A New Method for the Rapid Identification of sub-20nm Particles in UPW

by
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From Slava's IRDS and SEMI presentation
UPW Particles – High Risk that Needs Action

We have a problem:

- No effective metrology exists to accurately monitor 10nm particles
- Filtration capability at the killer particles size is marginal
  - <100% of removal at 15nm and smaller
  - UF integrity cannot be guaranteed
- High Molecular Weight Polymers may become killer particles
- Colloidal Silica Needs to be Effectively Controlled
  - Most difficult to detect and remove
  - Typically occurring in UPW

The high particle counts, in the millions per mL, as measured by the STPC indicate that we may have both “hard” and “soft” particles (high molecular weigh nm-sized organic particles) in UPW.

This presentation is the 1st phase, focusing on method feasibility, of the development work using a different approach to solve the problem of particle collection (both hard and soft) and particle identification.

SEM with EDX/EDS would seem to hold the answer, but how to collect 20nm and smaller particles on a SEM filter.

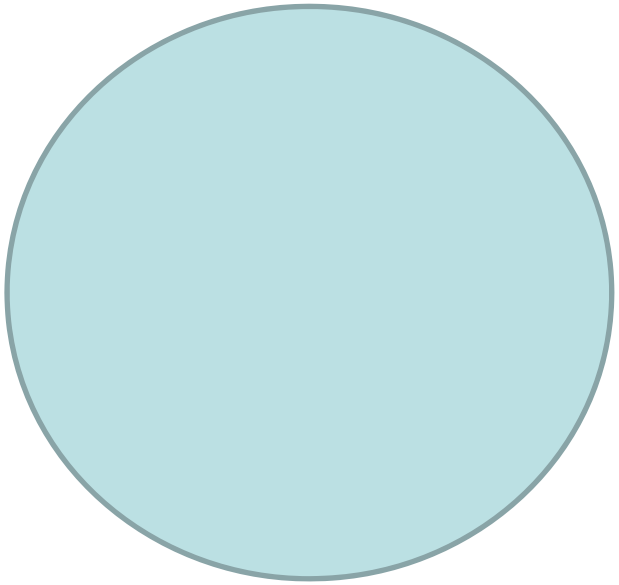
I (and others) have tried solving the problem of sub-20nm particle collection and identification before:
(Blackford, David, et al, NanoParticle Collection Device for Ultra-Pure Water, UPW Conference Portland OR, November 2009.)

A 10nm colloidal silica particle or HMW polymer about to land on a standard 25mm SEM filter

Polyethyleneimine

$(-CH_2CH_2NH-)_x-(CH_2CH_2N(CH_2CH_2NH_2)-)_y$

10nm colloidal silica particle

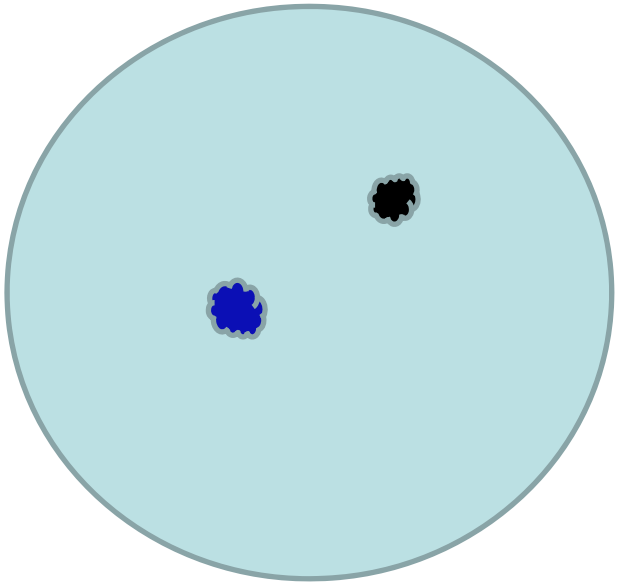


(Note, not to scale)

25 mm SEM filter

What percentage area does a 10nm particle occupy on a 25mm SEM filter?

0.000000000016%

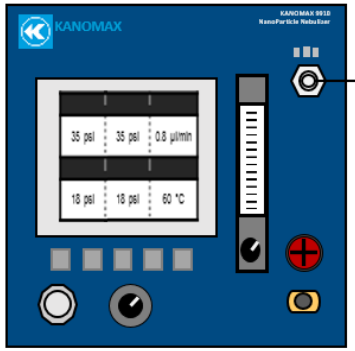


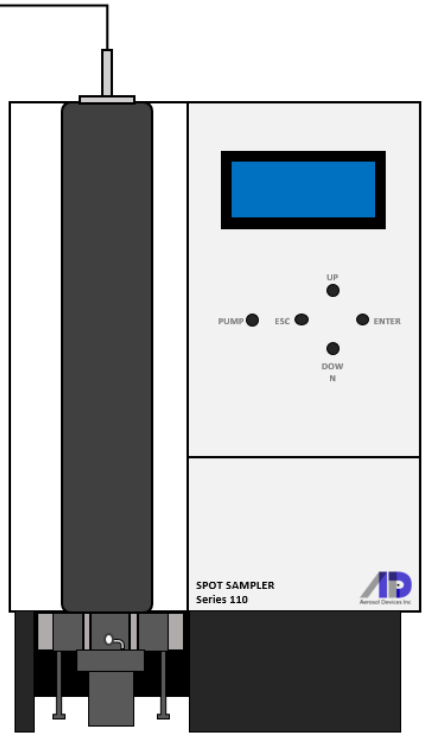
(Note, not to scale)

25 mm SEM filter

NanoParticle Nebulizer with Spot Sampler

NanoParticle Nebulizer
(KANOMAX Model 9110)

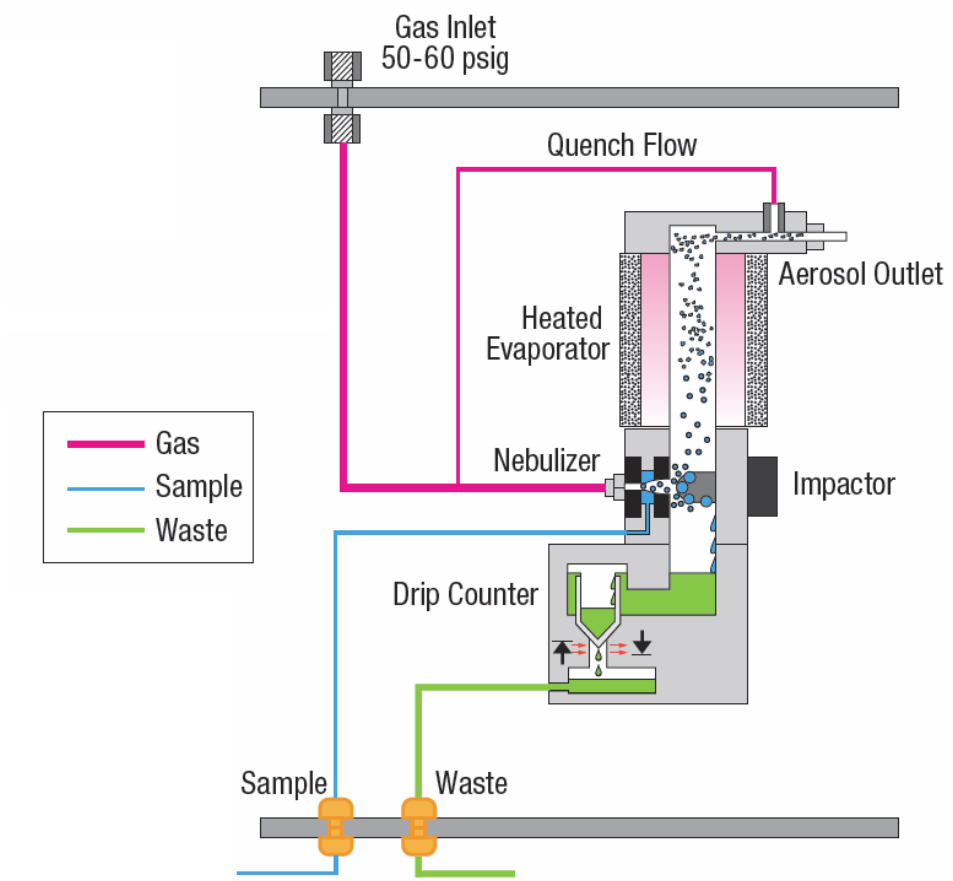




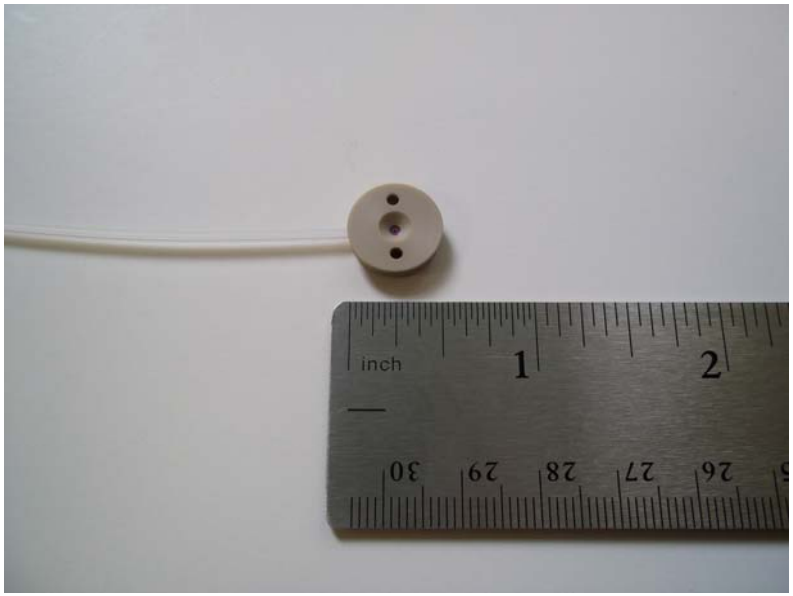
Sequential Spot Sampler
(ADI SSS110)

NanoParticle Nebulizer (NPN)

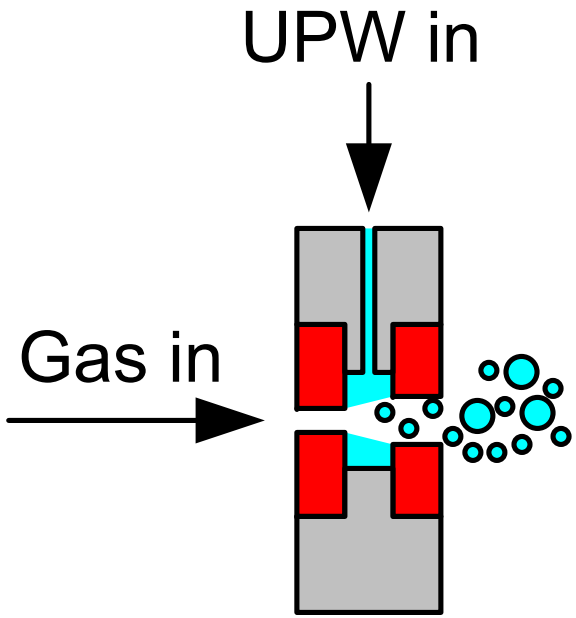
Continuous On-line dilution with UPW before Injection

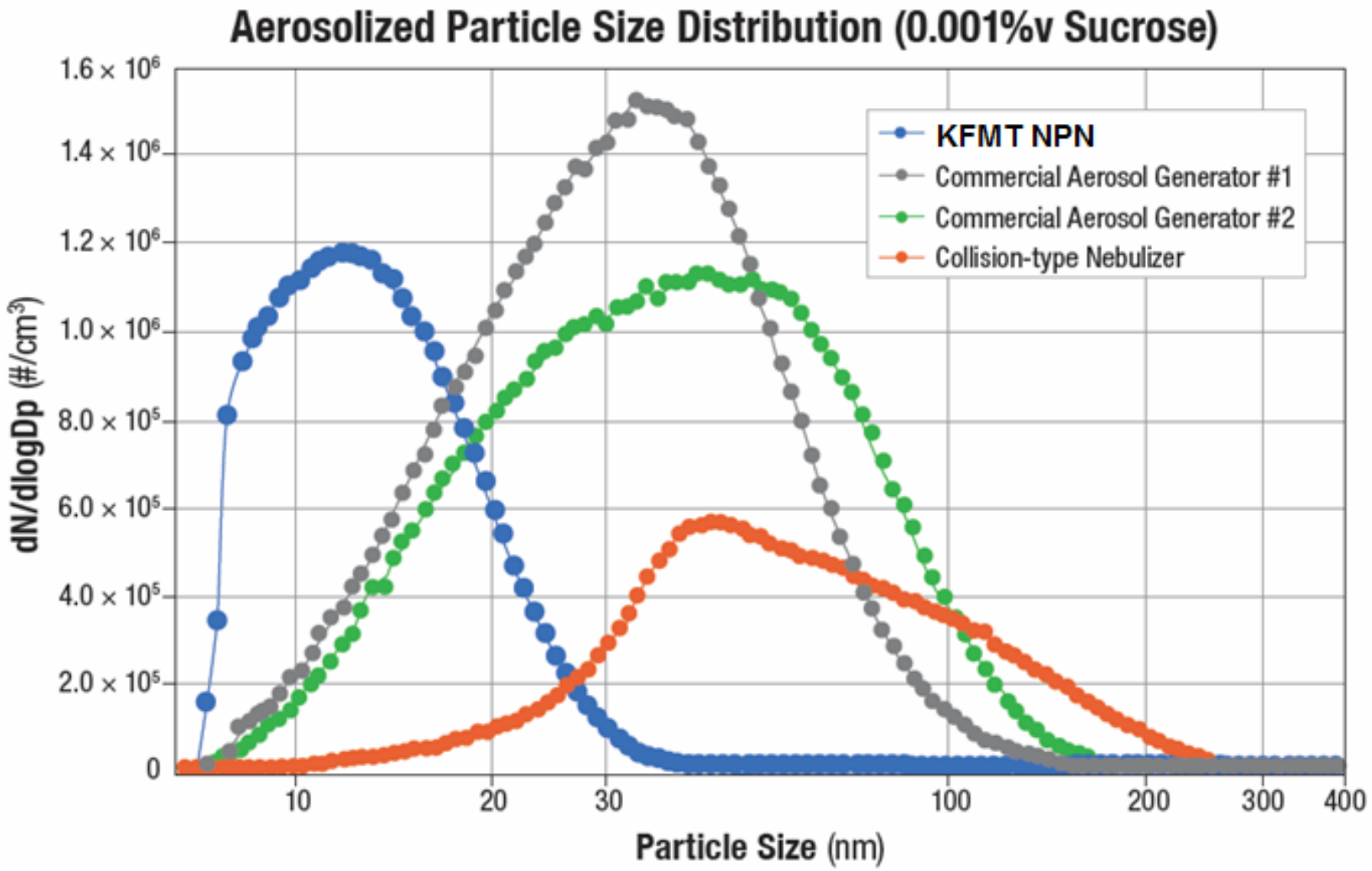


Nebulizer used in the NPN



Nebulizer used in the NPN



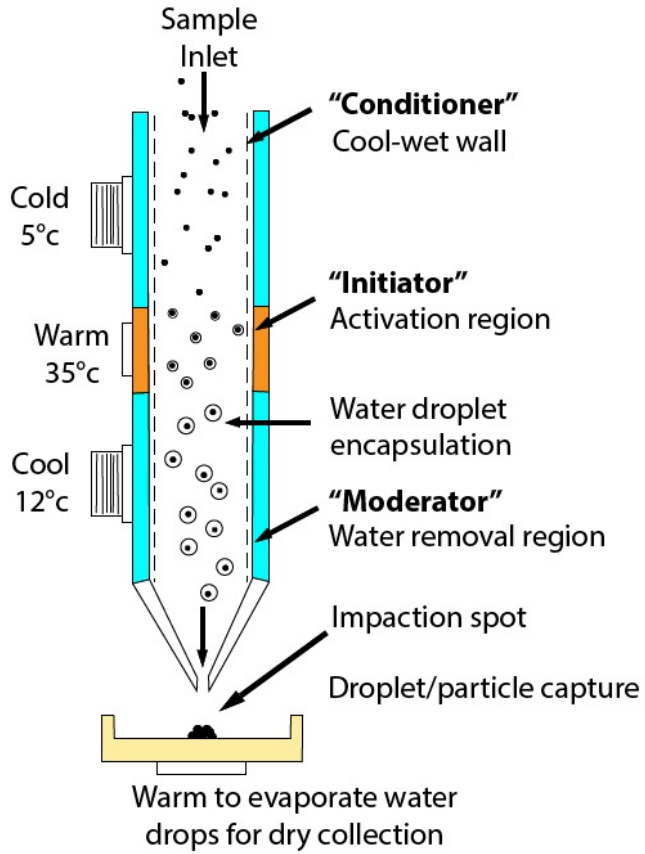

Aerosolized Particle Size Distribution (0.001%v Sucrose)
KFMT NPN
Commercial Aerosol Generator #1
Commercial Aerosol Generator #2
Collision-type Nebulizer
dN/dlogDp (#/cm³)
1.6 × 10⁶
1.4 × 10⁶
1.2 × 10⁶
1.0 × 10⁶
8.0 × 10⁵
6.0 × 10⁵
4.0 × 10⁵
2.0 × 10⁵
0
10
20
30
100
200
300
400
Particle Size (nm)

Spot Sampler aerosol particle collector

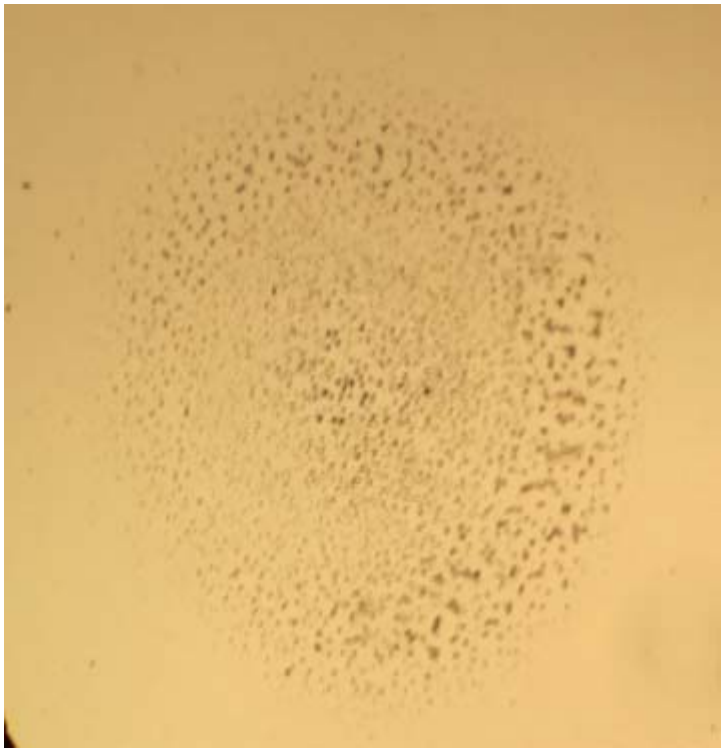
- High collection efficiency
- >95% from 5 nm to >2.5µm
- Concentrated sample

The Spot Sampler Uses Condensation Particle Growth with Gentle Impaction

We use proven technology and apply it in a new way



Spot pattern at 50X magnification

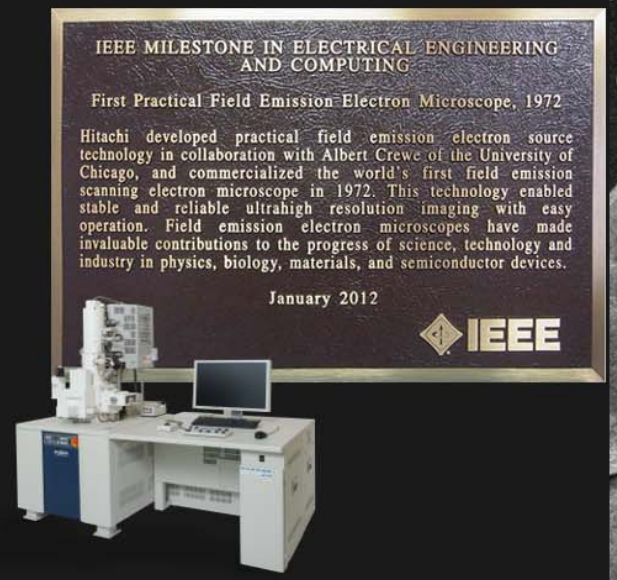


1mm

Hitachi Maryland Applications Lab Demonstration Data

Prepared for:

BALAZS™ nanoanalysis



Hitachi High Technologies America Inc.
Nanotechnology Systems Division

SU8200 Series FE-SEM

Oxford Instruments latest Extreme EDS/EDX analysis

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

Sample Overview

The particles are collected onto the carbon tape with a glass substrate used only for easier transportation.

#2 is particle samples collected from UPW nebulization after a filter change event.

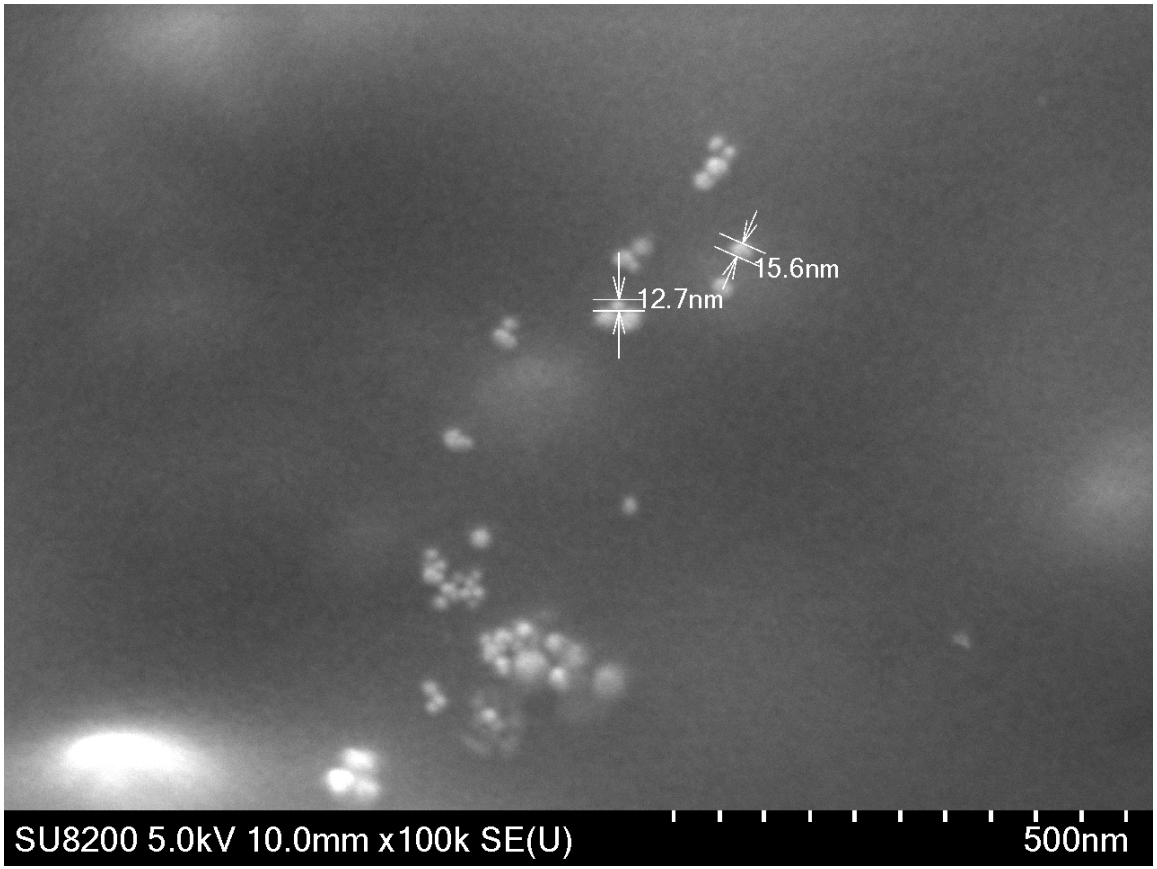
#10: 10nm colloidal silica

Imaging of particle collection during filter rinse on UPW system

Vacc=5kV, WD=10mm, Mag=50kX----

24 hour collection time

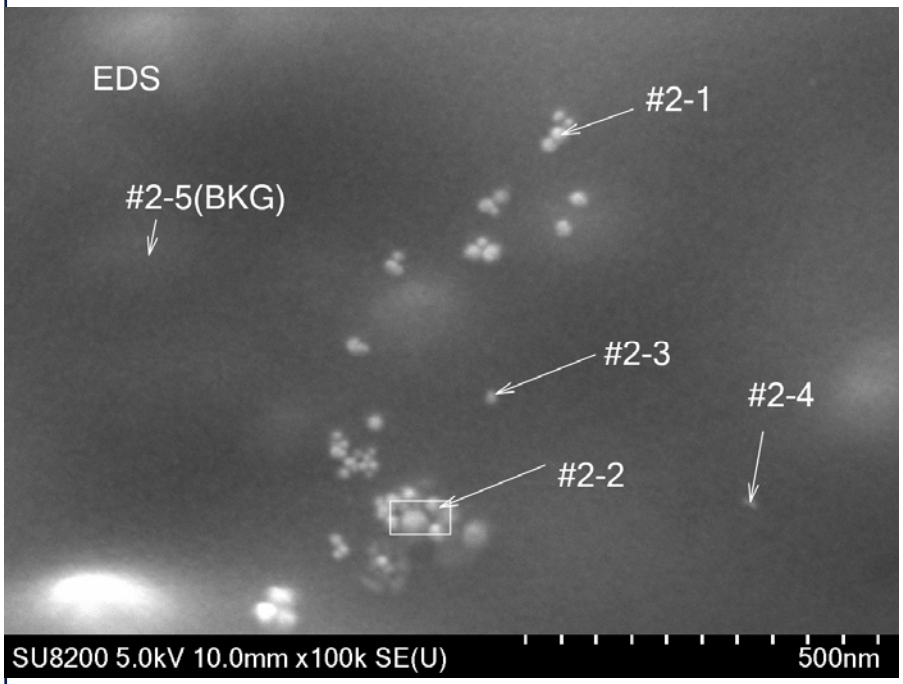
Measurement of particles

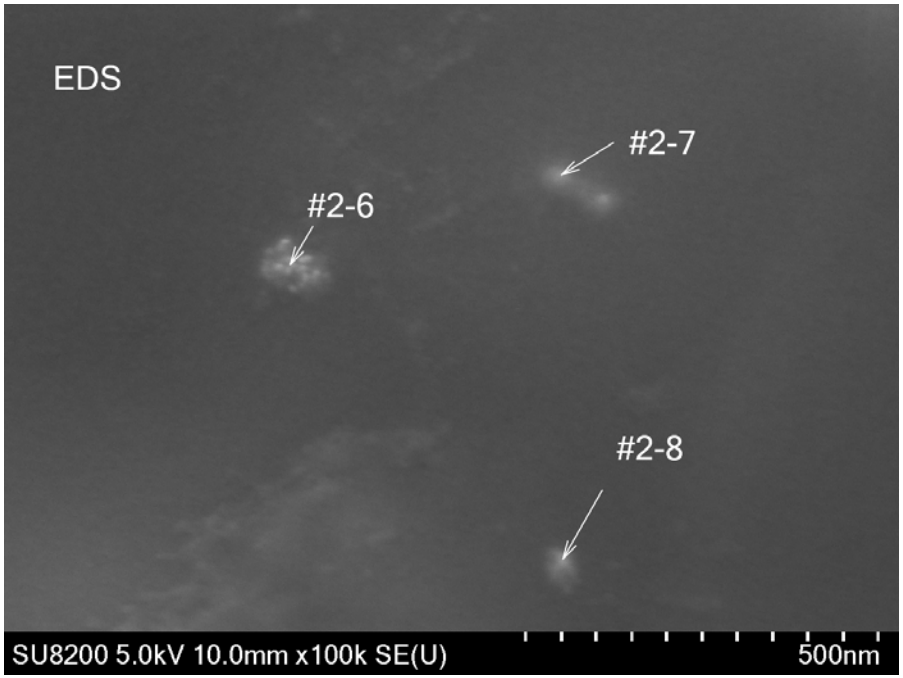


Imaging of particle collection during filter rinse on UPW system

Vacc=5kV, WD=10mm, Mag=50kX----

24 hour collection time



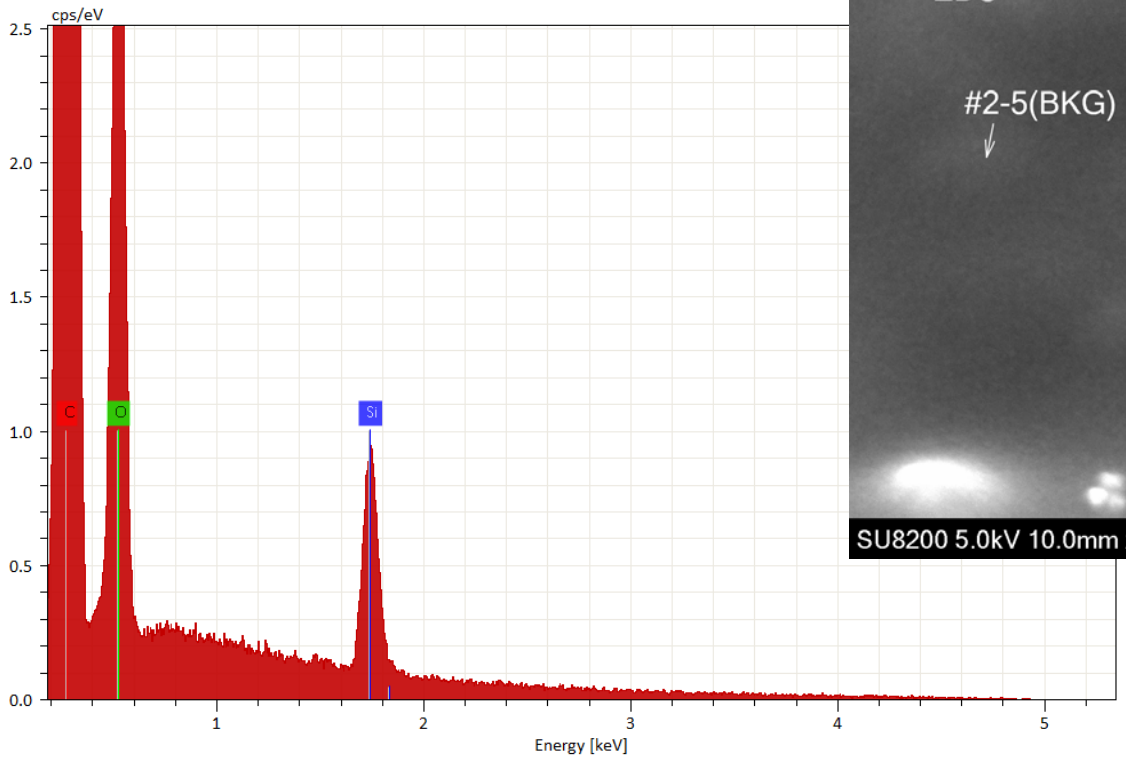


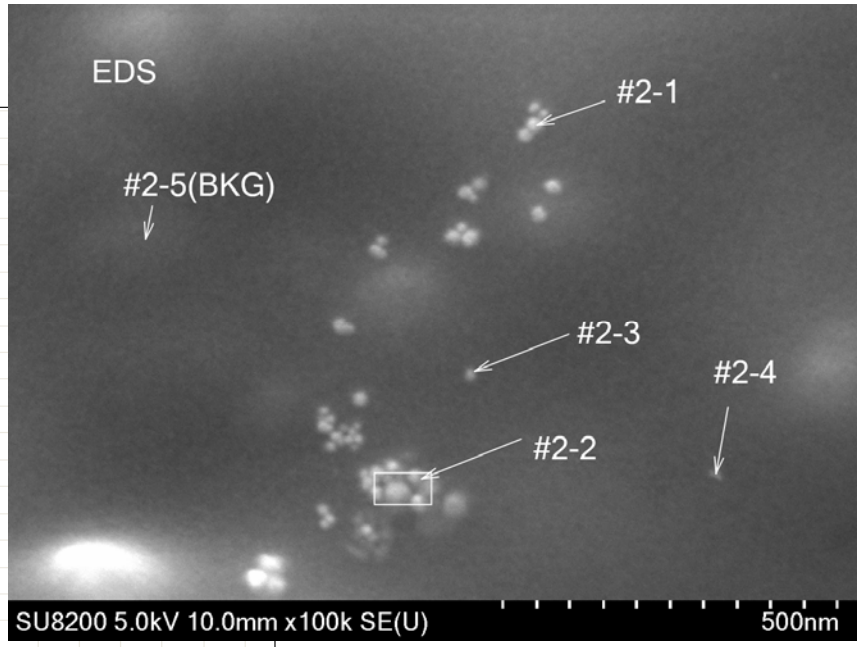
Imaging of particle collection during filter rinse on UPW system

Vacc=5kV, WD=10mm, Mag=50kX----

24 hour collection time

2-2

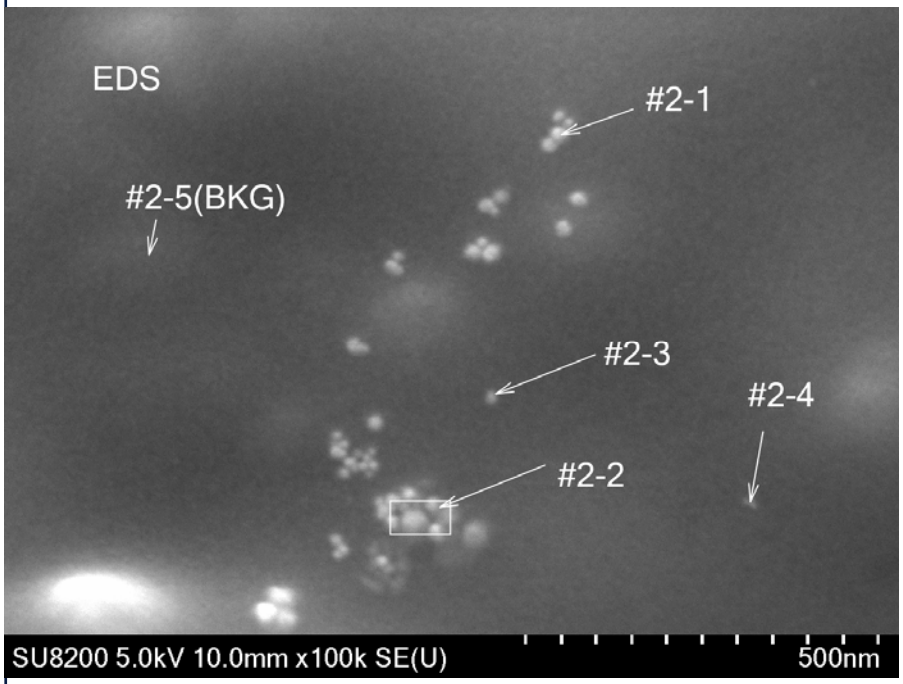


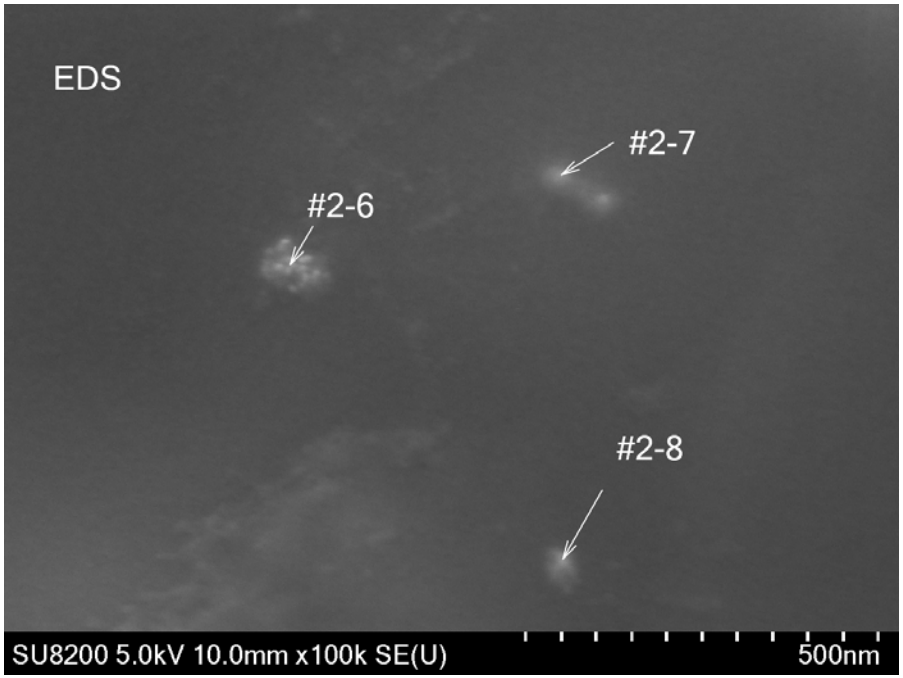


Imaging of particle collection during filter rinse on UPW system

Vacc=5kV, WD=10mm, Mag=50kX----

24 hour collection time

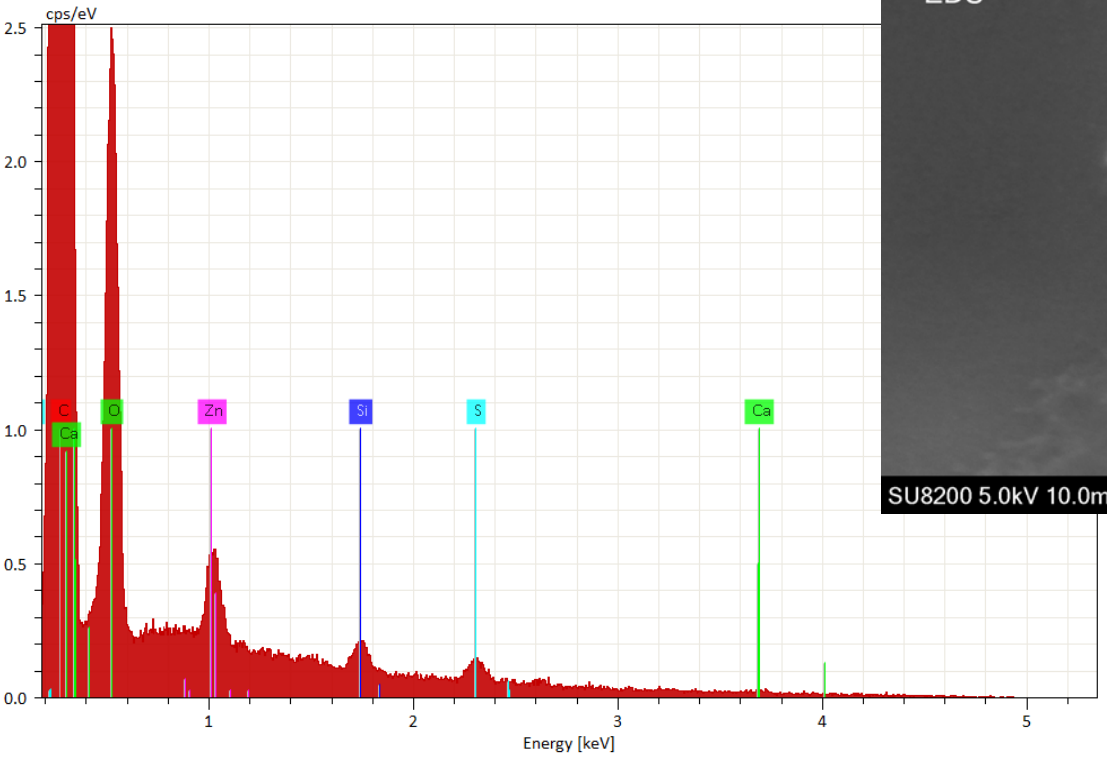


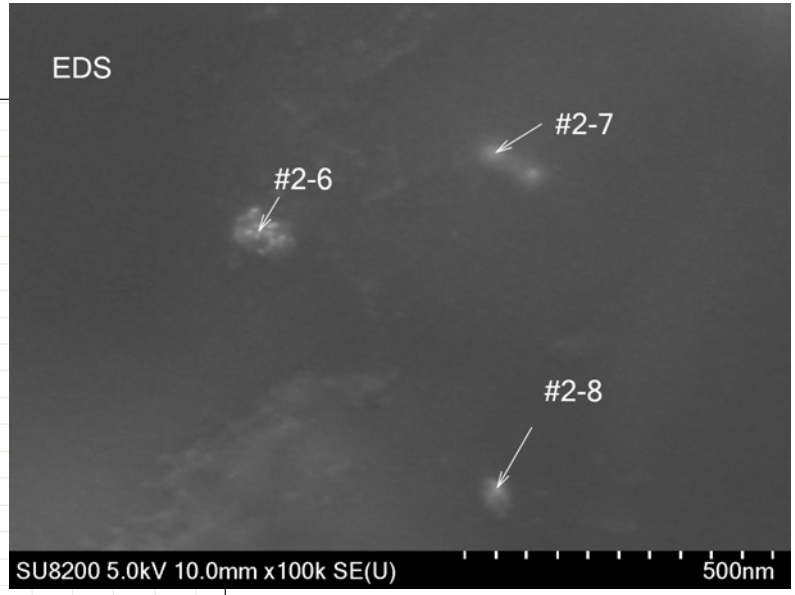


Imaging of #2 Real sample----Vacc=5kV, WD=10mm, Mag=100kX----

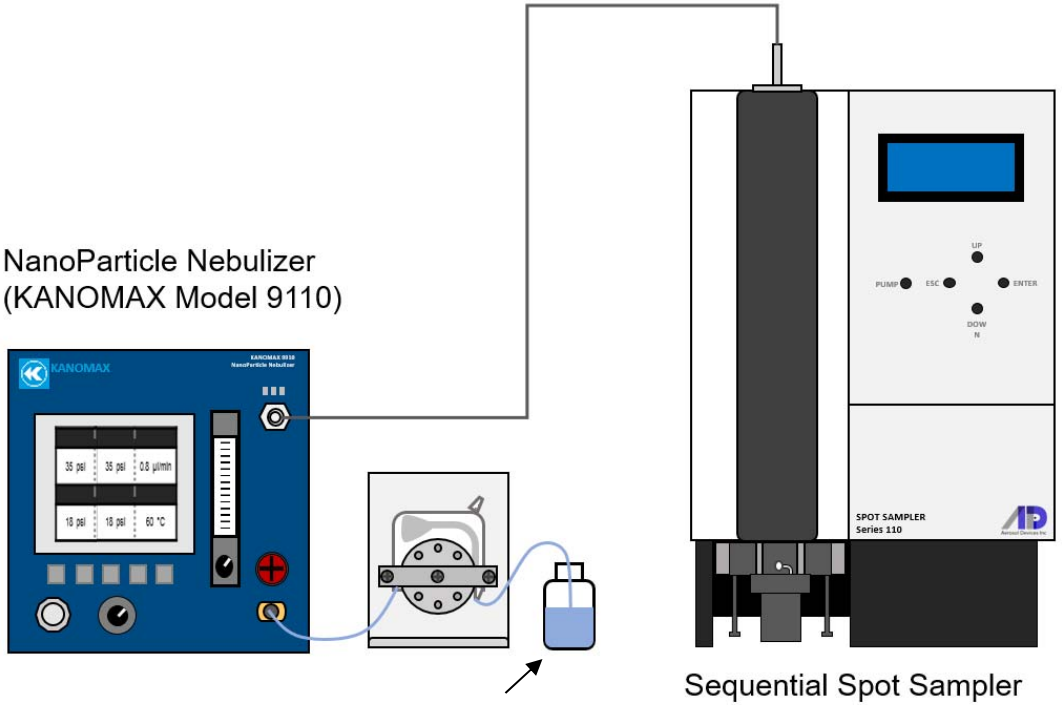
24 hour collection time

2-8

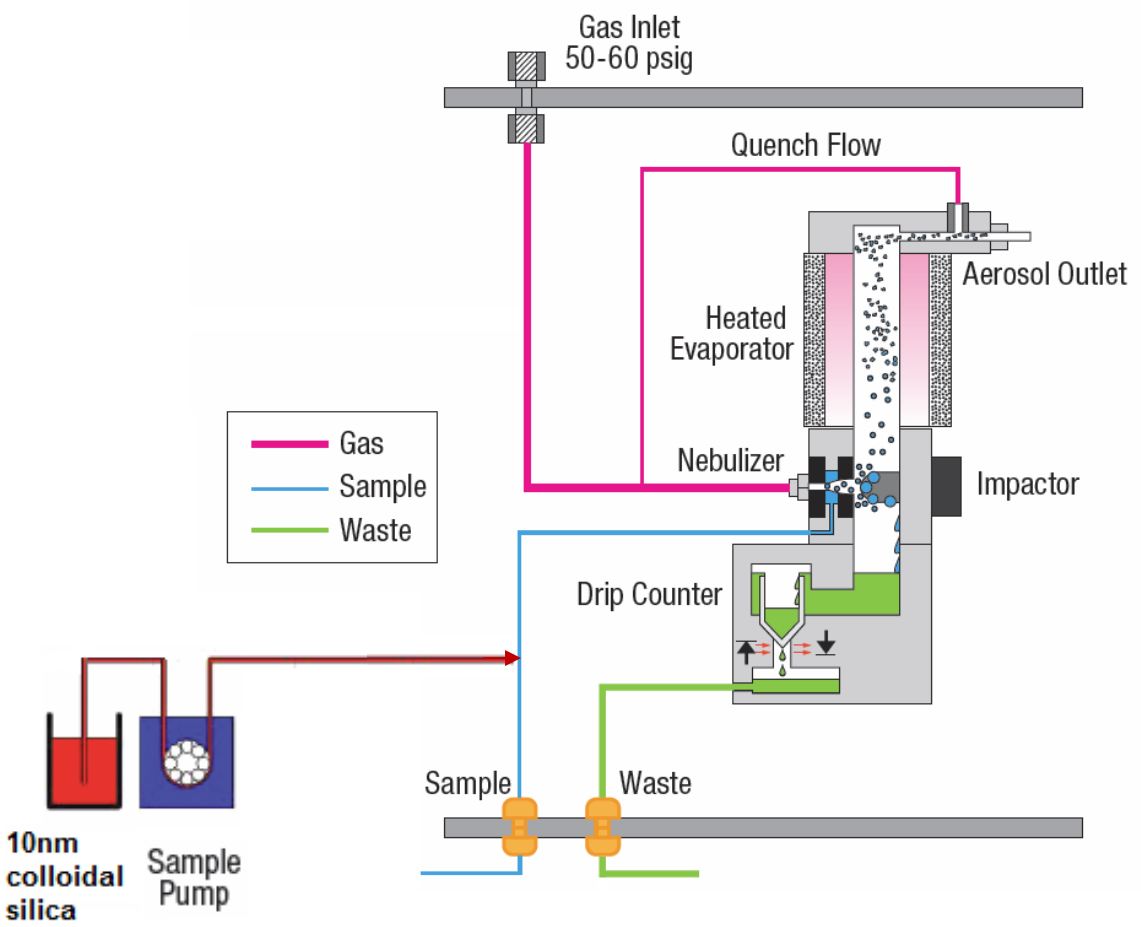




NanoParticle Nebulizer with Spot Sampler and Peristaltic injection pump

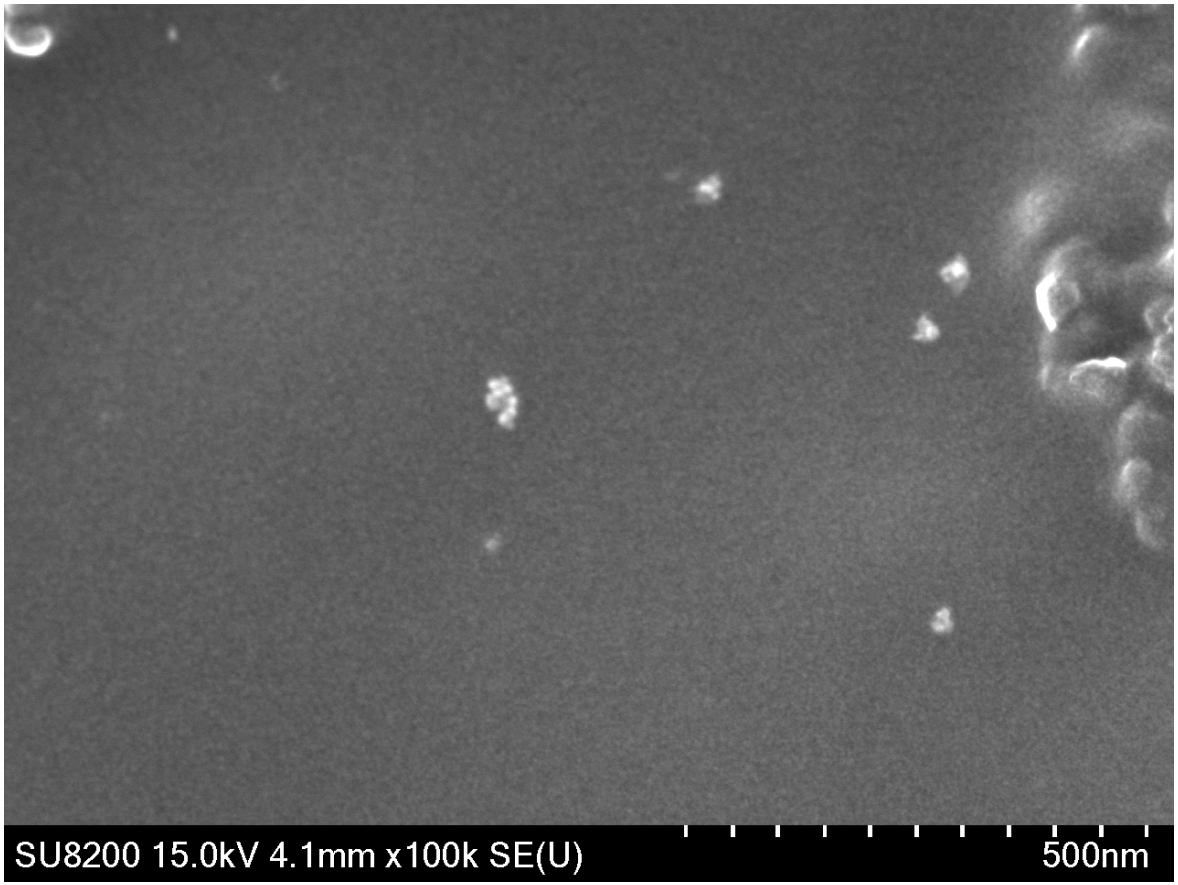


NanoParticle Nebulizer (NPN)
with 10nm colloidal silica injection



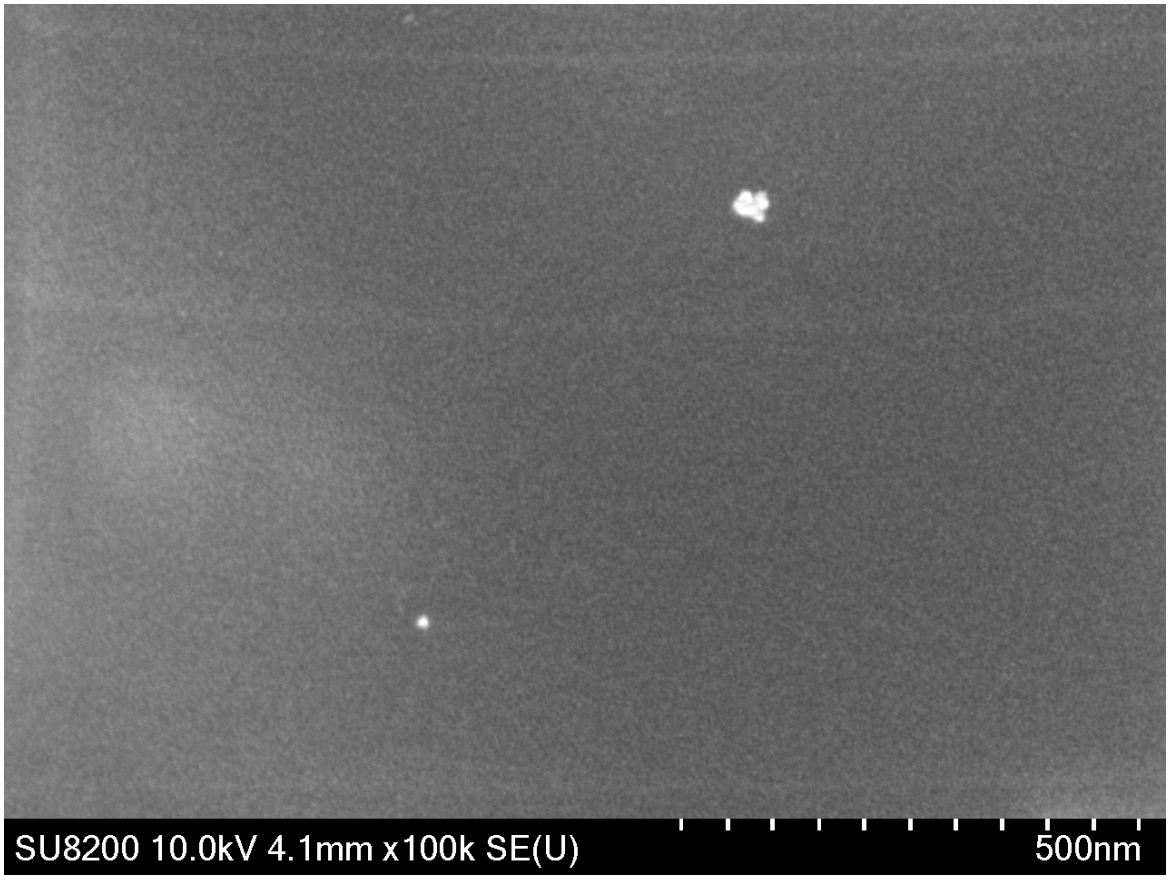
Imaging of injected 10nm Colloidal Silica----Vacc=15kV, WD=4mm, Mag=100kX----
10 minute collection time, concentration 1E9 particles per mL

Fine particles around 10nm
(some are aggregated) were confirmed at 50kX Using SE image with passive
voltage contrast.



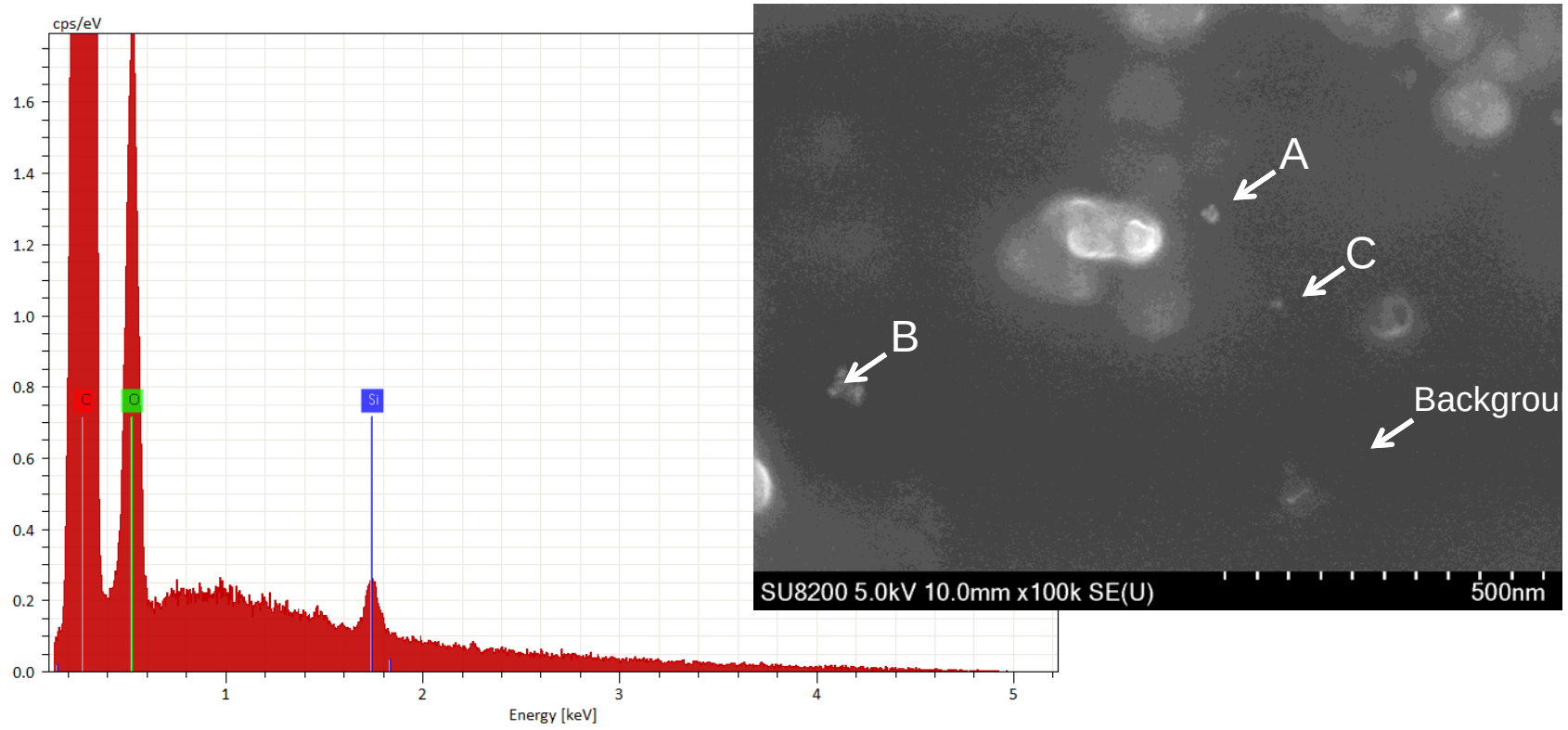
Imaging of injected 10nm Colloidal Silica----Vacc=10kV, WD=4mm, Mag=100kX---
10 minute collection time, concentration 1E9 particles per mL

Fine particles around 10nm
(some are aggregated)
were confirmed at 50kX
Using SE image with passive
voltage contrast.

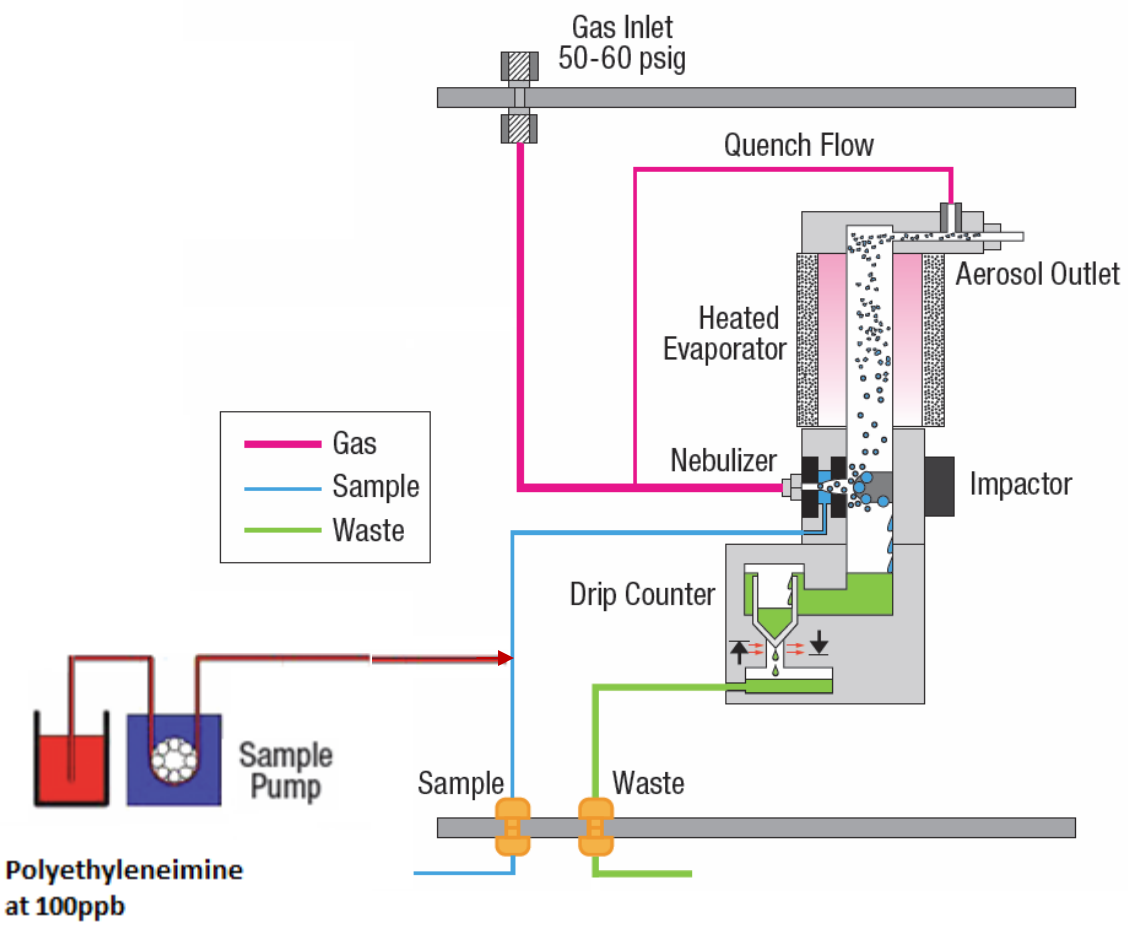


Imaging of injected 10nm Colloidal Silica----Vacc=5kV, WD=10mm, Mag=50kX----
10 minute collection time, concentration 1E9 particles per mL

Particle B

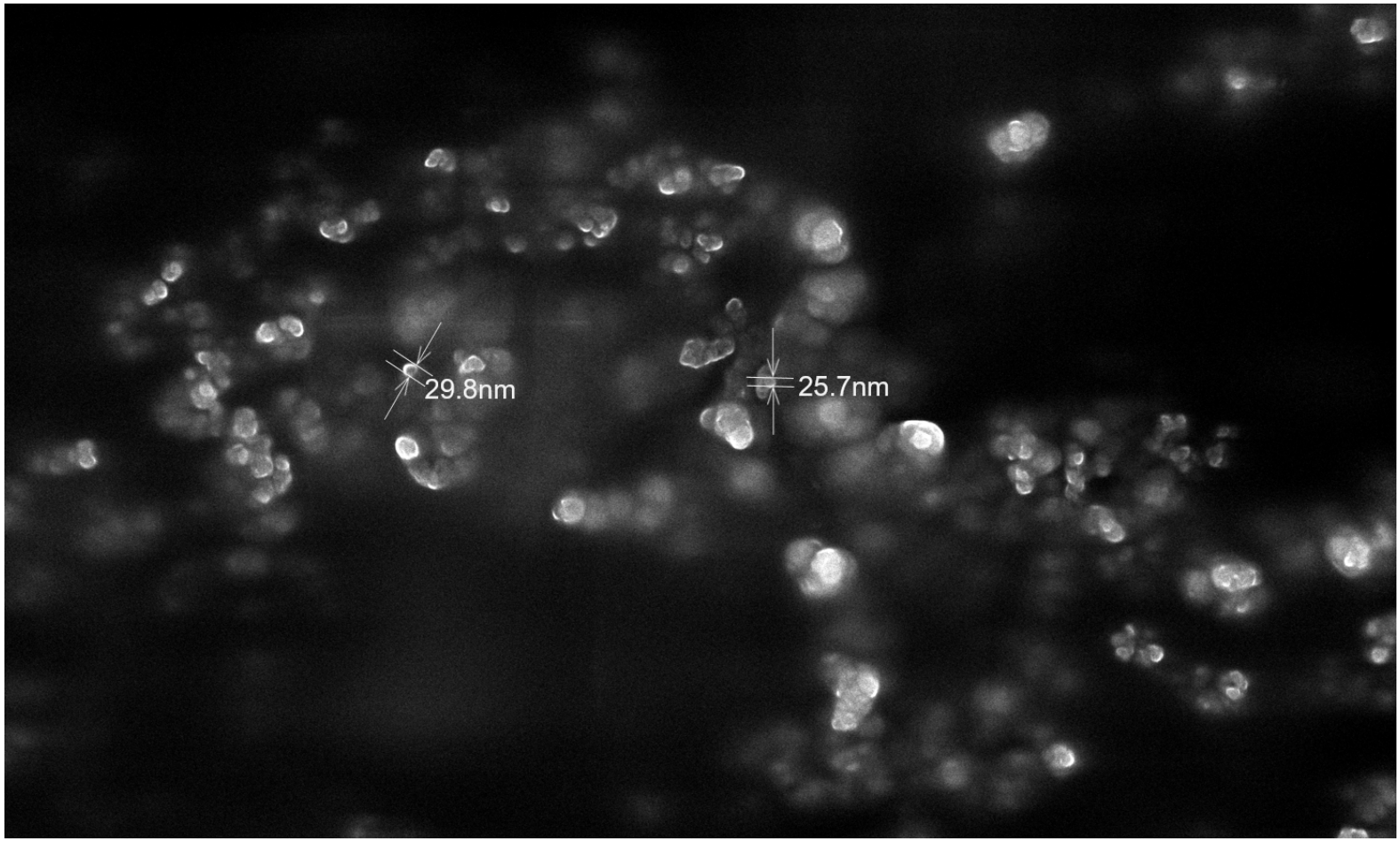


NanoParticle Nebulizer (NPN) with HMW Polymer injection



Polyethyleneimine at 100ppb concentration injected for 15 minutes

Carbon tape substrate



Need to explore using other target materials to collect both “hard” and “soft” (HMW polymer) particles.

Performed a second round of testing with a variety of target materials, including a Nucleopure filter, Substratek Gold Mesh, Silicon wafer, Carbon Tape of different thicknesses and Aluminum Tape.

Surface roughness proved to be critical

Sample Summary

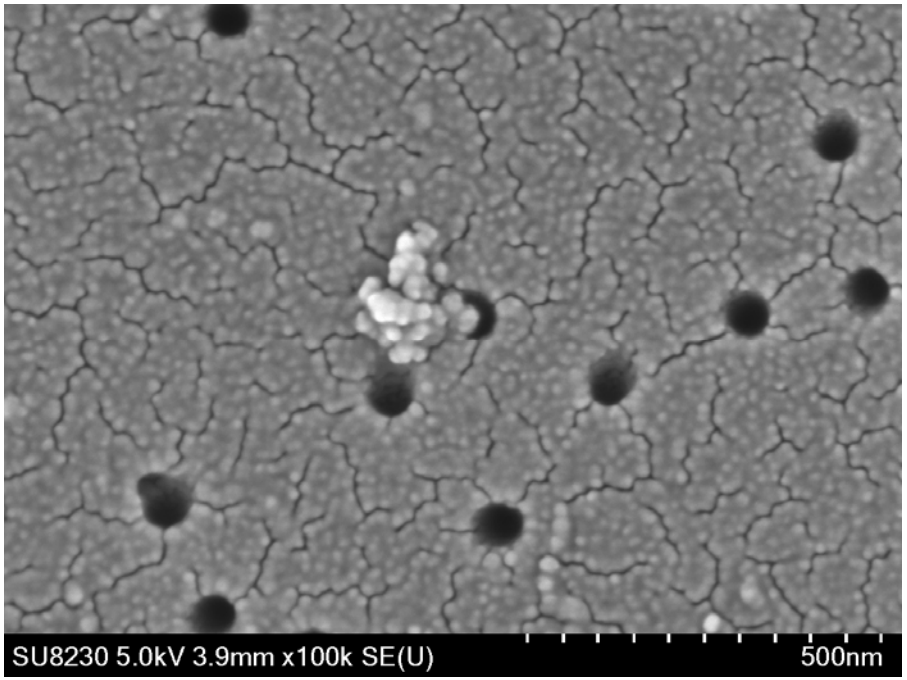
Type of Substrate	Source	Background uniformity	Contrast uniformity	Surface cleanness	Comment
A	Ted Pella	No good	No good	No good	Blank surface is dirty and topographic
B	Ted Pella	No good	No good	Good	Tough point : less contrast uniformity, charge up and image drift by beam damage
C	Ted Pella	No good	No good	Good	Tough point : less contrast uniformity, charge up and image drift by beam damage
D	Ted Pella	Good	Good	Good	Tough point: less contrast when we try to find Si Al type materials
E	Ted Pella	No Good	No Good	Good	Contrast of Au coating
F	Whatman	No Good	No Good	Good	Contrast of Au coating

Conclusion: Substrate D has possibility to be used for EDS particle analysis +Automation activity

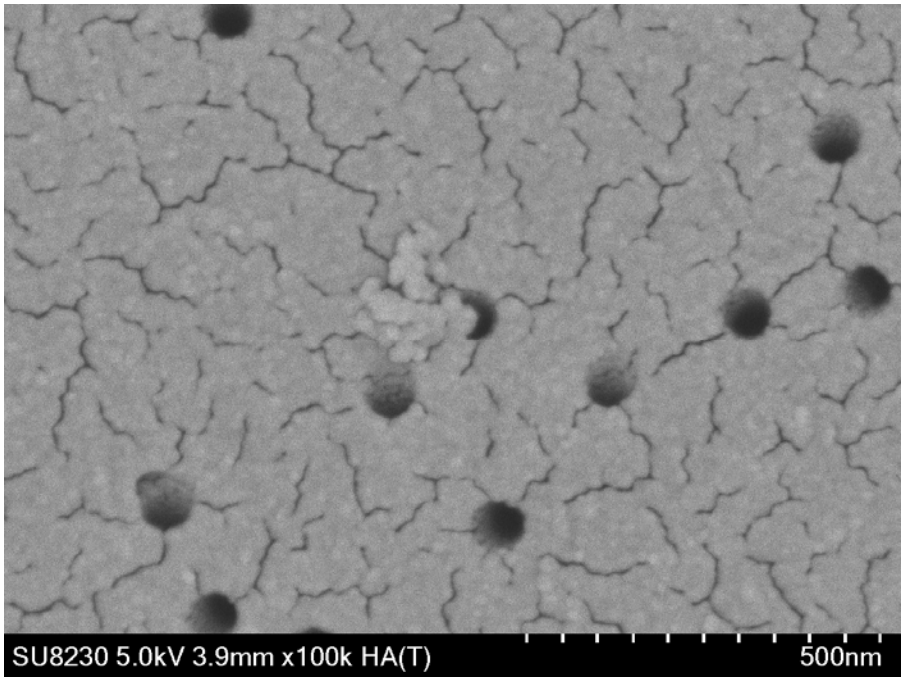
Imaging of 10nm colloidal silica on Gold coated Nucleopore ----Vacc=5kV, WD=4mm

5 hour collection time

100kX



SE: Secondary electron image
highlight topographic and static information

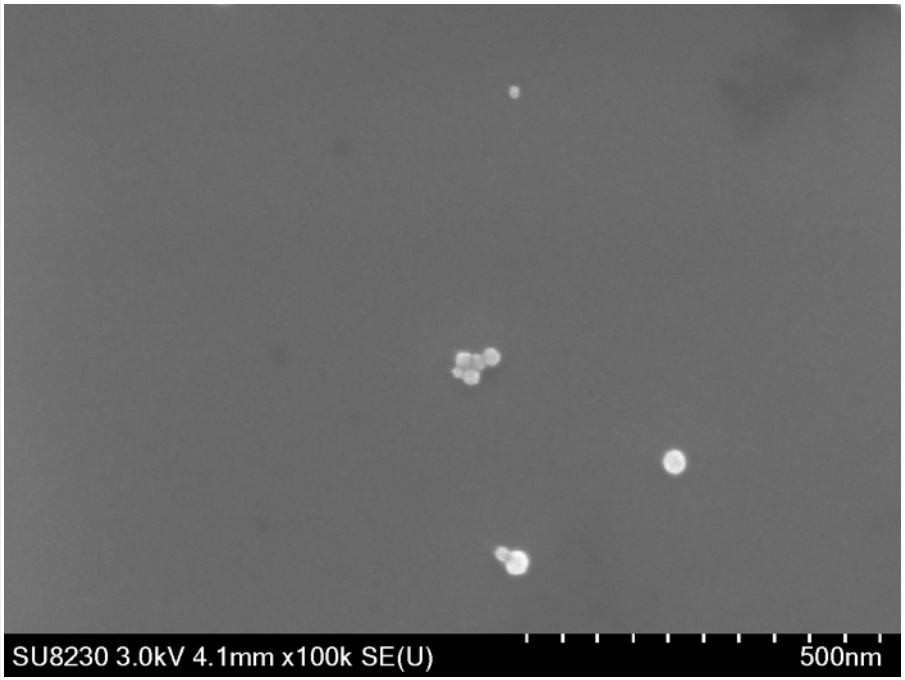


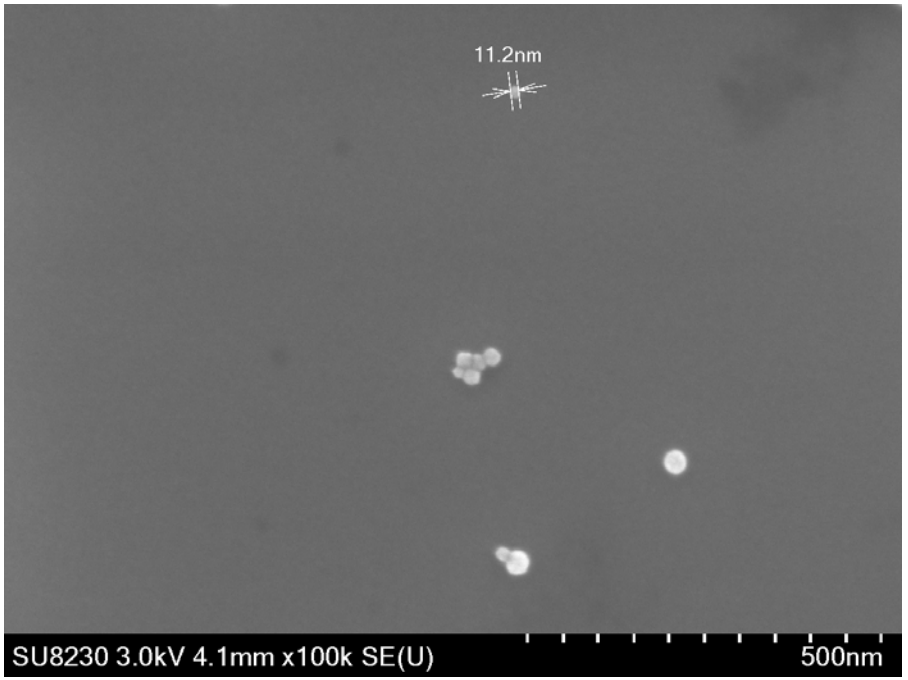
BSE: Backscattered electron image
highlights composition (chemical) information

Not a good surface for topographic or compositional uniformity

Imaging of 10nm colloidal silica ----Vacc=5kV, WD=4mm

3 hour collection time, substrate D

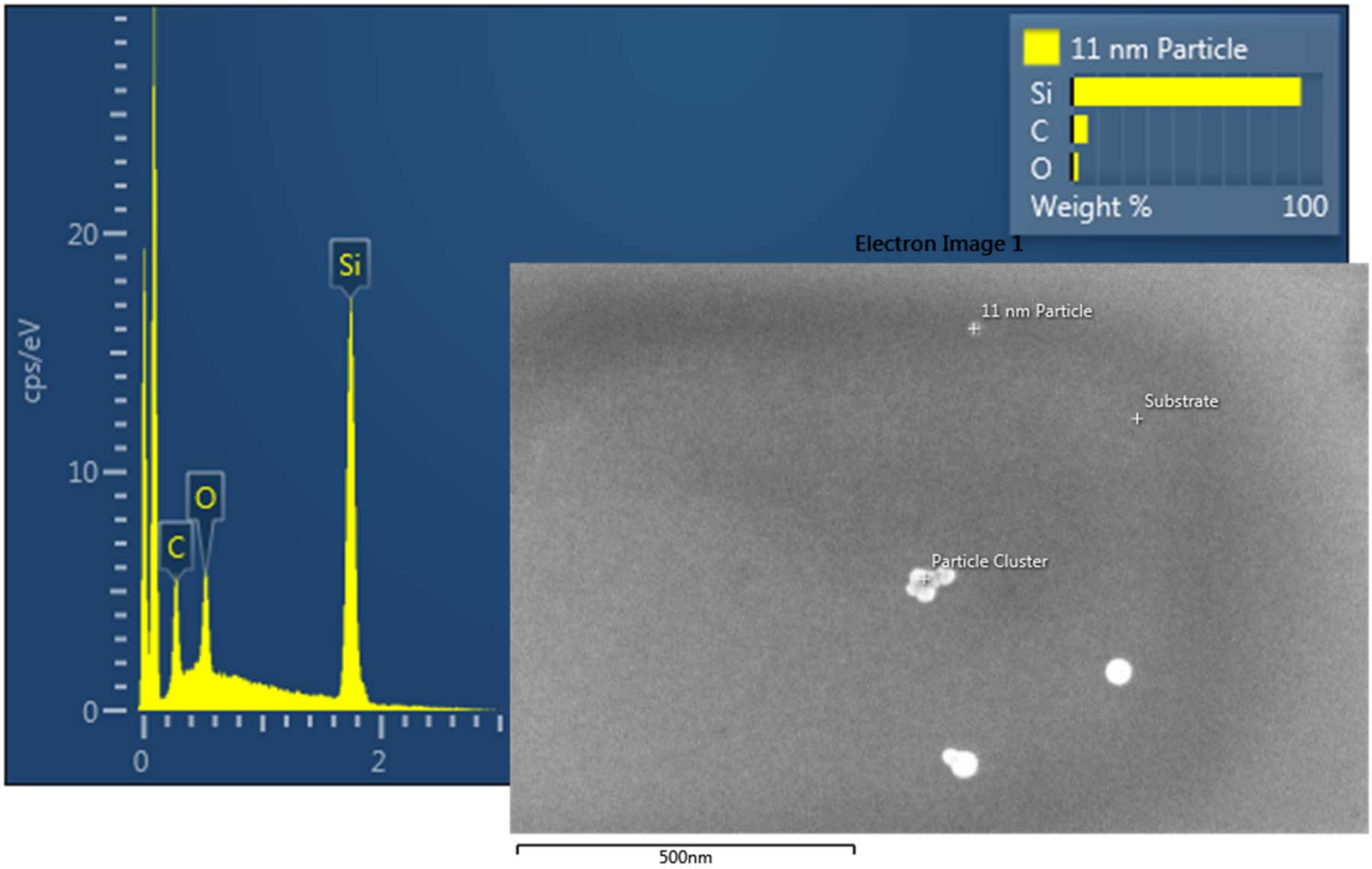




SE for topography/static contrast

Using static voltage contrast, we can identify Silica around 10nm with very high contrast intensity.

Substrate D may be the ideal material for EDS, and for collecting and identifying both hard and soft particles



Conclusions

The combination of two commercially available instruments does indeed look very promising for the collection, identification and quantification of 10nm particles in UPW.

Native (UPW) particles around 12nm were successfully confirmed and elemental information of particles were identified by EDS. Sample collection time was 24 hours.

A 10 minute challenge of 10nm silica particles (smallest particles in this sample preparation) were successfully collected and their composition confirmed by EDS. A 15 minute Polyethyleneimine injection also resulted in approximately 30nm particle collection.

Working to identify the best type of collection material: need to collect traditional particles and collect and identify soft particles (high-molecular weight organic particles) as measured by the STPC.

As the author list implies, complex problems require collaborative solutions.

Acknowledgements

- *The authors wish to acknowledge Air Liquide Balazs for their participation in arranging all the SEM work used in this presentation.*
- *Hitachi provided all the SEM analysis*
- *Oxford Instruments for the EDS/EDX analysis*