STRONGER TOGETHER

Identification of Organic Particle Precursors using ATR-IR, SERS and AFM-IR

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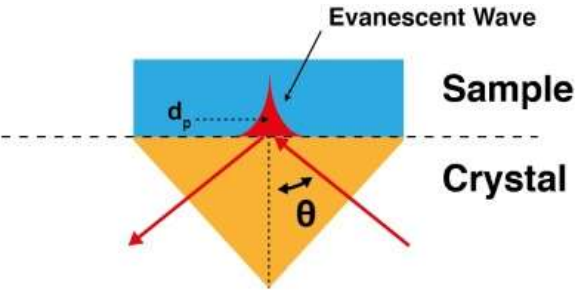
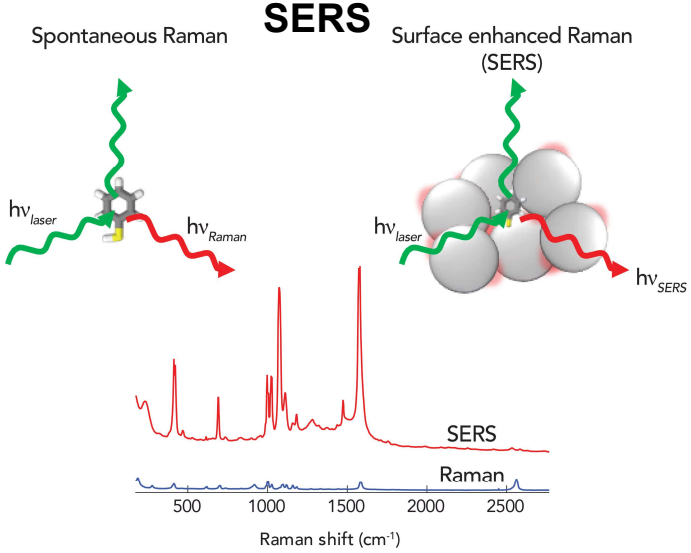
Some Vibrational Spectroscopy Methods

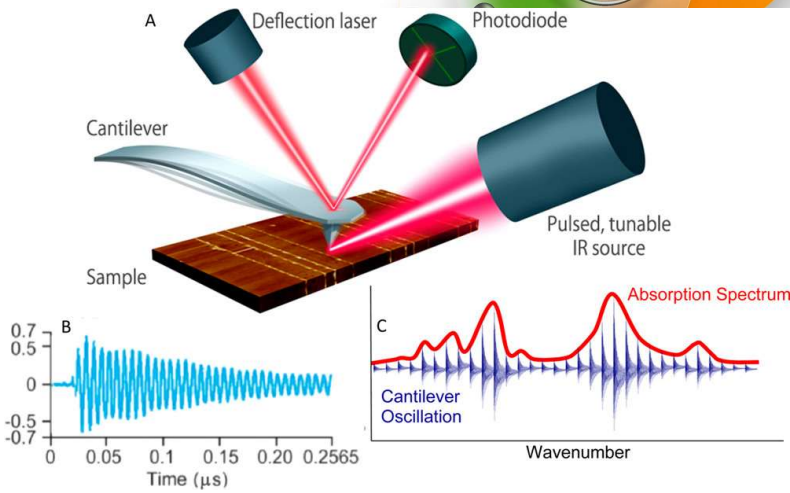
ATR-IR



SERS



AFM-IR



Vibrational spectroscopy methods chemically speciate semi-volatile and non-volatile contaminants present as thin films, particles or monolayers on surfaces.

All **three of these analytical methods can detect specific chemical bonds in a wide range of organic and inorganic contaminants**.

The underlying **physics and instrumentation of these analytical techniques are quite different**.

Previous work on particle precursors

Identification of Organic Particle Precursors in MBIX "Extract" and Ultrapure Water

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Note: Collaboration needed for multiple analytical methods approach

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What We Know and a Problem Statement

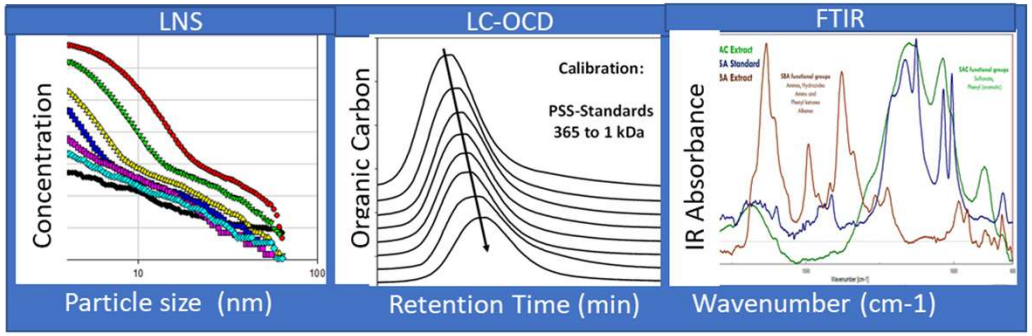
- Particle precursors (dissolved compounds) are present in UPW and pose a risk of depositing on wafers.
- Mixed bed (MB) ion exchange (IX) is a known potential source of particle precursors.
- To mitigate the risk, the SEMI UPW Task Force is developing a particle precursor challenge based on IX resin to evaluate sub-15 nm filters used for ultrapure water (UPW).
- Size, composition and reactivity data from extract is needed to identify potential particle precursors and to develop organic particle precursor challenges.

MBIX "Extract" Technical Objectives

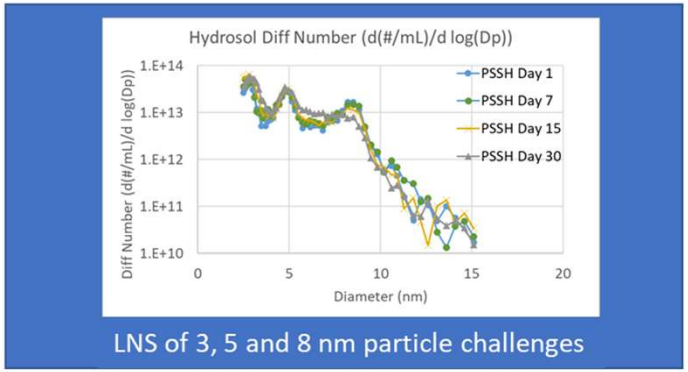
1. Extract "useful" concentrations of organics from isolated SAC and SBA resins

Extract organics from Ion Exchange Resin (UPW 80°C, 7 days)

2. Characterize the size, chemical composition and reactivity of organic particles and particle precursors
   - Liquid Nanoparticle Sizing (LNS)
   - Size Exclusion Liquid Chromatography with Organic Carbon Detection (LC-OCD)
   - Attenuated Total Reflection Infrared (ATR-IR)



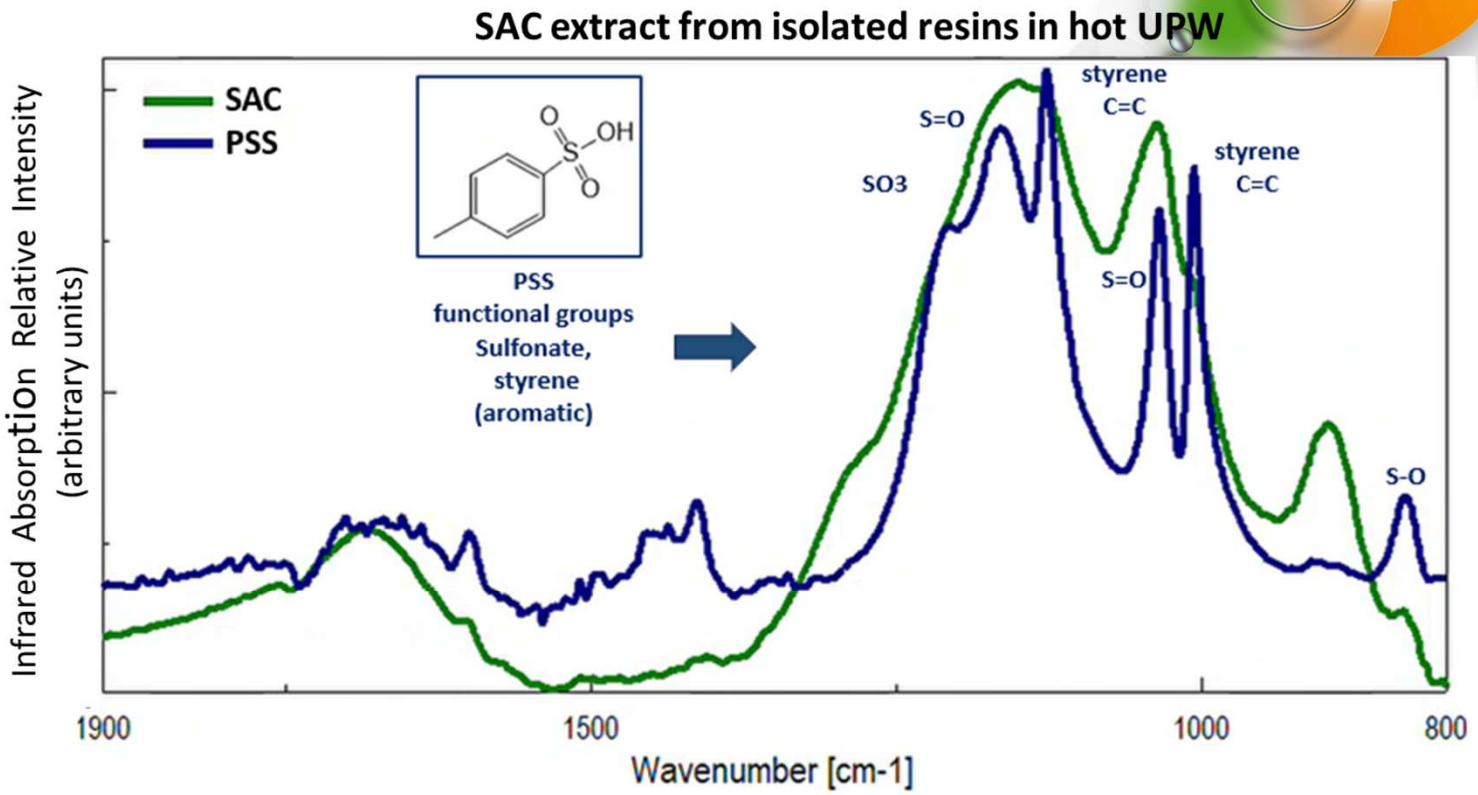
3. Provide knowledge to develop nanoparticle challenges for sub 15 nm filter devices



LNS of 3, 5 and 8 nm particle challenges

Potential Particle Precursors according to ATR-IR

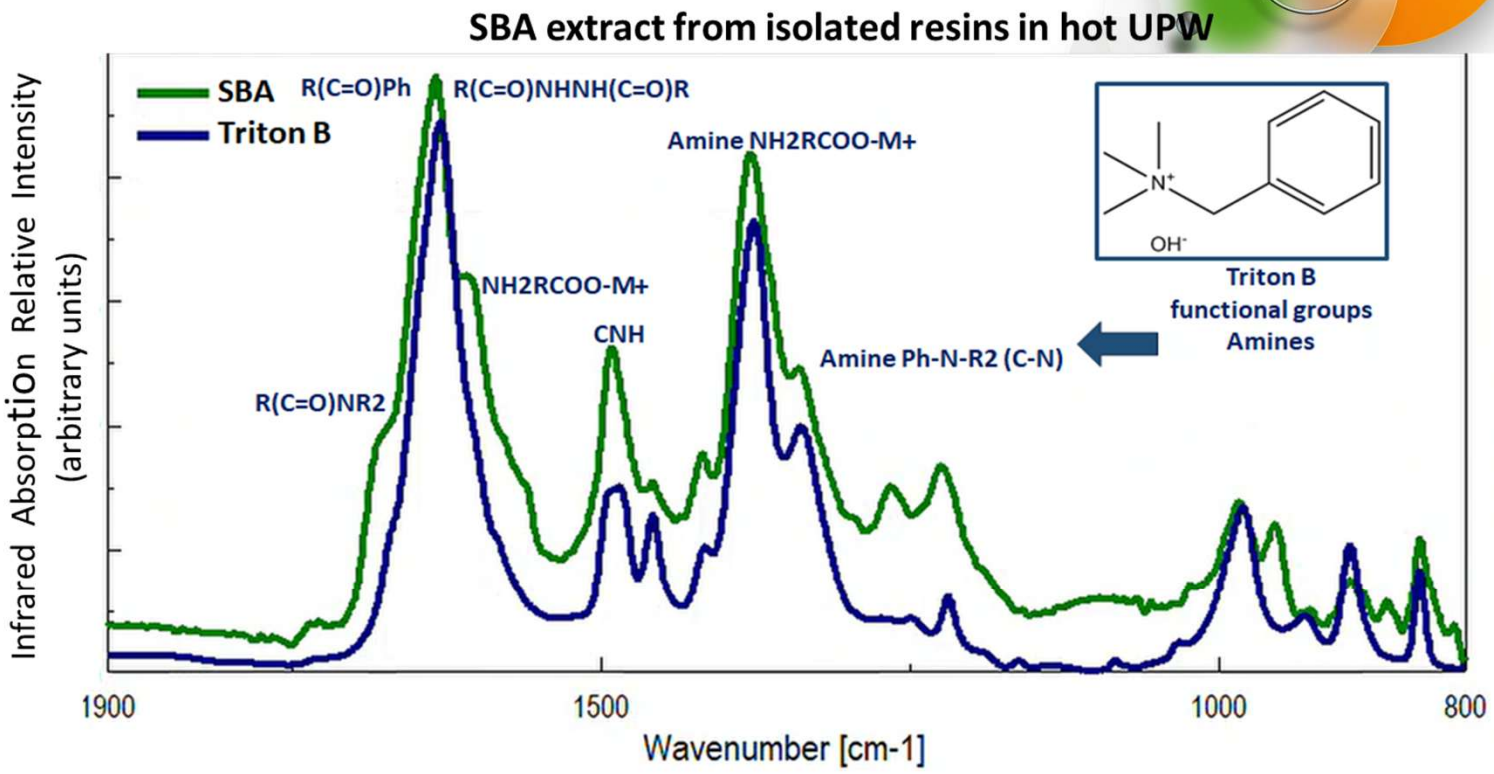
- **SAC Extract** shows organic sulfonate and styrene peaks **like polystyrene sulfonic acid (PSS)** standard.



Clear similarities between SAC and PSS standard

Potential Particle Precursors according to ATR-IR

- **SBA Extract** shows organic nitrogen peaks like **benzyltrimethyl ammonium hydroxide (Triton B)** standard.

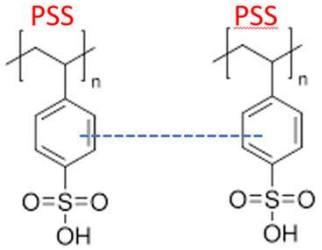


Clear similarities between SBA and Triton B standard

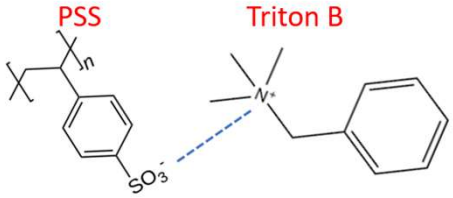
Identification of Organic Particle Precursors in MBIX "Extract" Summary

- SAC extract contains low molecular weight (LMW) and high-molecular weight (HMW) PSS and is an obvious source of potential particle precursors.
- SBA extract contains LMW organic nitrogen which is not an obvious particle precursor.
- SAC and SBA extracts can react upon drying to form new HMW material.
- We proposed three pathways to transform potential particle precursors to particles on wafers.

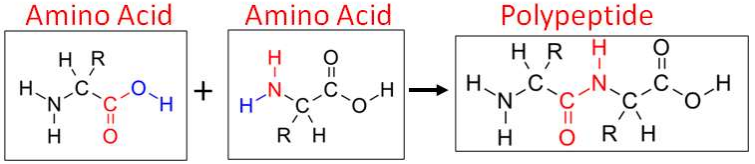
1. "Pi-stacking" of PSS from SAC



2. "Ion pairing" of anionic PSS from SAC with cationic Triton B from SBA



3. "Condensation polymerization" of amino acids from SBA

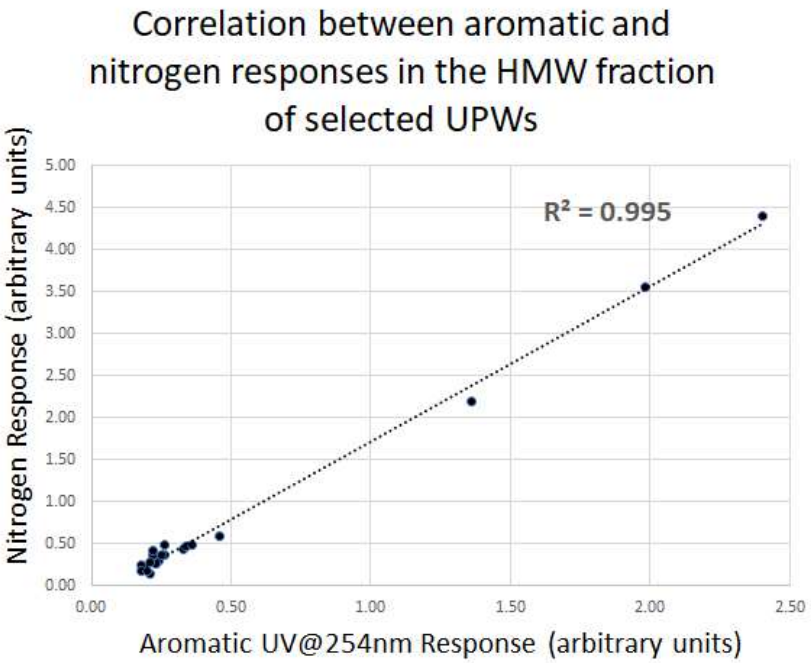


UPW Technical Objective

1. **Collect** UPW samples from different facilities
   - Not high concentrated extract from isolated SAC and SBA resins
2. **Measure** size and composition of trace organics in UPW
   - Size exclusion Liquid Chromatography with organic carbon detection (LC-OCD)
3. **Measure** composition of trace organics on wafers
   - Surface Enhanced Raman Spectroscopy (SERS)

Can we find high molecular weight (HMW) organics from polishing MB in UPW and on wafers?

UPW Data

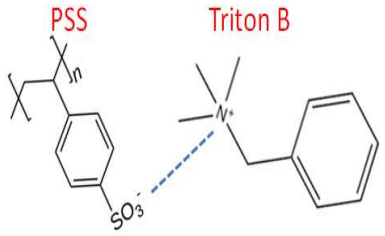


DOC-LABOR has conducted some 1000 analyses of UPWs.

- Samples cover plant monitoring, plant commissioning, and at out-of-spec situations.

The relationship between the aromatic and nitrogen responses suggest a common source:

- PSS anions and Triton B cations are in direct contact in the MBIX and undergo ion pairing.
- The ion pair complexes travel through the MBIX unnoticed as non-ionic particles.

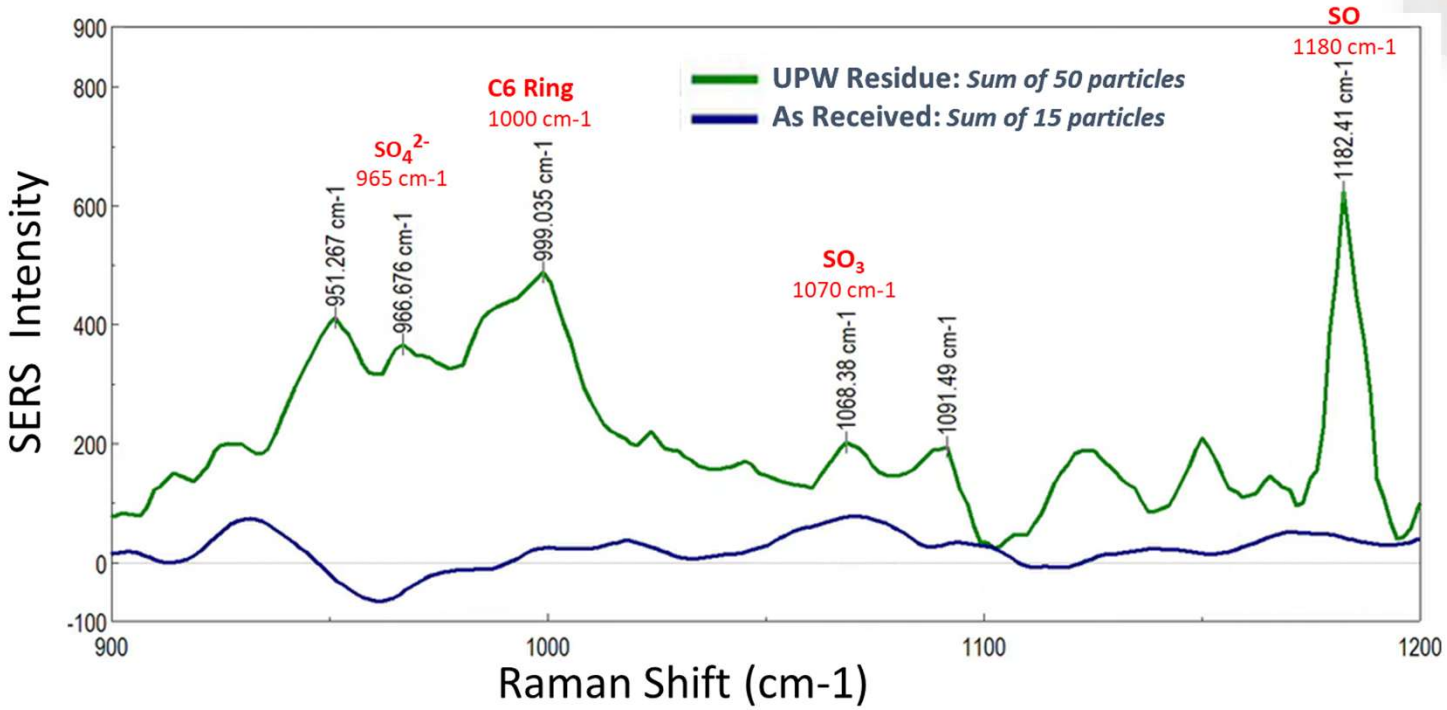


Ion pair complex

Correlation suggests the LMW organic nitrogen (Triton B) is associated with PSS

Particles on wafers according to SERS

CTA UPW drip-dried onto "as received" silicon wafer



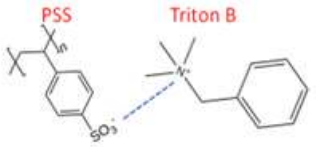
Particles in <u>UPW</u> residue show styrene and sulfonate. Still looking for amines on wafer.

Identification of Organic Particle Precursors in Ultrapure Water - Summary

Previously we proposed three pathways to transform LMW organic leachates from polishing MBIX to HMW organic particles on wafers:

Then we asked: Can we also find HMW organics from polishing MB in UPW?

- UPW from different fabs show LMW and HMW organics.
- A correlation between nitrogen and aromatic LC-OCD responses in the HMW fraction suggest that ion pair complexes travel through the MB IX as non-ionic particles.
- UPW residues on wafers (SERS) showed styrene and sulfate but no amines on wafers.



Ion pair complex

We found HMW organics in UPW that are consistent with MB IX leachates.

Surface Analysis Techniques –What makes AFM-IR special?

AFM-IR performance in the scientific literature and instrument manufacturers application notes are of interest to nano contamination studies

Method	Chemical Bond Information	Nanometer Scale Localized	Non-Destructive	Correlated electrical or mechanical properties
AFM-IR	●	●	●	●
AFM	●	●	●	●
FTIR	●	●	●	●
EM/EDS	●	●	●	●
XPS	●	●	●	●
Tof-SIMS	●	●	●	●

CTA's scope of AFM-IR work at University of Minnesota

1. **90nm diameter PSL nanoparticle standard on a silicon wafer**
2. **Image, size and IR spectra of single particles**
3. **Compare AFM-IR size distribution to CTA SEPS data**
4. **Compare AFM-IR spectra to CTA ATR-IR spectra**

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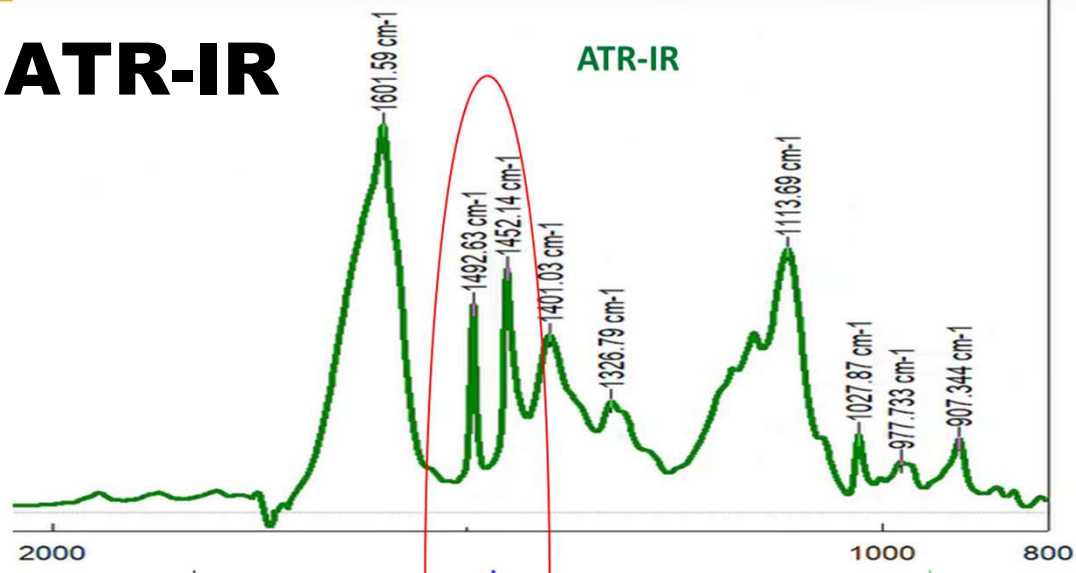
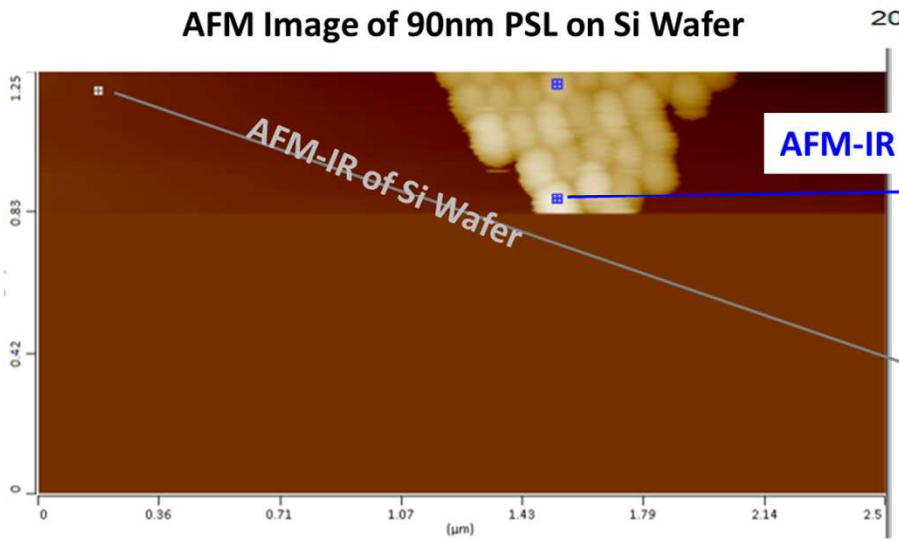
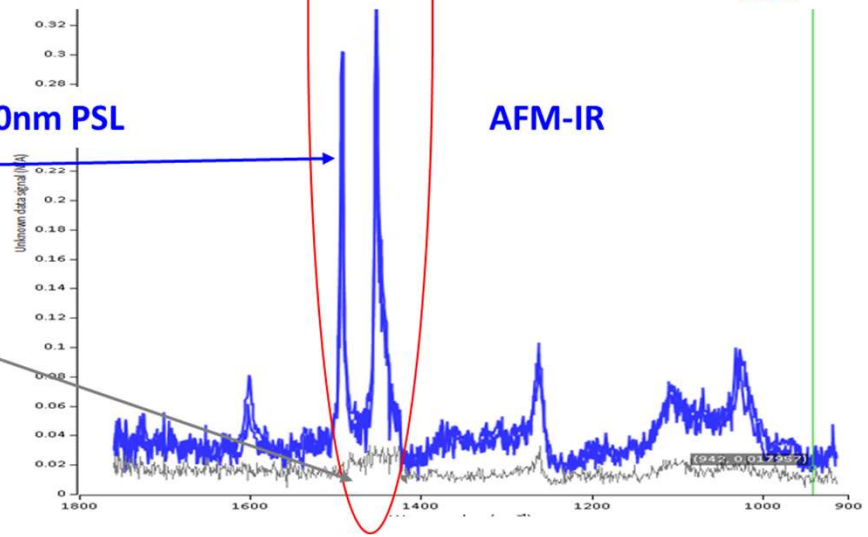
90nm PSL by AFM-IR and ATR-IR

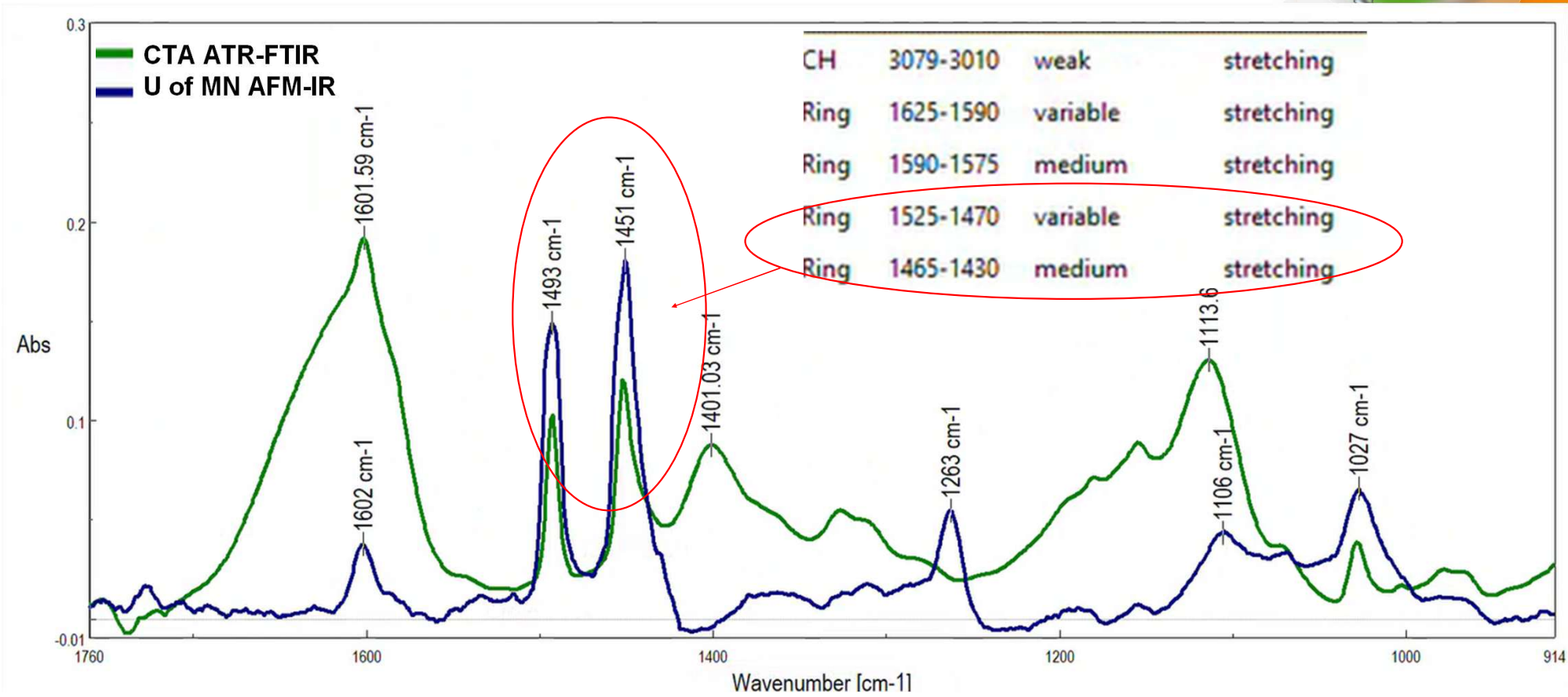
PSL organic nanoparticles can be imaged, and chemical composition can be determined.





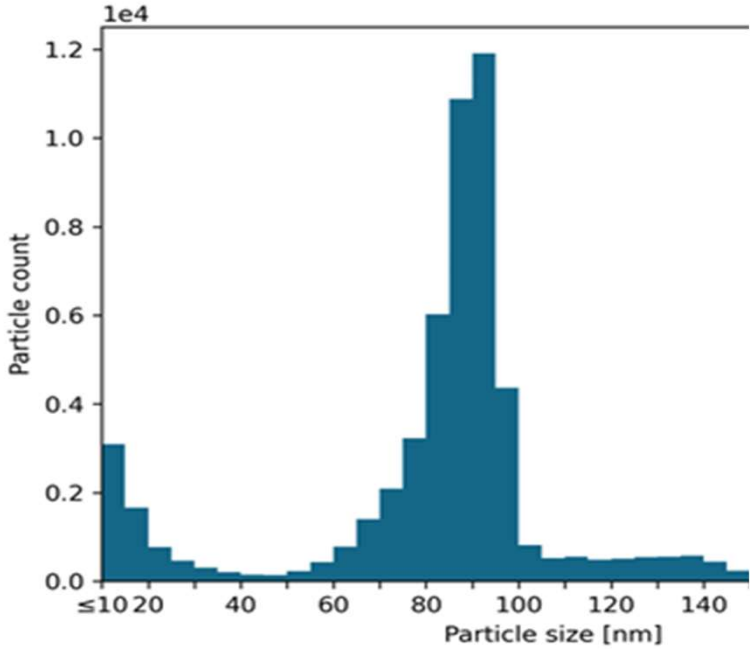


AFM-IR and ATR-IR Spectra of 90nm PSL Show chemically characteristic IR Peaks

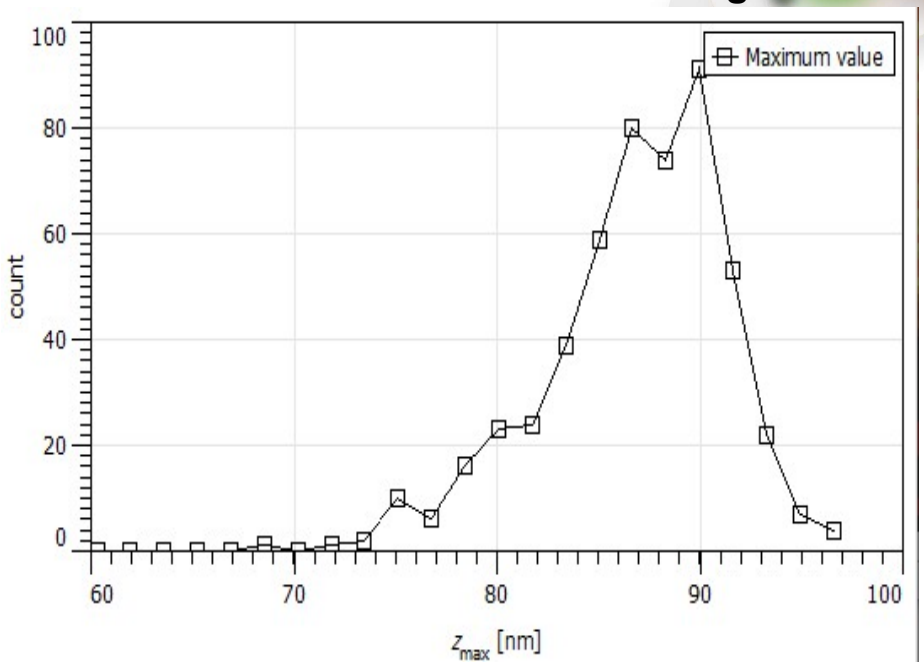


90nm PSL Particle Size Distribution

CTA Surface Enhanced Particle Sizing (SEPS)



U of MN AFM-IR Particle Sizing



Particle size distributions measured on wafers by SEPS and AFM-IR are similar!

SUMMARY: Identification of Organic Particle Precursors using ATR-IR, SERS and AFM-IR

- Particle Precursors from mixed bed Ion Exchange (MBIX) are an unquantified risk to wafer yield.
- Vibrational spectroscopies are part of a multiple analytical method approach to chemically speciate particle precursors.
- Recent advances in vibrational spectroscopy are an opportunity to obtain fundamental knowledge on critical organics that adhere to wafers.
  - AFM-IR sized, counted and matched the ATR-IR spectra for 90nm PSLs
- Analytical methods that meet the challenge to size, count and chemically speciate below <15 nm are needed to quantify risks to wafer yield.