higher ratio of particle precursor to native particles.

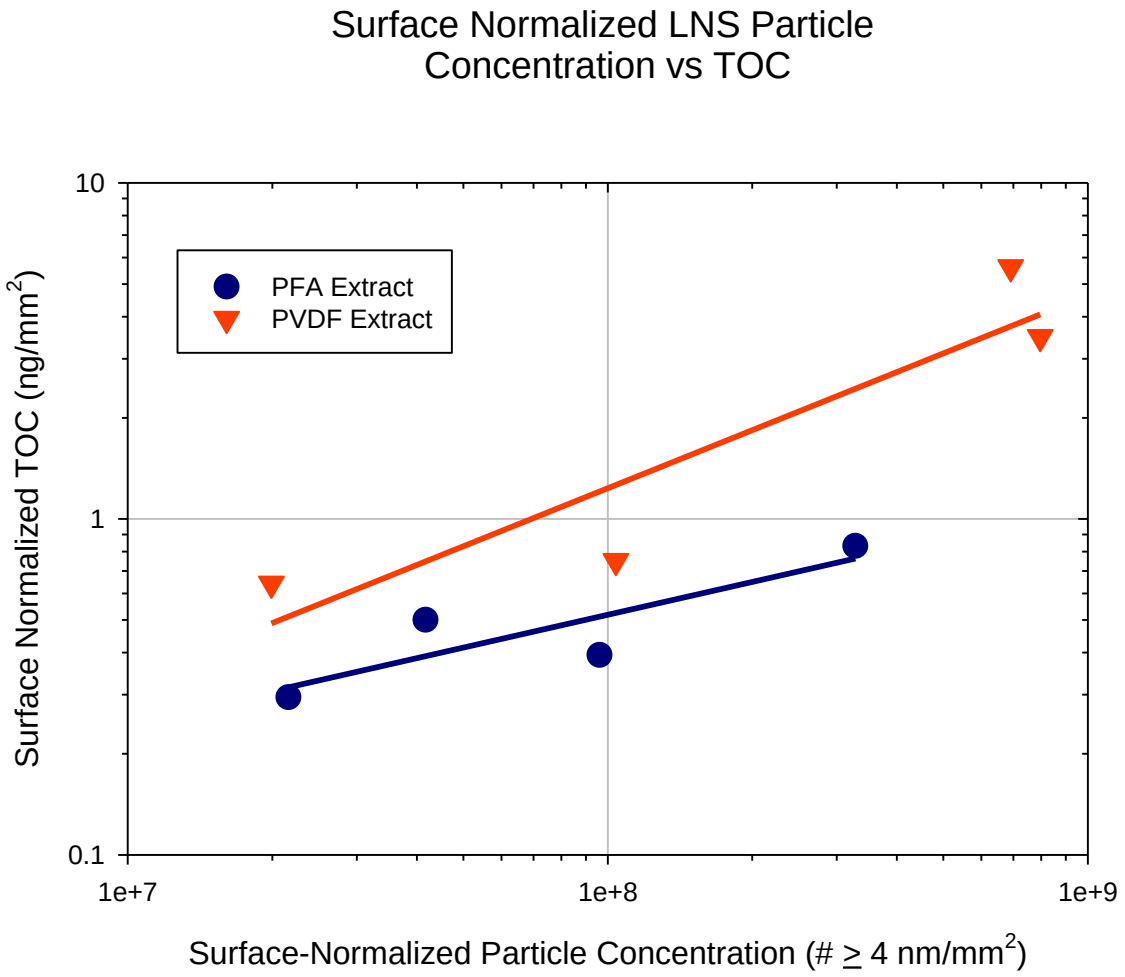
LNS Analysis of PFA and PVDF Extract, 14 Day at 85˚C





- Similar particle size distribution curves observed for both PFA and PVDF.
- Particle precursors are evident in both extracts. PVDF may have a higher ratio of particle precursor to native particles.
- Good signal to noise between extracts and method blank.

Total Organic Carbon Comparison

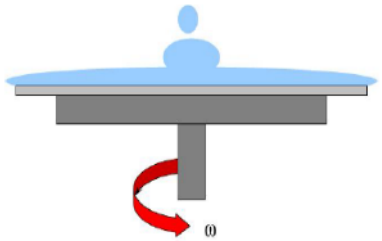


PVDF particle and particle precursors appear to be more susceptible to oxidation by UV than those in the PFA extract.*

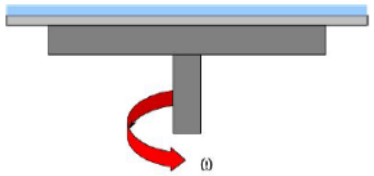
* This may be related to differences in the ratio of particle precursor and native particles between PFA and PVDF extract. More study is need here.

Wafer Prep and Surface Particle Analysis

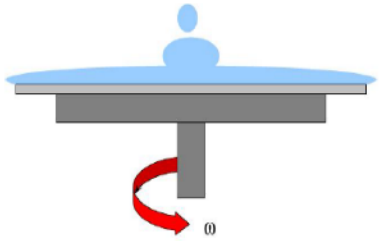
30-sec UPW pre-rinse - 80 RPM



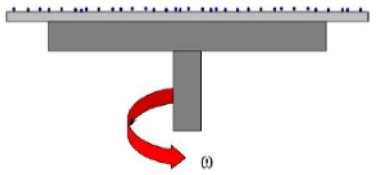
Spin dry at 1,500 rpm



120 mL extract hand pour at 80 RPM

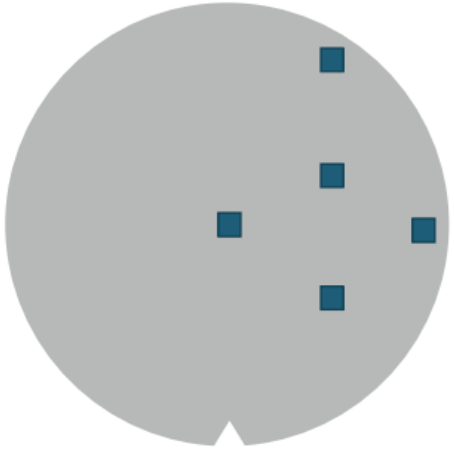


Spin dry at 1,500 rpm

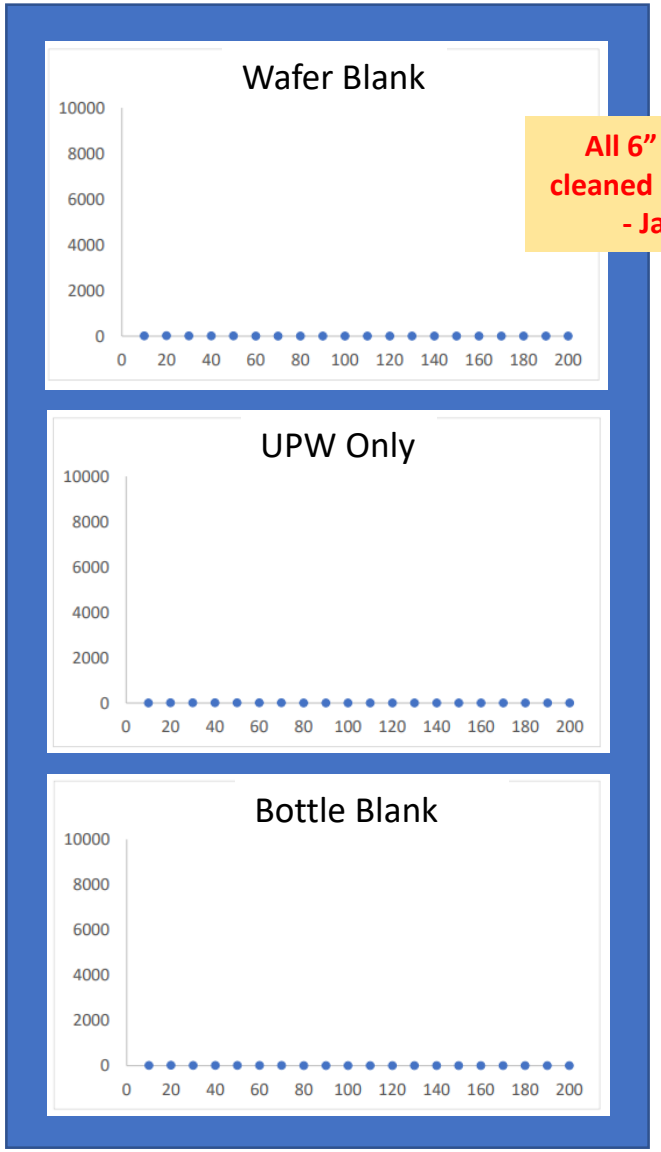


UNISERS Surface Enhanced Particle Sizing

5 scan areas, each are 1cmx1cm



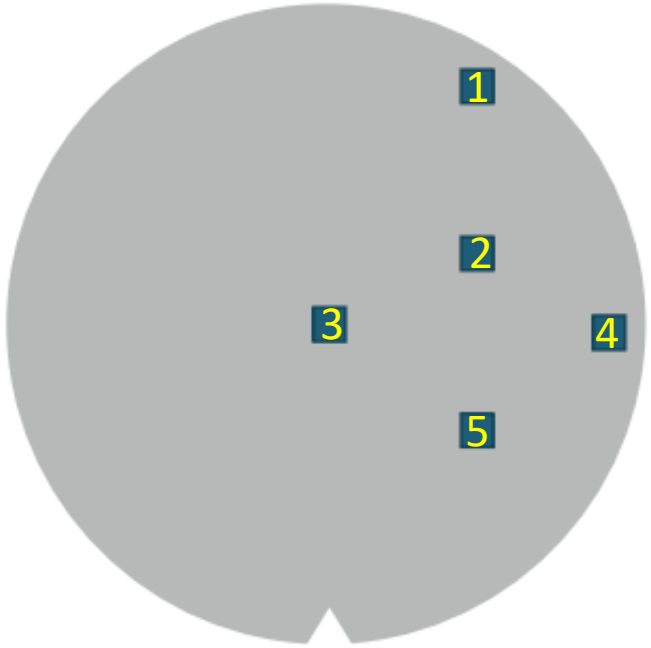
Low background levels for all control wafers and control depositions



All 6” wafers cleaned by Screen - Japan

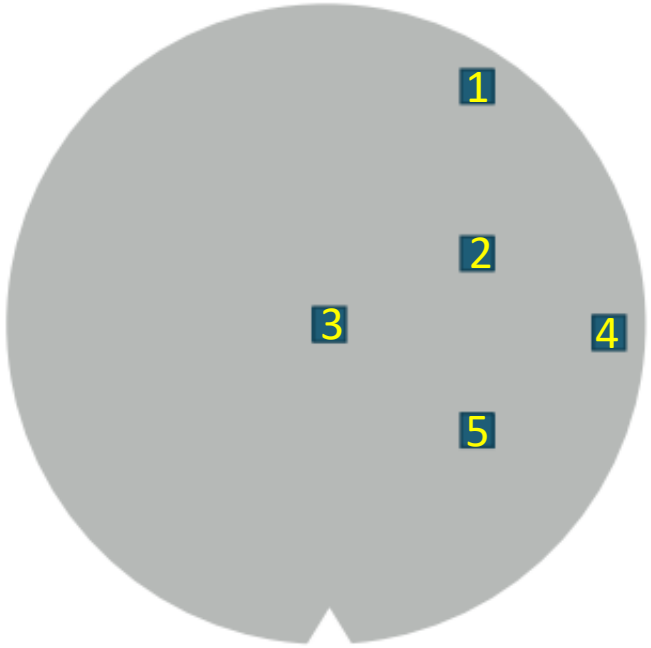
Surface Particle Scan Summary

1 cm x 1 cm scan areas



Wafer	Preparation	Total Particle (8 - 540 nm)	Wafer Location				
			1	2	3	4	5
1	None	36					
2	UPW	41					
3	Bottle Blank	55					
4	Method Blank (no dilution)	4270					
5	PVDF extract 100:1	306	80	68	115	1,165	100
6	PVDF extract 100:1	128	84	147	168	160	81
7	PVDF extract 10:1	12537	468	2,003	1,676	42,184	16,356
8	PVDF extract 10:1	16621	260	56,508	9,648	64	16,627
9	PFA extract 100:1	16897	3,296	55,724	10,584	3,296	11,585
10	PFA extract 100:1	10335	9,152	11,480	9,276	9,656	12,110
11	PFA extract 10:1	19548	1,456	11,044	51,576	336	33,328
12	PFA extract 10:1	13840	13,064	16,396	9,848	12,396	17,496
13	UPW	27					

Surface Particle Scan Summary



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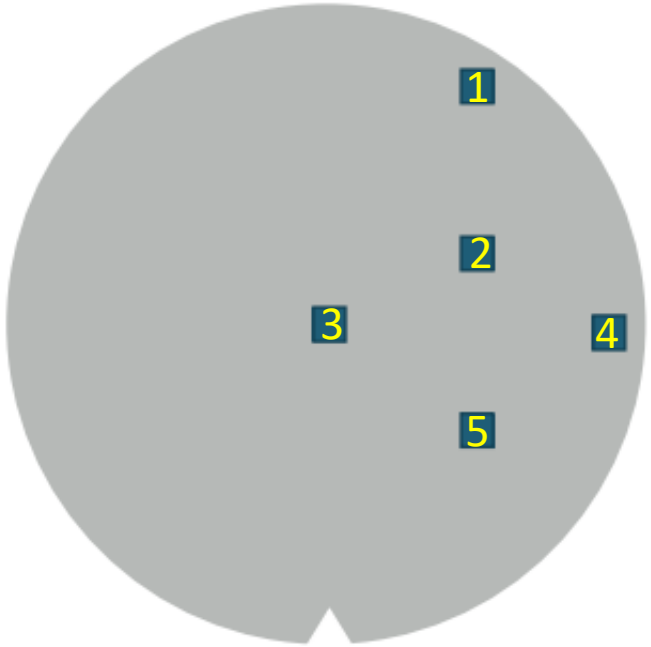
PVDF particle concentration on the wafer is not consistent with change in concentration

Surface Particle Scan Summary



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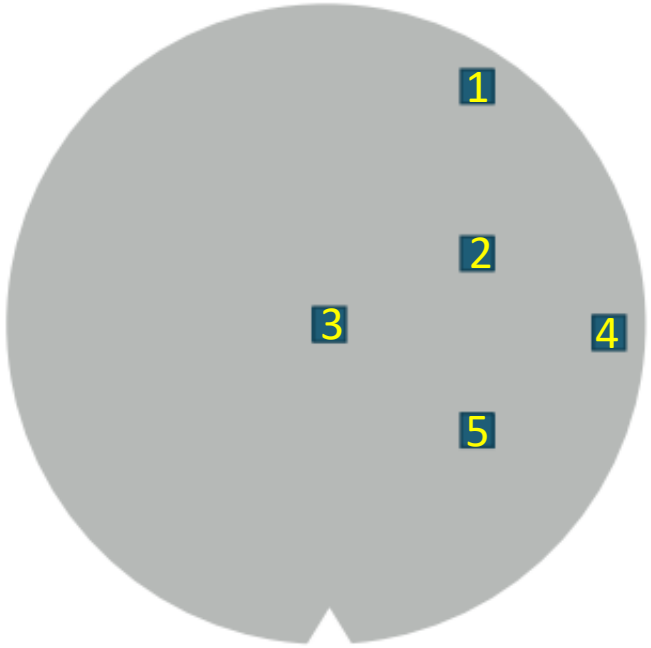
PFA particle concentration on the wafer is not consistent with change in concentration

Surface Particle Scan Summary



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13	UPW	27					

Extremely high variability over the wafer surface.

Surface Enhanced Raman Summary

Wafer	Preparation	Total Particle (8 - 540 nm)	Wafer Location				
			1	2	3	4	5
1	None	36					
2	UPW	41					
3	Bottle Blank	55					
4	Method Blank (no dilution)	4270					
5	PVDF extract 100:1	306	80	68	115	1,165	100
6	PVDF extract 100:1	128	84	147	168	160	8
7	PVDF extract 10:1	12537	468	2,003	1,676	42,184	16,356
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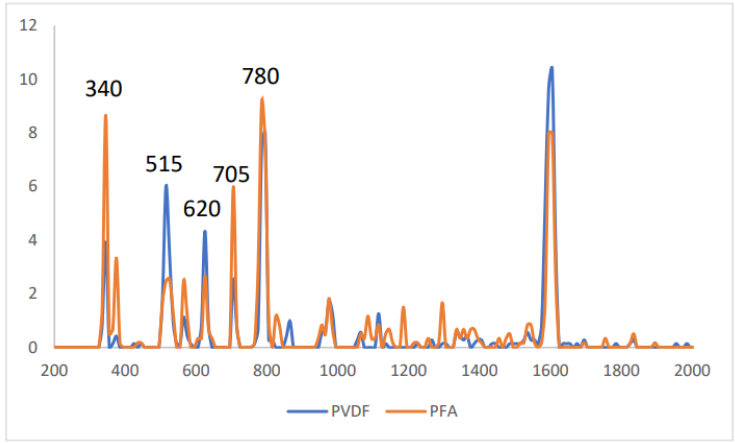
13	UPW	27					

However…it is clear that particles from PFA and PVDF extract adhere to the wafer surface!!



Reference Raman peaks:
340cm^{-1}
515cm^{-1}
620cm^{-1}
705cm^{-1}
780cm^{-1}

PFA Reference

PVDF Reference

Wafer	Method blank (W4)	PVDF-extract 10:1 (W6)	PFA Extract 10:1 (W9)
Spectra acquired	21	51	62
Inorganic spectra	42.9%	8.3%	10.9%
Organic spectra with 5 of the reference bands	0.0%	6.3%	1.8%
Organic spectra with 4 of the reference bands	4.8%	25.0%	14.5%
Organic spectra with 3 of the reference bands	9.5%	56.3%	29.1%

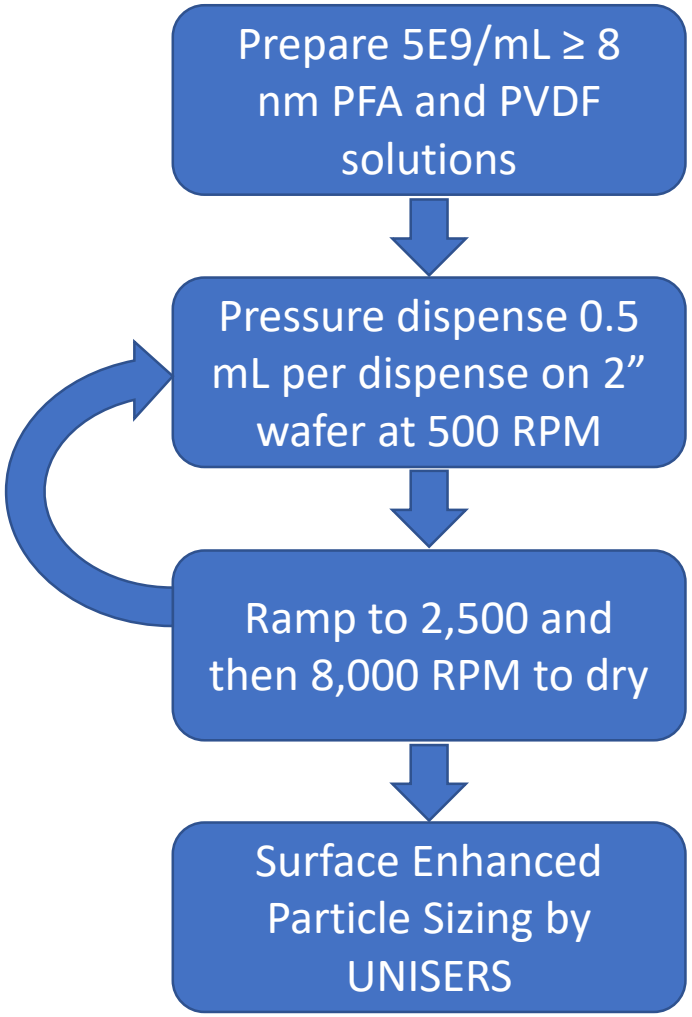
Three or more reference peaks identified in spectra

87.6% PVDF

45.4% PFA

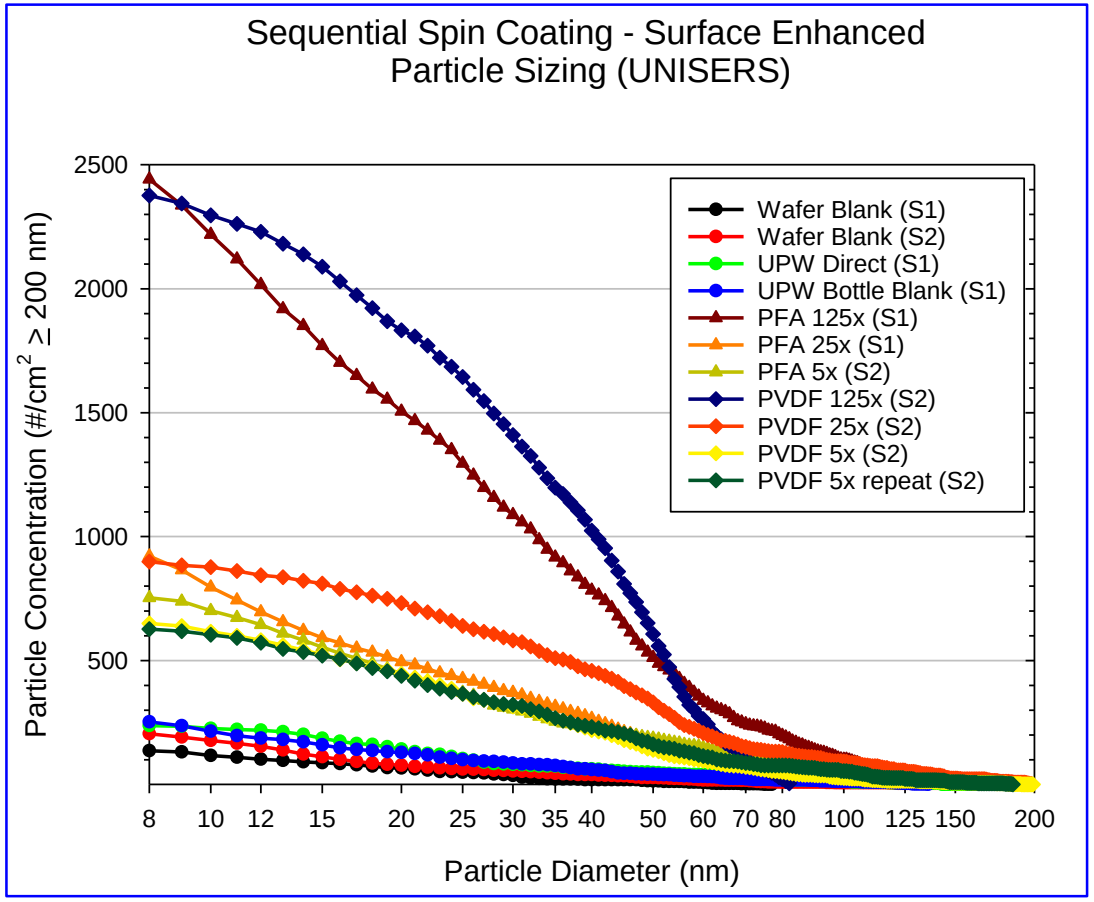
Alternate Approach to Wafer Preparation – Sequential Spin Coating

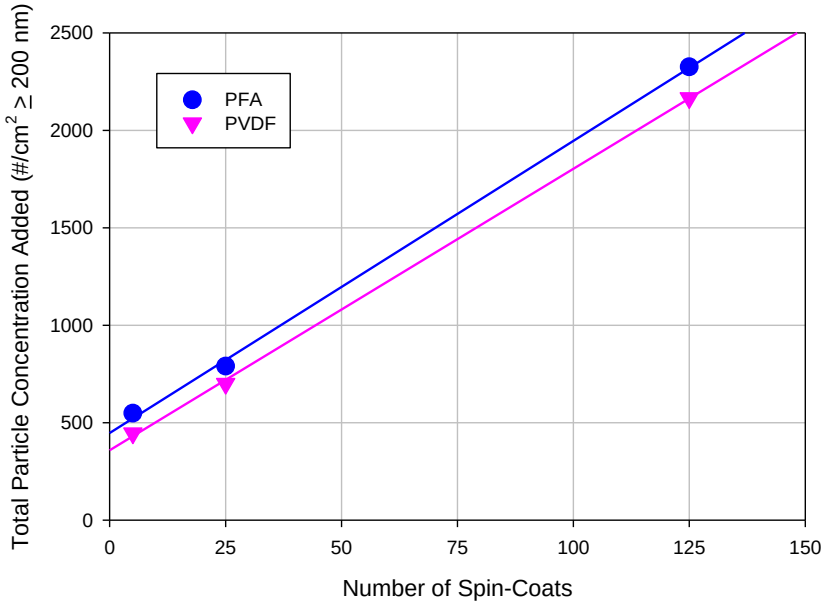
- **Objective:** Demonstrate feasibility of preparing a uniform PSD using automated sequential spin coating on 2” wafer.



Alternate Approach to Wafer Preparation – Sequential Spin Coating

Sample ID
Wafer Blank W1
UPW Direct 125x
UPW Bottle 125x
PFA 125x
PFA 25x
PFA 5x
PVDF 125x
PVDF 25x
PVDF 5x
PVDF 5x(2)
Wafer Blank W14



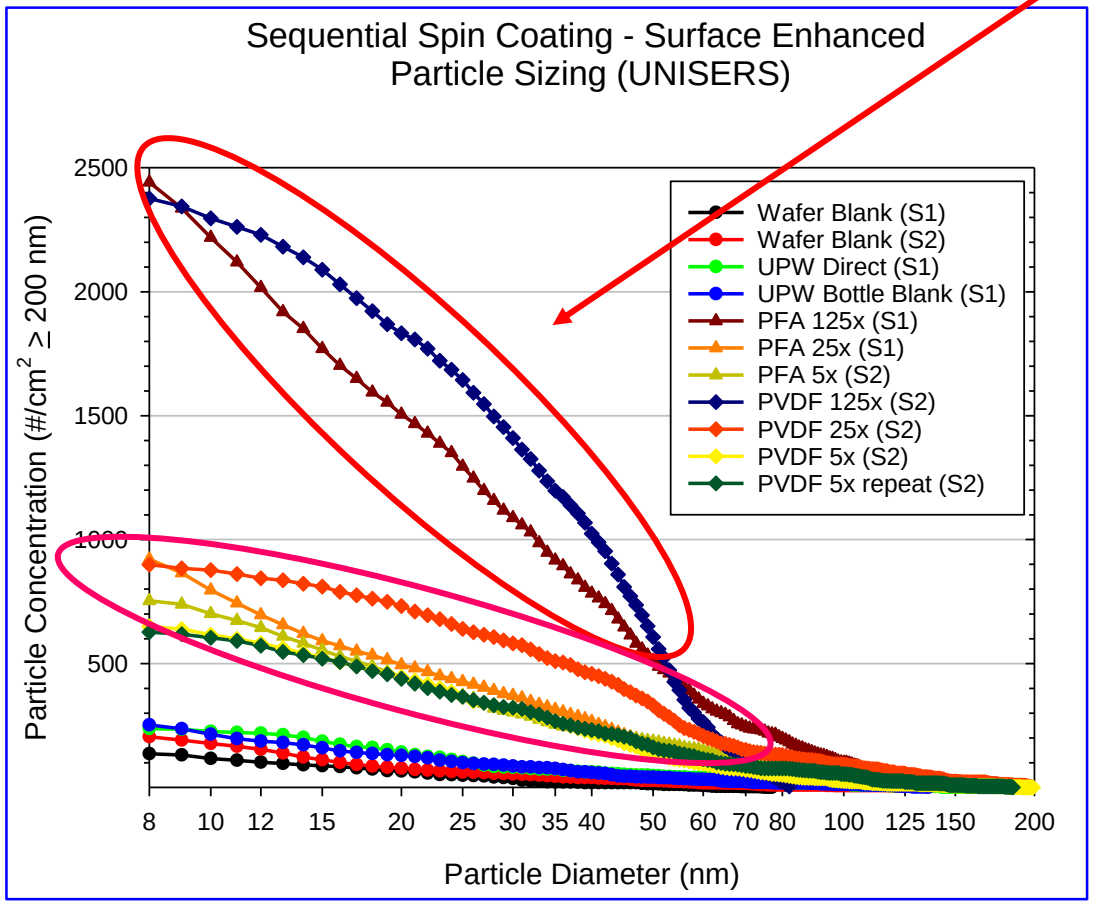


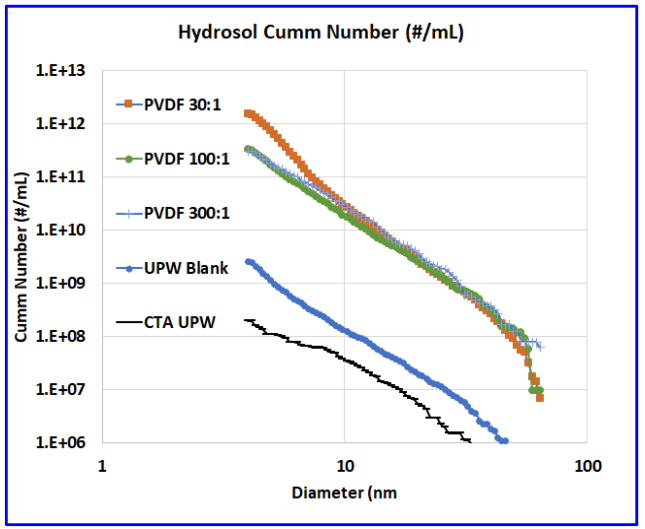
2” wafers cleaned by Screen – Japan
10-fold reduction in background level compared to as-received.

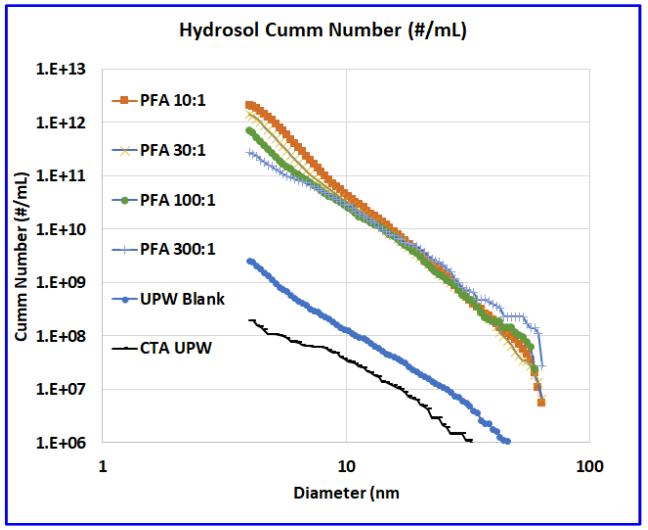
Alternate Approach to Wafer Preparation – Sequential Spin Coating

Different on-wafer PSD for PFA and PVDF

Sample ID
Wafer Blank W1
UPW Direct 125x
UPW Bottle 125x
PFA 125x
PFA 25x
PFA 5x
PVDF 125x
PVDF 25x
PVDF 5x
PVDF 5x(2)
Wafer Blank W14

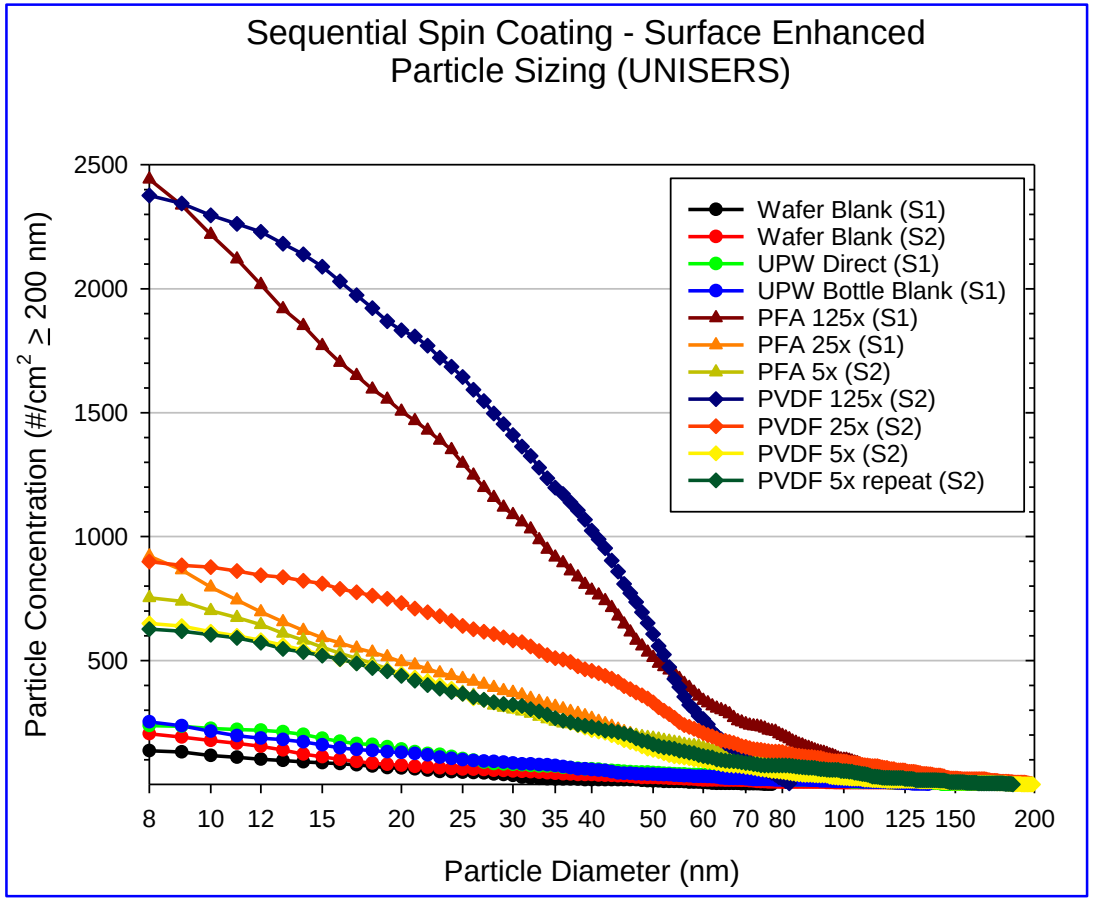




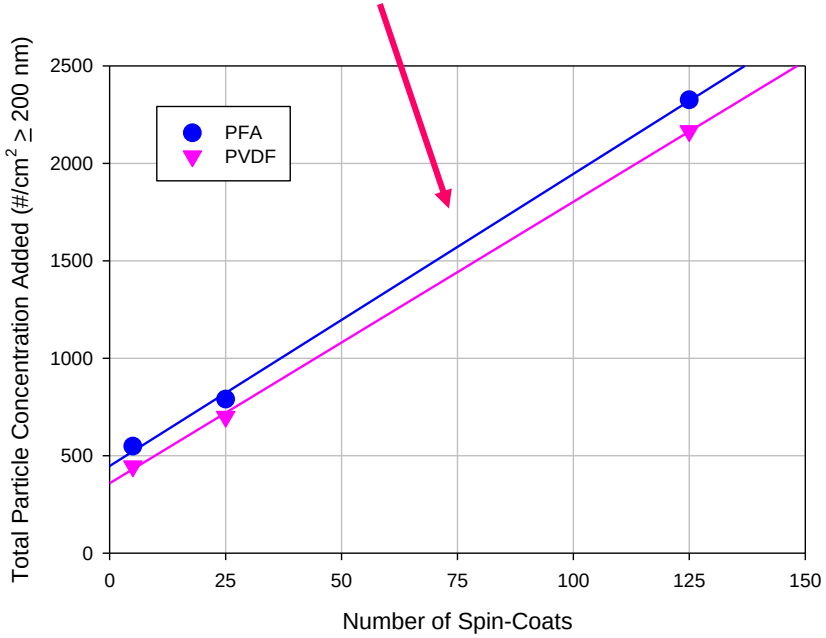


Future Approach to Wafer Preparation – Sequential Spin Coating

Sample ID
Wafer Blank W1
UPW Direct 125x
UPW Bottle 125x
PFA 125x
PFA 25x
PFA 5x
PVDF 125x
PVDF 25x
PVDF 5x
PVDF 5x(2)
Wafer Blank W14

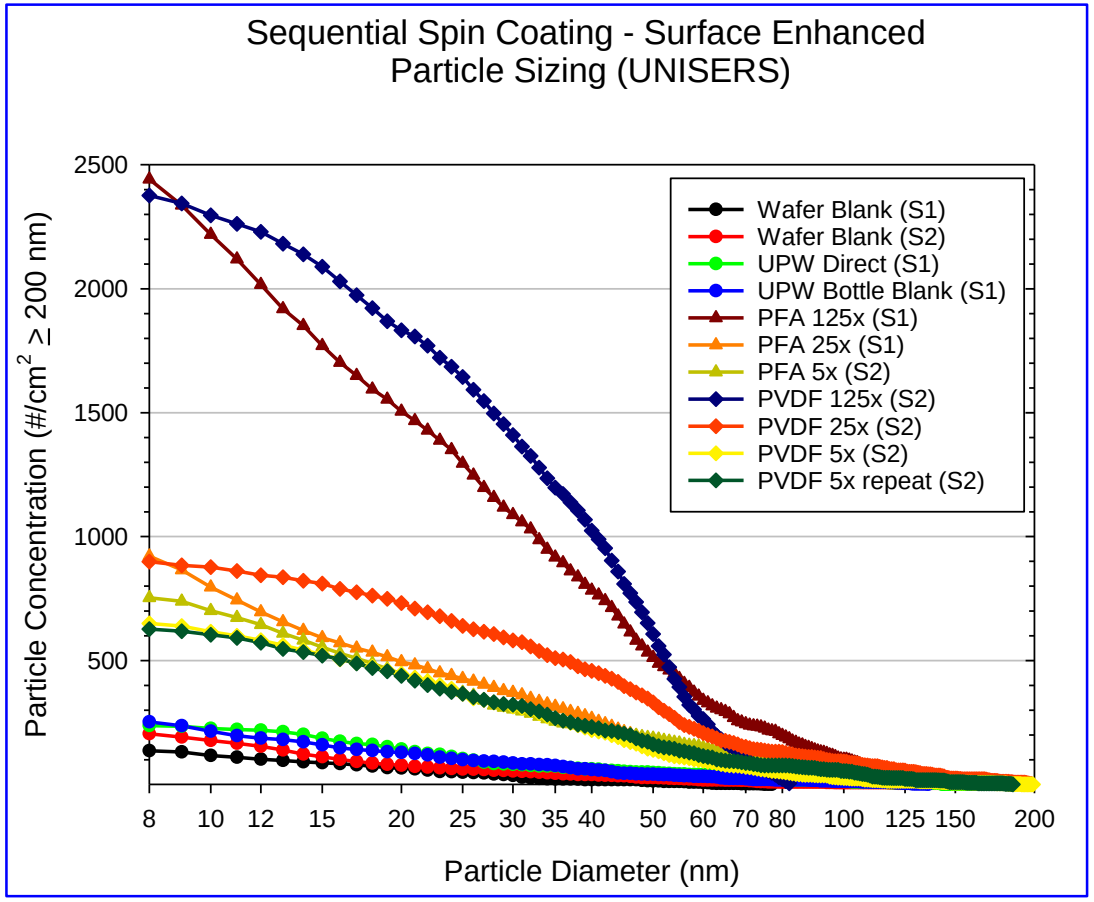


- Different on-wafer PSD for PFA and PVDF
- Linear increase in particle concentration with # of coats

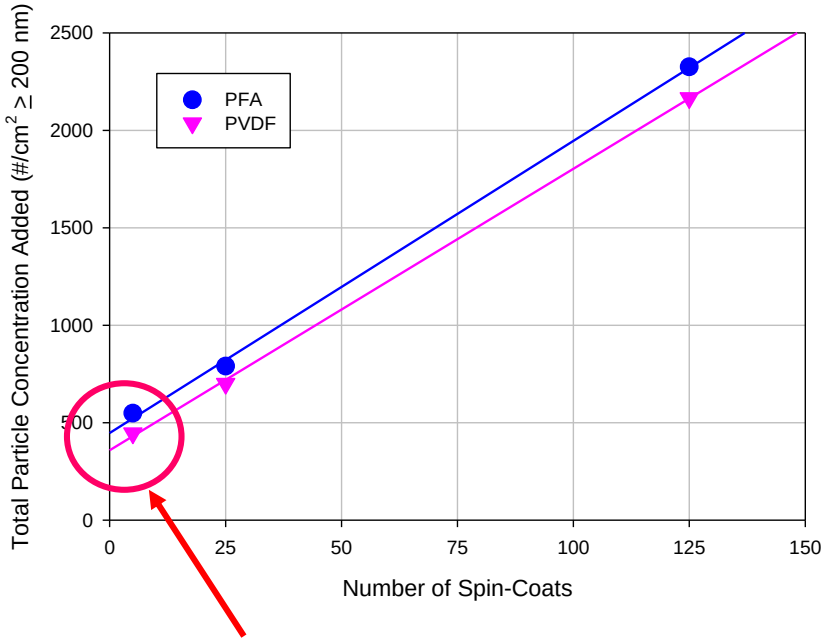


Future Approach to Wafer Preparation – Sequential Spin Coating

Sample ID
Wafer Blank W1
UPW Direct 125x
UPW Bottle 125x
PFA 125x
PFA 25x
PFA 5x
PVDF 125x
PVDF 25x
PVDF 5x
PVDF 5x(2)
Wafer Blank W14



- Different on wafer PSD for PFA and PVDF
- Linear increase in particle concentration with # of coats

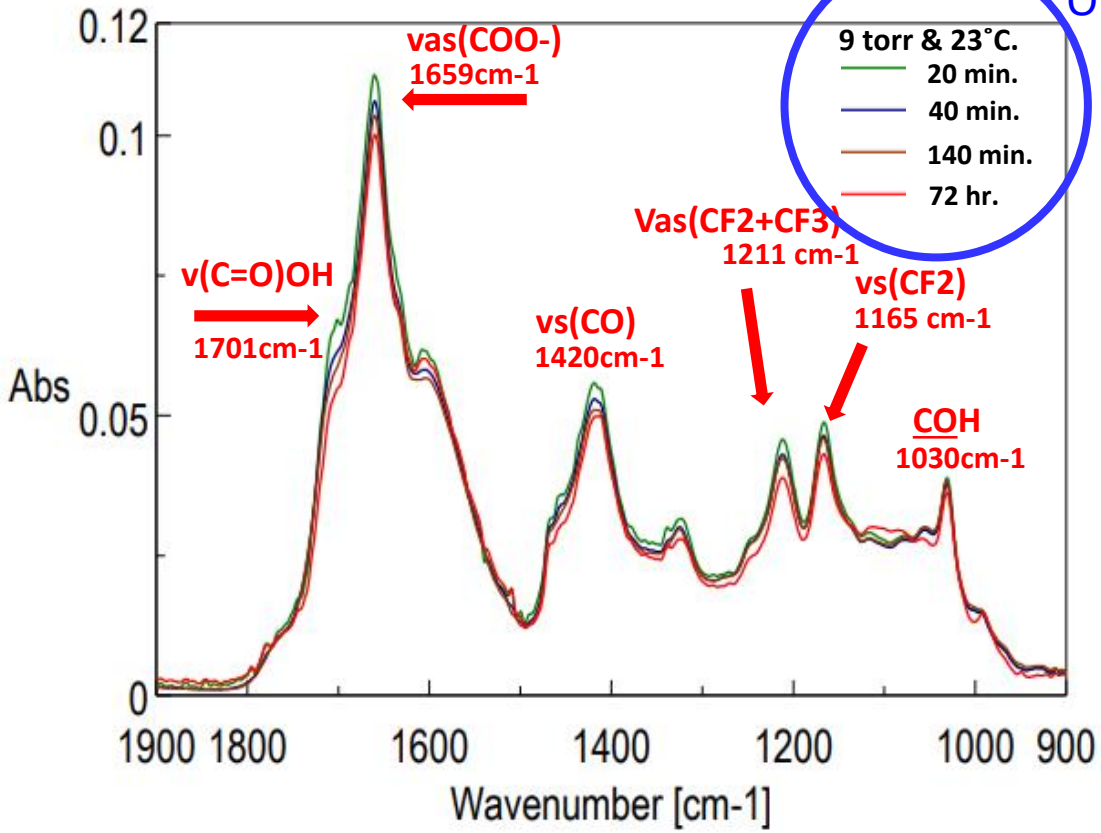


- Important to understand the reason for the intercept offset before we can use this as a proactive tool.

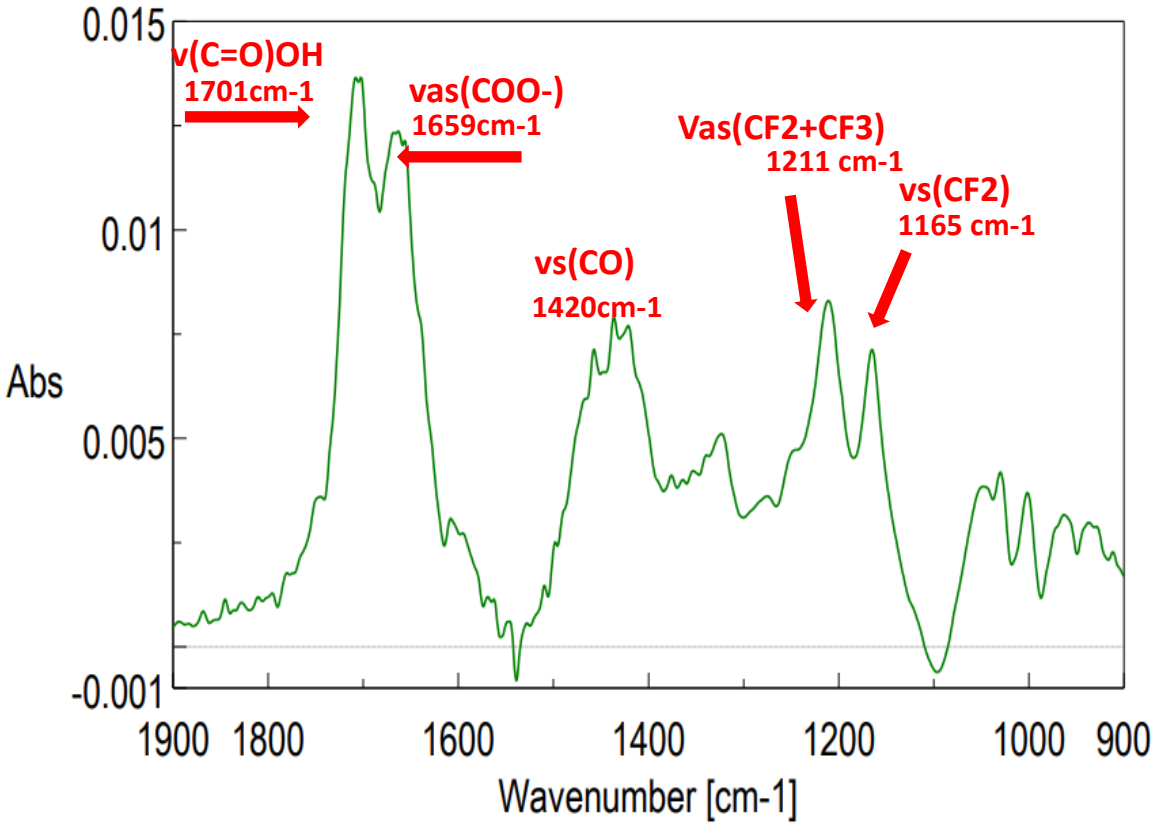
Candidate Approach to ID Critical Organics – Thermal and Vacuum Desorption by FTIR (PFA Example)

FTIR Spectra as Measured

Vacuum Only



FTIR Desorption Spectra



IR peak intensity decreases with extract evaporation; lower volatiles "critical organic" remain.

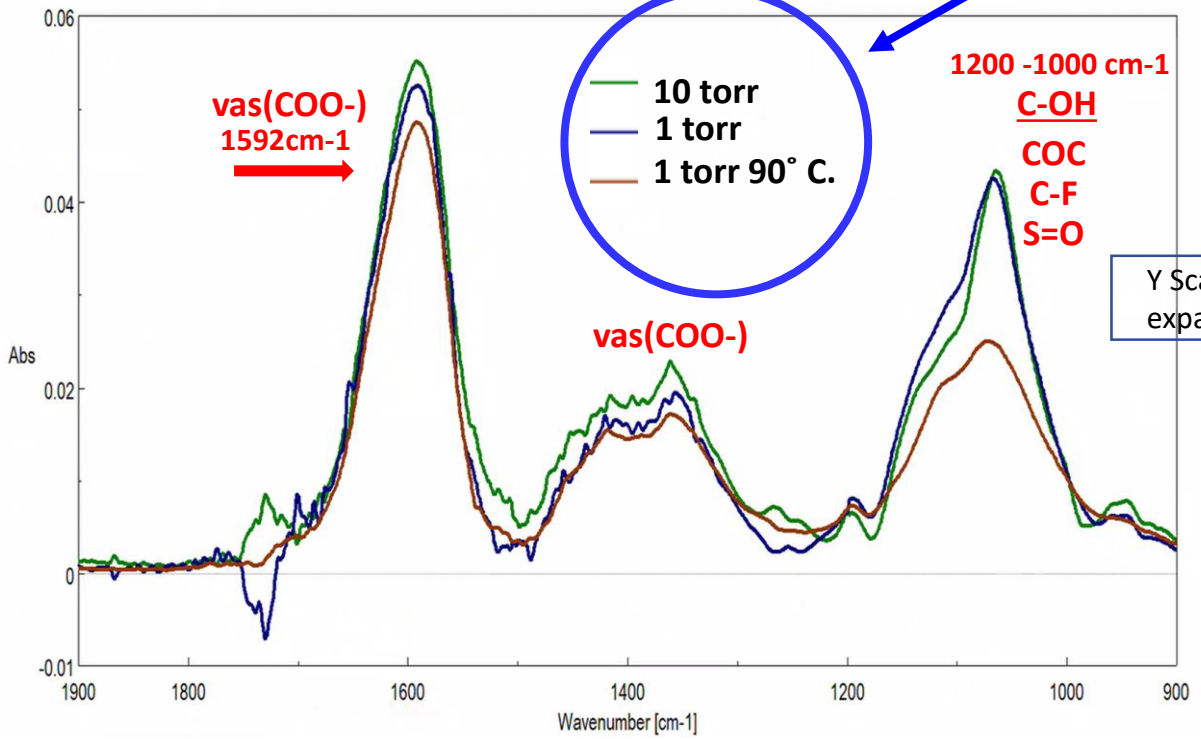
Released PFA volatiles calculated by subtracting 72-hr. spectrum from 20 min spectrum.

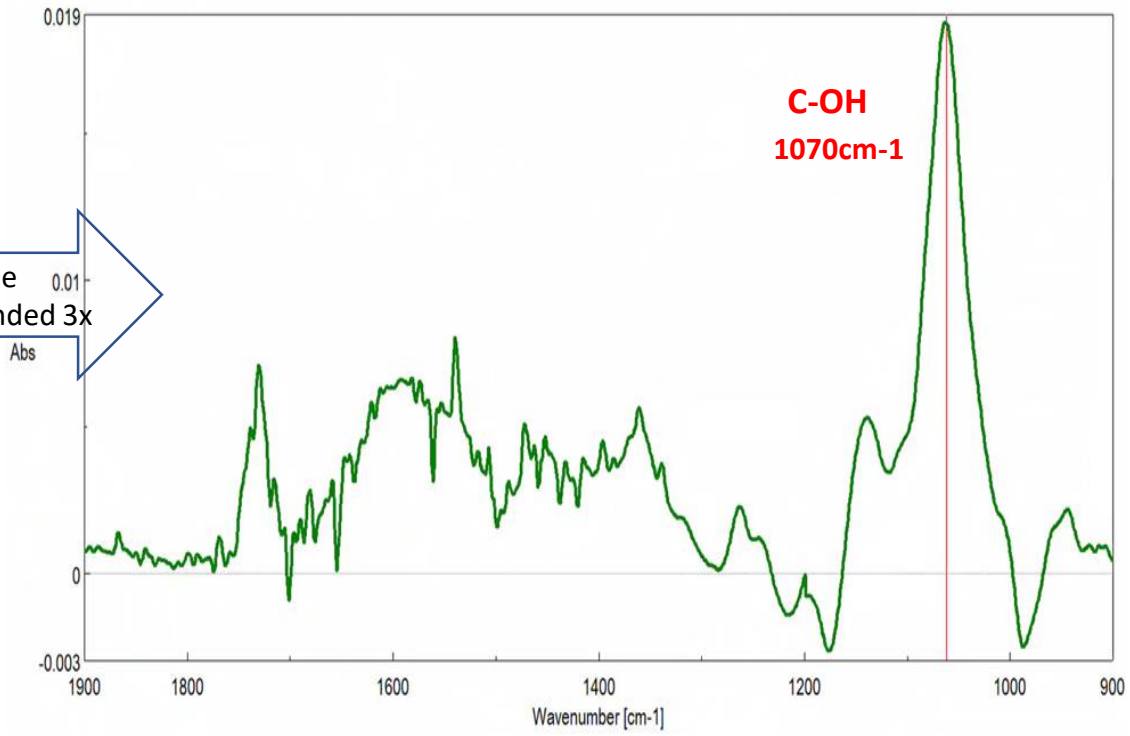
Candidate Approach to ID Critical Organics – Thermal and Vacuum Desorption by FTIR (PVDF Example)

FTIR Spectra as Measured

Vacuum and temperature

FTIR Desorption Spectra





IR peak intensity decreases with extract evaporation; lower volatiles "critical organic" remain.

Released PVDF volatiles calculated by subtracting 1 Torr, 90°C spectrum from 10 Torr spectrum.

Summary and Take-aways

- Extended SEMI F40 extraction* of PFA tube and PVDF pipe provides an extract solution with particle and particle precursor concentrations suitable for quantification by LNS and TOC analysis.
- Particle and particle precursor extracts extracted by hot UPW adhere to the wafer surface under spin-coat processing as measured by Surface Enhanced Particle Sizing (SEPS) and Surface Enhanced Raman Spectroscopy (SERS) and therefore present a yield risk.
- Single, hand-pour deposition of the extract solution fails to provide a uniform distribution of particles over the surface.
- Sequential spin coating in conjunction with SEPS may have potential for quantifying particle adhesion risk with the particle concentration in the solution. Additional work is needed to validate repeatability and understand the reason for the intercept offset.
- FTIR with varied temperature and vacuum is showing promise in identifying desorbed and residual organics (i.e. critical organics).

*with concentrated surface to volume ratio

Thank you for your attention!!