Development of a Nanoparticle Sampler for Particle Speciation Using Electron Microscopy

Quantifying Exposure to Engineered Nanomaterials (QEEN) from Manufactured Products Workshop

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RJ LEE GROUP
DELIVERING SCIENTIFIC RESOLUTION

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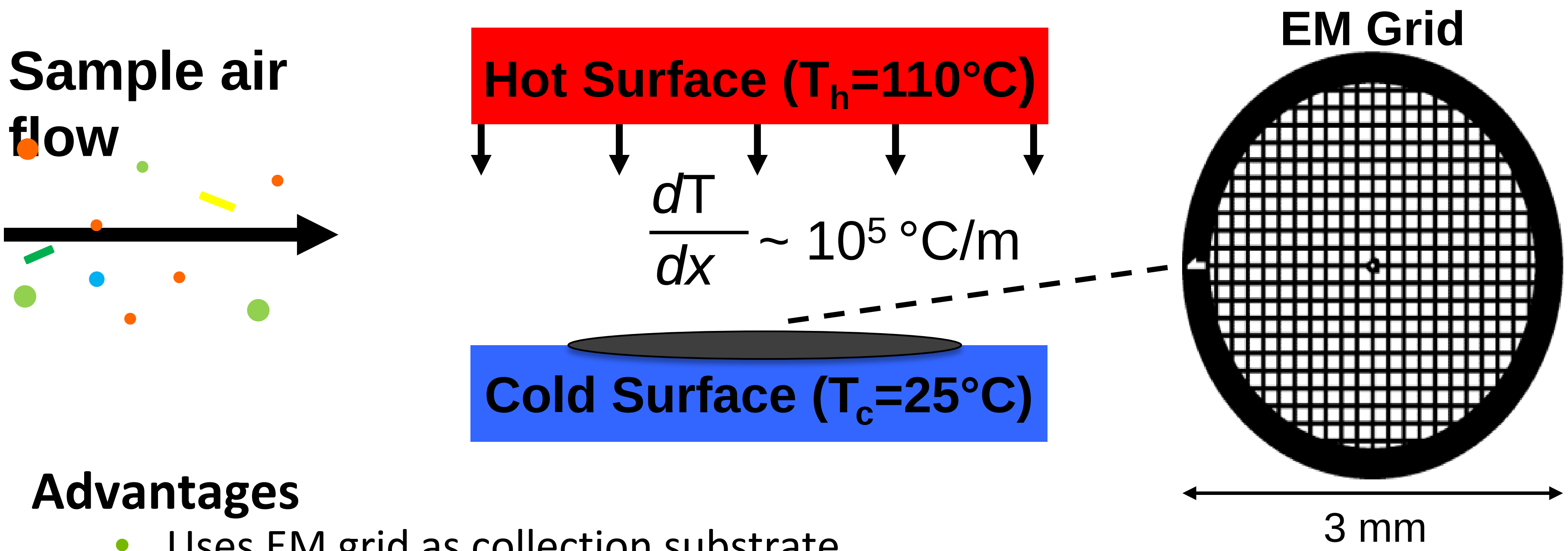
The TPS100

Total weight	320g
Sampler Dimensions	122mm x 63mm x 38mm
Sample Cartridge Dimensions (3mm Diameter EM Grid)	46mm x 18mm x 15mm
Battery Duration (from full charge)	~8 hours
Charging Time	<3 hours
Battery Lifespan	>300 complete charge/discharge cycles
Recommended Hot Side Temperature Range	85 to 120°C
Recommended Cold Side Temperature Range	25 to 35°C
Volumetric Flow Rate	5 mL/min

Thermophoretic Collection



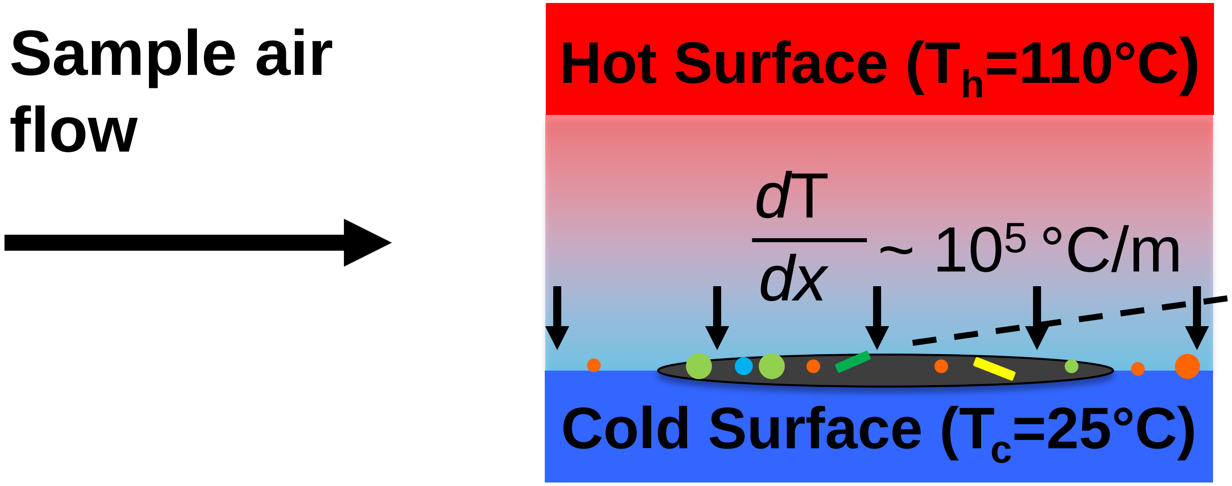
Advantages

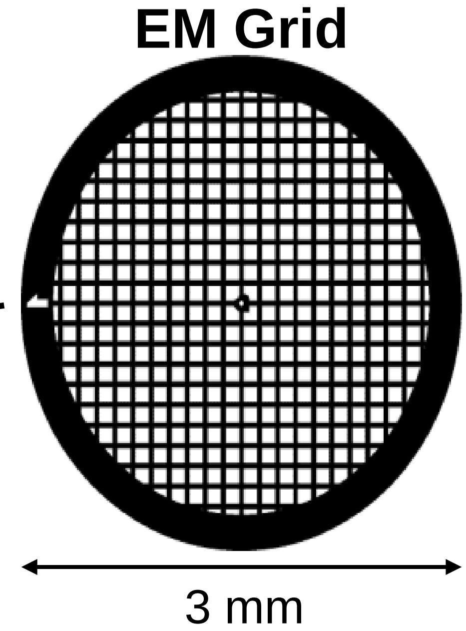
- Uses EM grid as collection substrate
- EM analysis gives size distribution, concentration, and elemental composition
- Thermophoresis is thought to be benign to particle composition/morphology

Disadvantages

- Not direct-reading - secondary analysis required
- Lower collection rate may challenge very short sample times

Thermophoretic Collection





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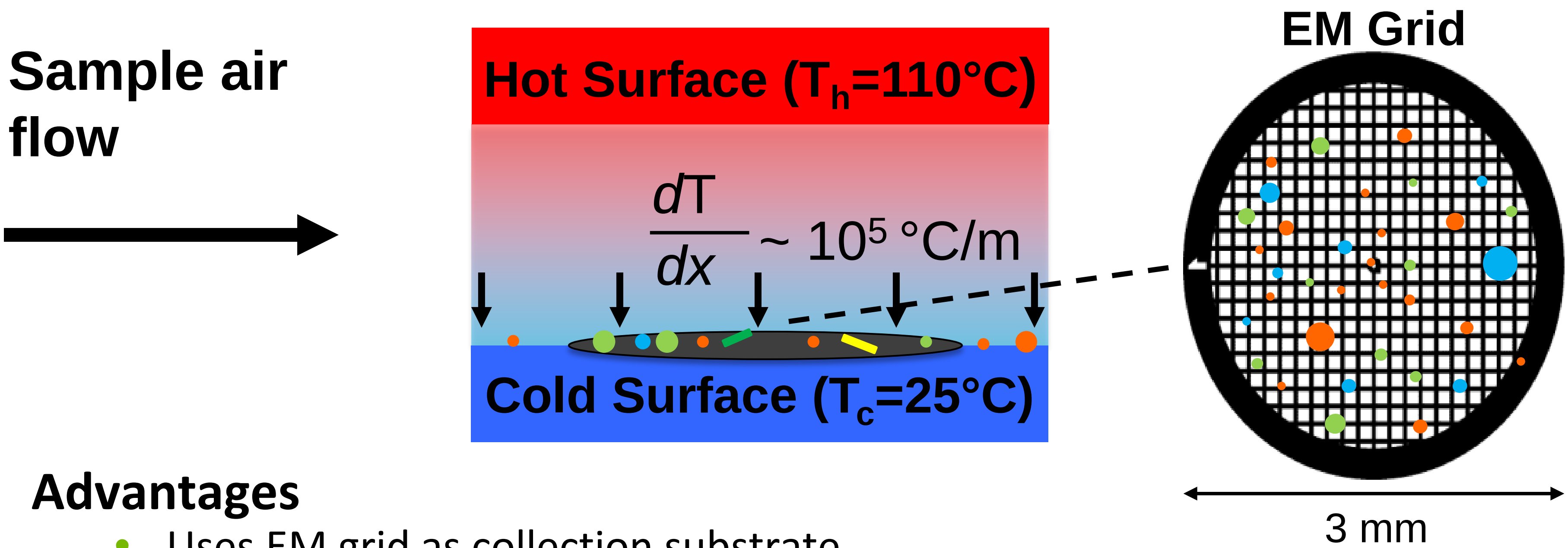
Thermophoretic Collection

Sample air flow



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The Need for the TPS100

- The same properties that make engineered nanoparticles useful may lead to problems for humans, animals, and the environment
  - How do we assess and manage exposures?
  - Are engineered nanoparticles hazardous?
- The need to speciate nanoparticles
  - Direct reading instrumentation (eg., CPC, OPC, SMPS) does not speciate particles

The Potential of Electron Microscopy (EM)

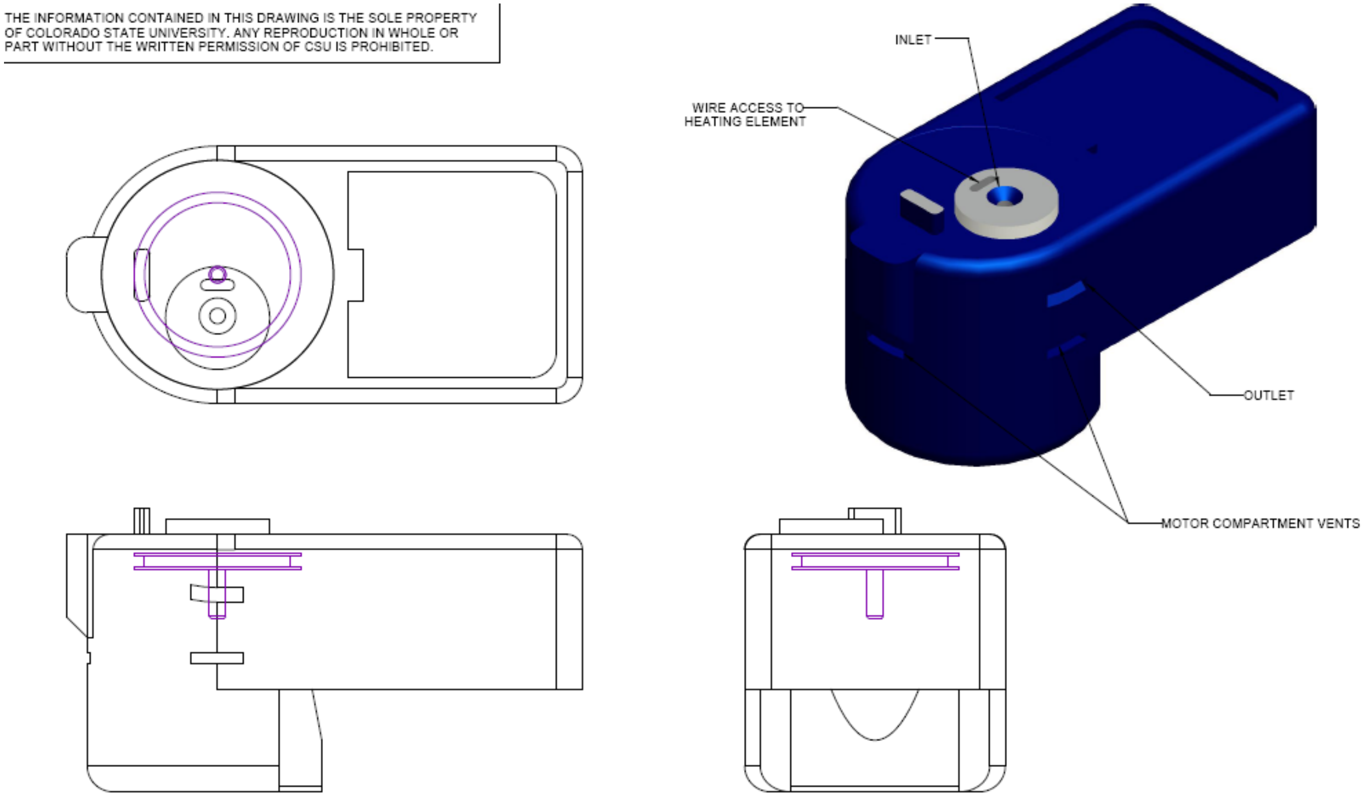
- EM has the capability to speciate nanoparticles
  - Potential issues associated related to sample collection, preparation and analysis of the nanoparticles
- Issues related to widespread use of EM
  - Ability to provide statistical data on nanoparticles
  - Ability to provide data in a cost effective manner

Nanoparticle Speciation Using EM

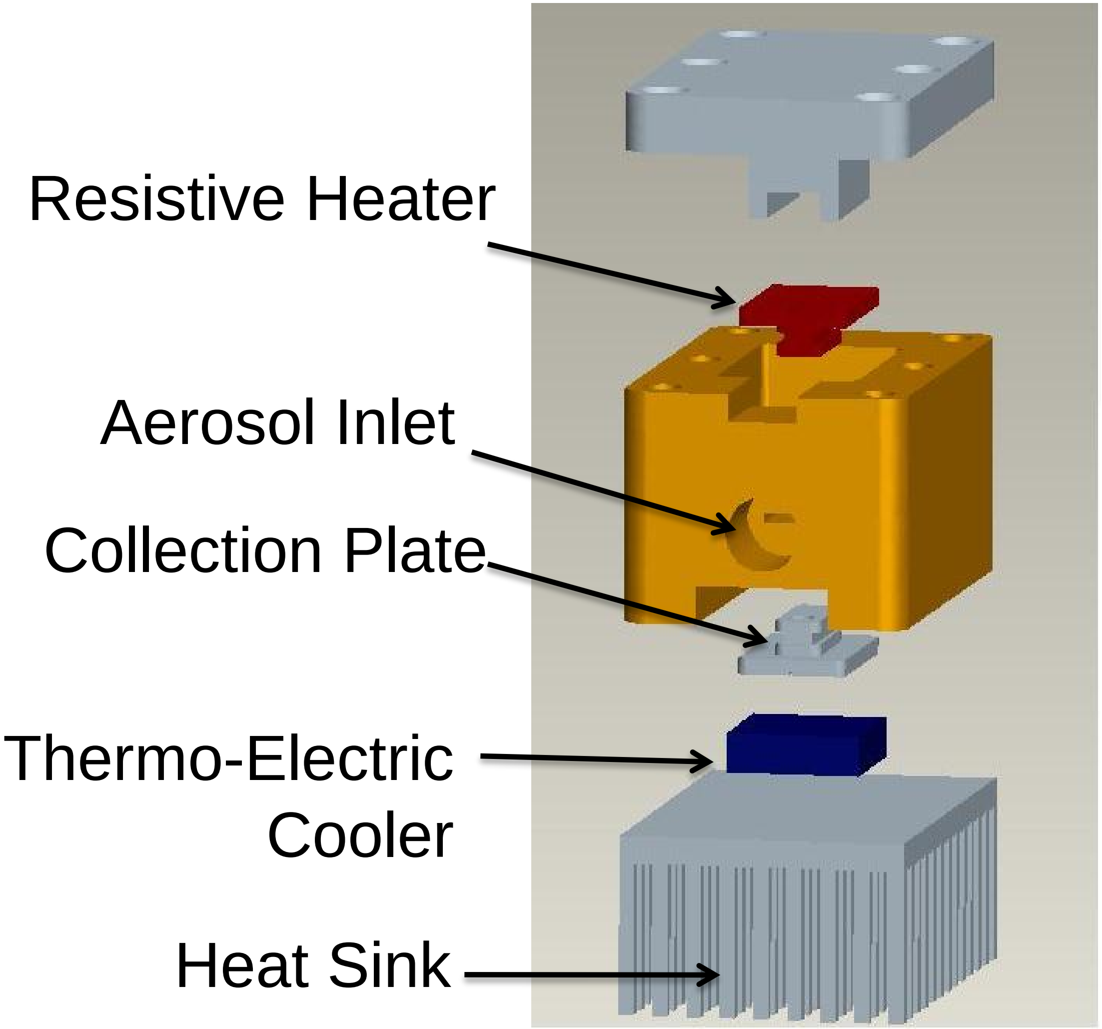
- The key to success in particle speciation is related to collection of a sample on a substrate that is well suited for EM analysis
  - An ideal sampler would collect particles directly on a EM grid (no preparation required)
  - The sample would have uniform particle loading (monolayer)
  - The sample would have a minimum number of particles in contact

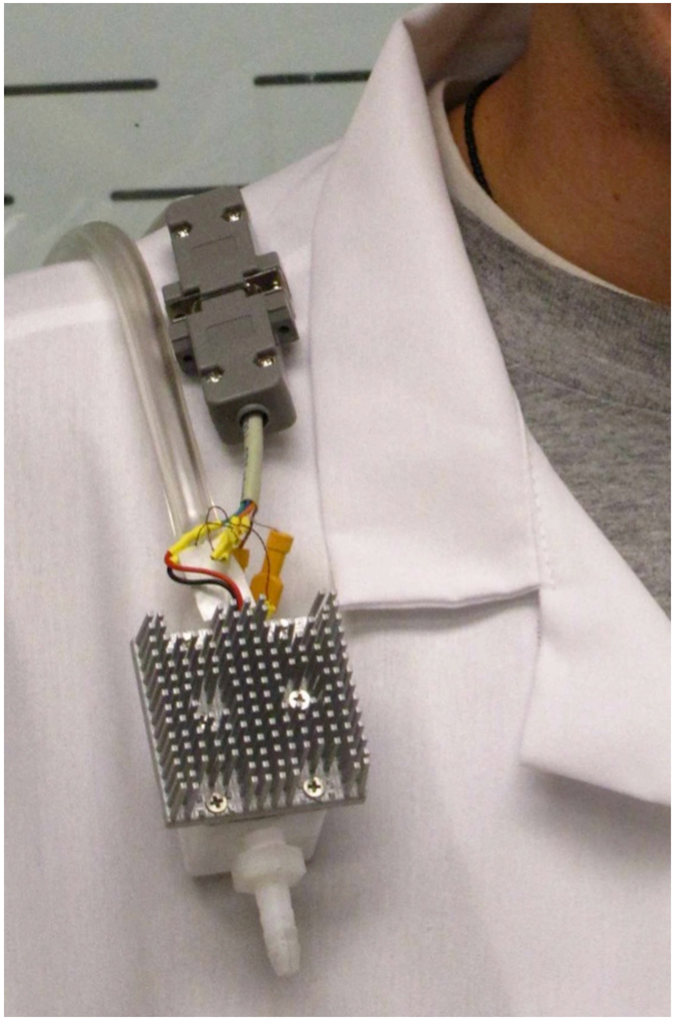
Evolution of the TPS100

- NIOSH small grant (R03OH009381, 2008-2010) awarded to John Volckens (CSU)
- 1st Technical Drawing



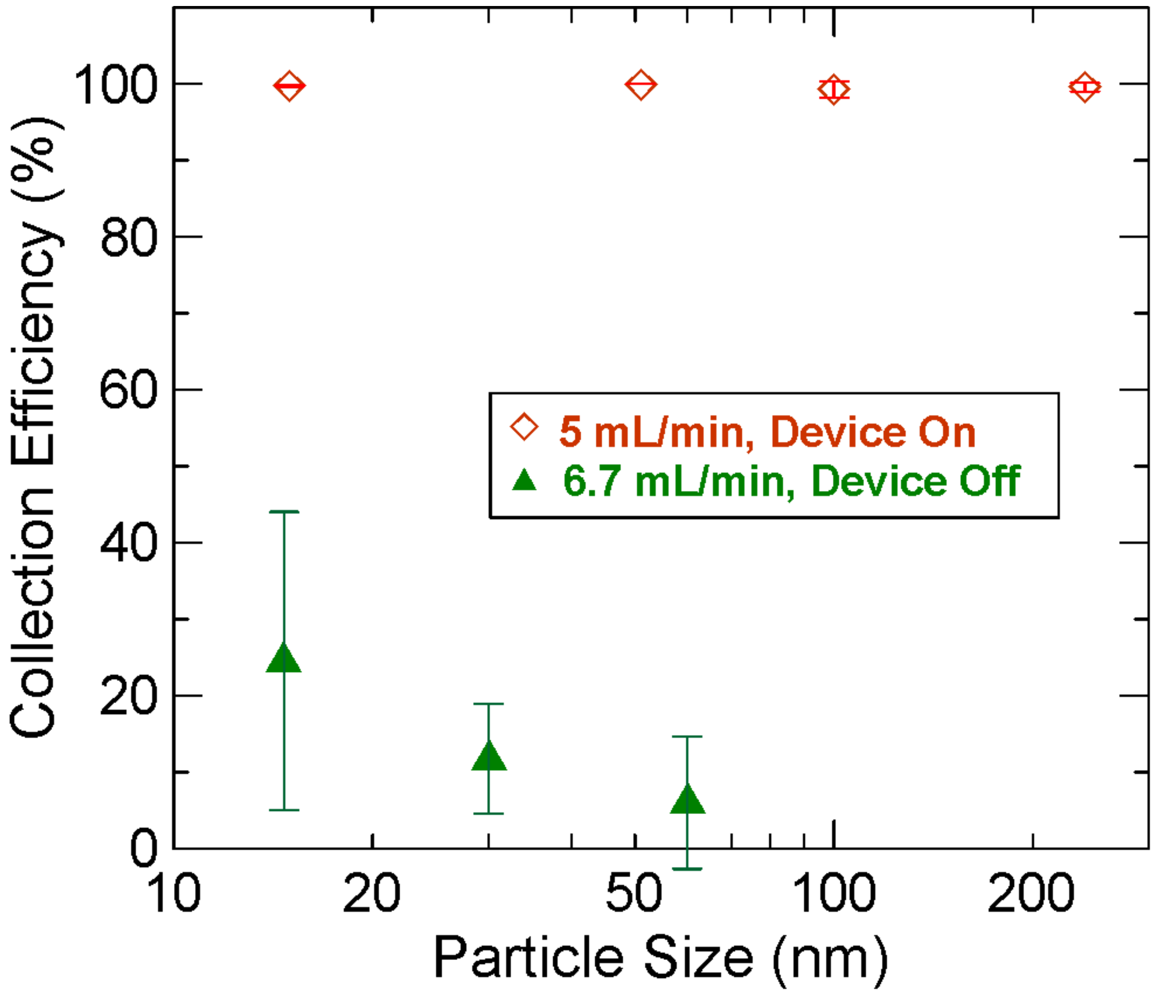
Proof of Concept of the CSU TPS





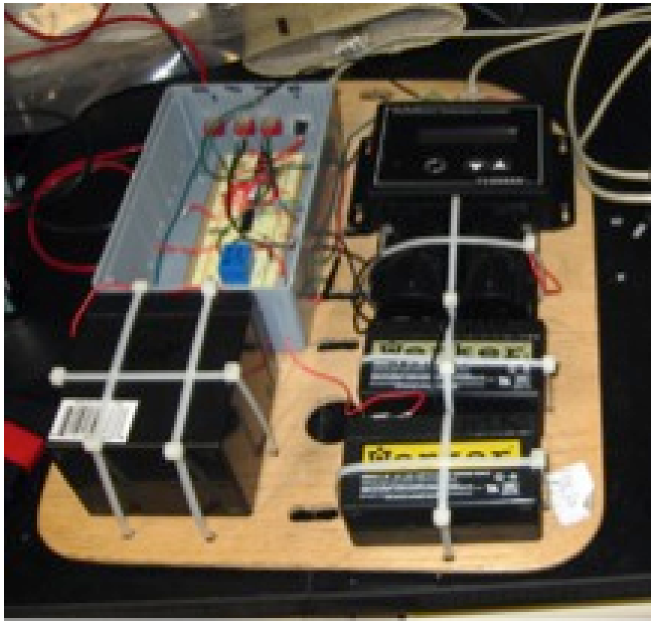
Laboratory Testing: Good Collection Efficiency

- 10 – 300 nm sizes
- 100% at 5 mL/min



Thayer et al., Aerosol Sci. Tech. (2011)

CSU Prototype Thermal Precipitator



The Good: It works! *(Thayer et al., AS&T 2009)*

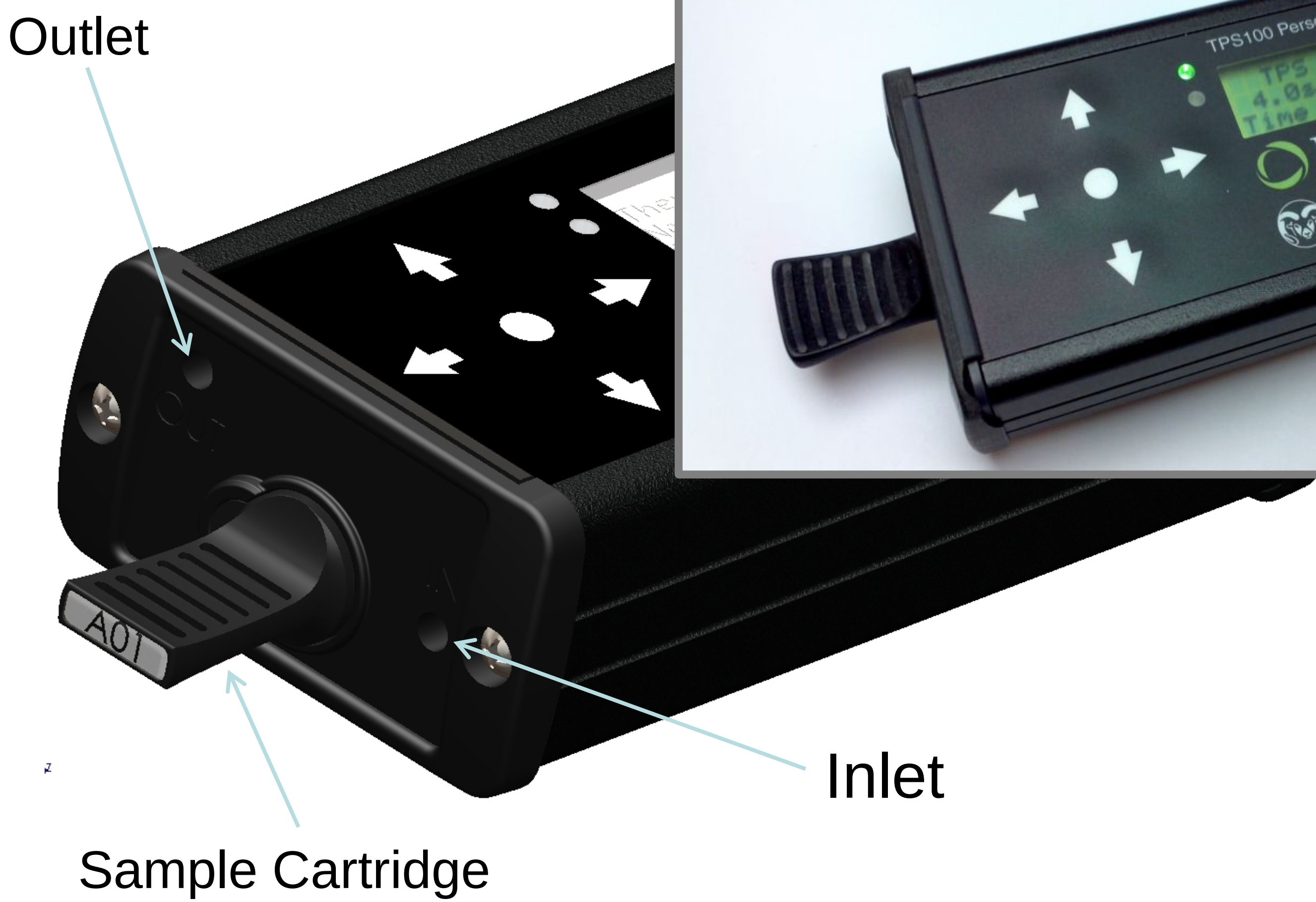
The Bad: Too big, too heavy for 8 hour run time

The Ugly: Not user friendly and not practical for personal sampling

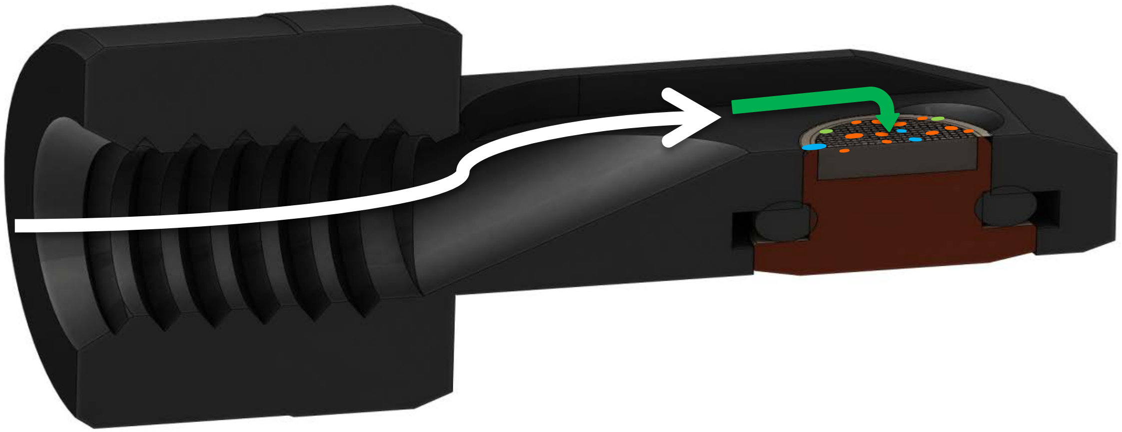
Development of a Personal TPS

- CSU partners with RJ Lee Group
- RJ Lee Group obtains funding from Pennsylvania NanoCommercialization Center
- Work begins on development of an integrated sampler
  – Dan Miller-Lionberg (CSU): mechanical engineering
  – Hank Lentz (RJLG): electrical engineering

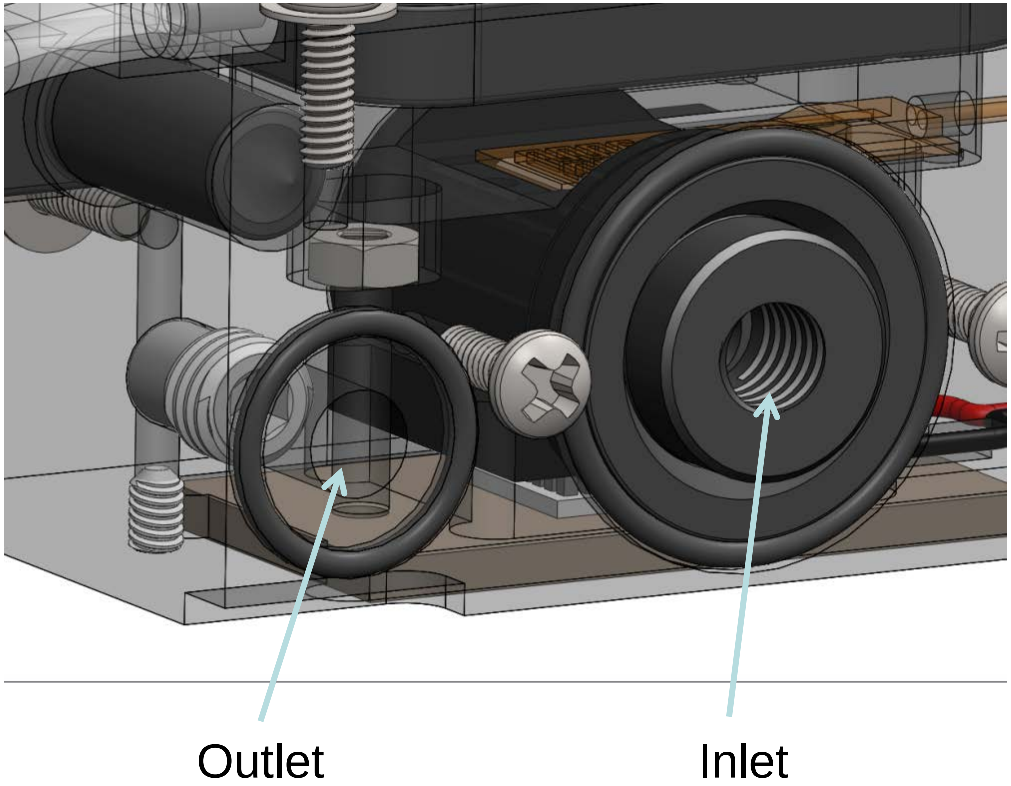
Prototype Integrated TPS100



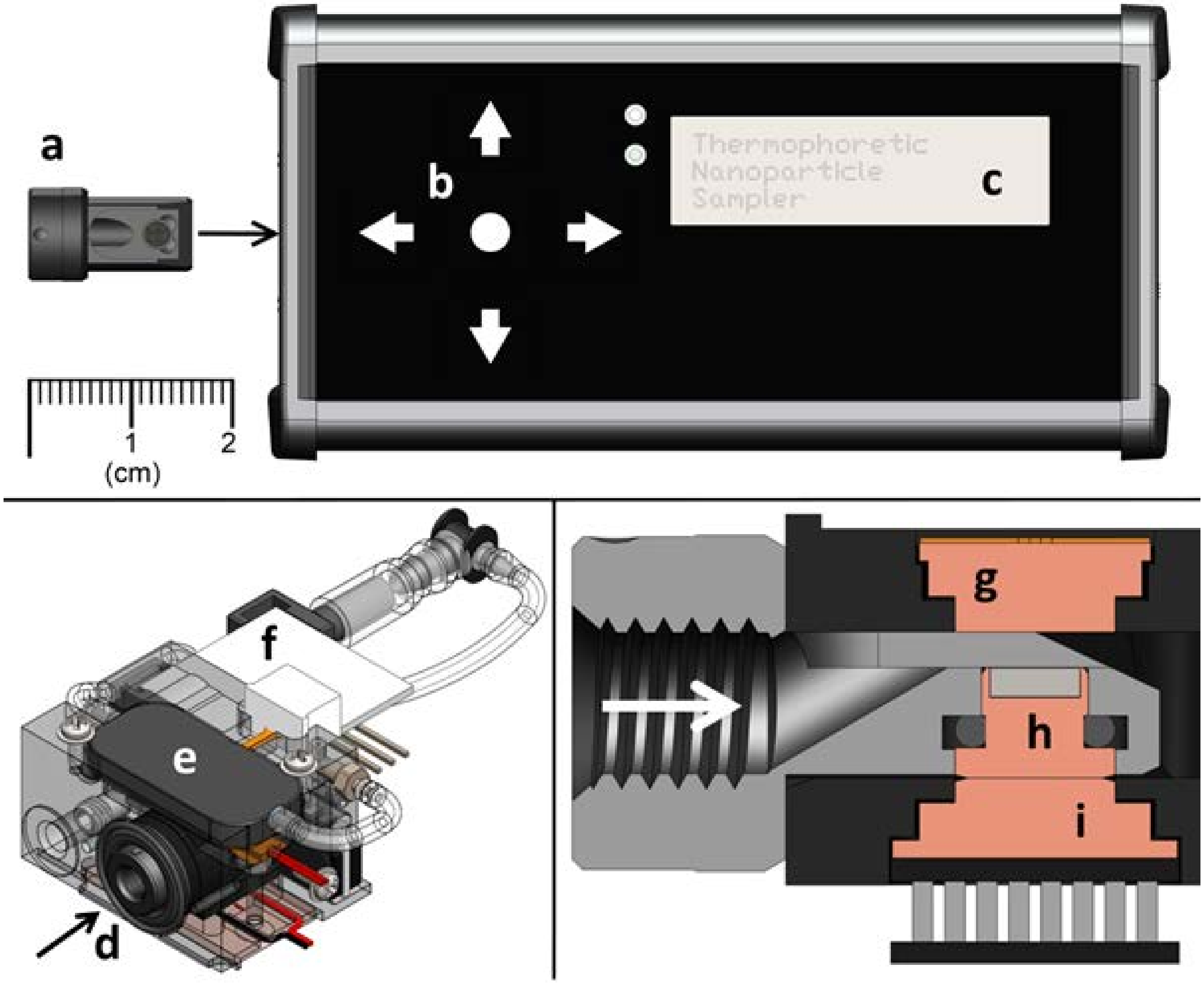
Redesign of the TPS100 Cartridge
The Cartridge becomes the Inlet



Re-design of the TPS100 Sampling Core



Key Components of the TPS100

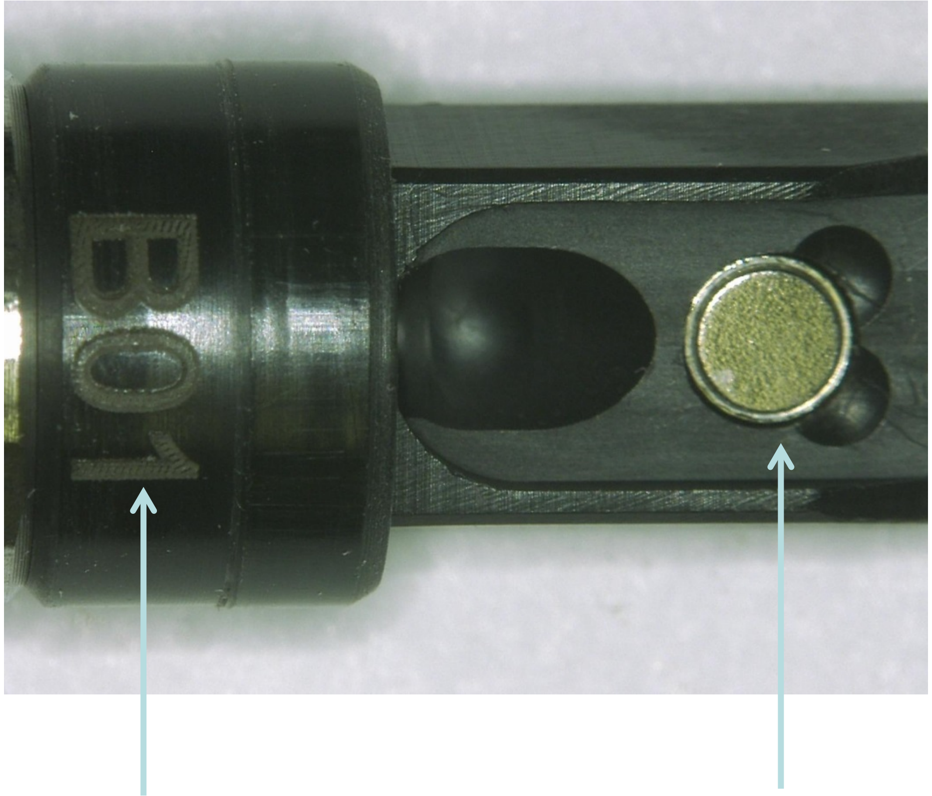


Sampling Core

[a] Sample key
[b]interface panel
[c] status screen
[d] inlet
[e] pump
[f] mass flow sensor
[g] hot plate
[h] grid holder
[i] cold plate

Leith et al., *Aerosol Sci. Tech*. (2013)

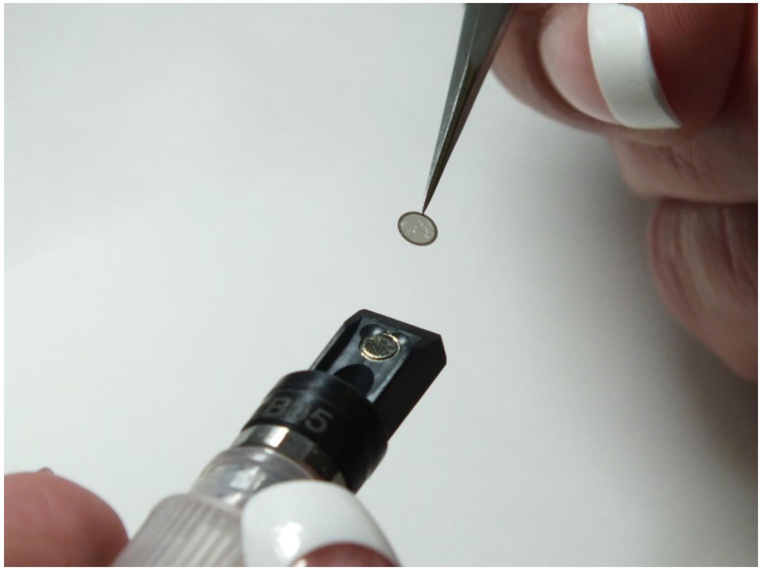
Photo of the TPS100 Sample Cartridge

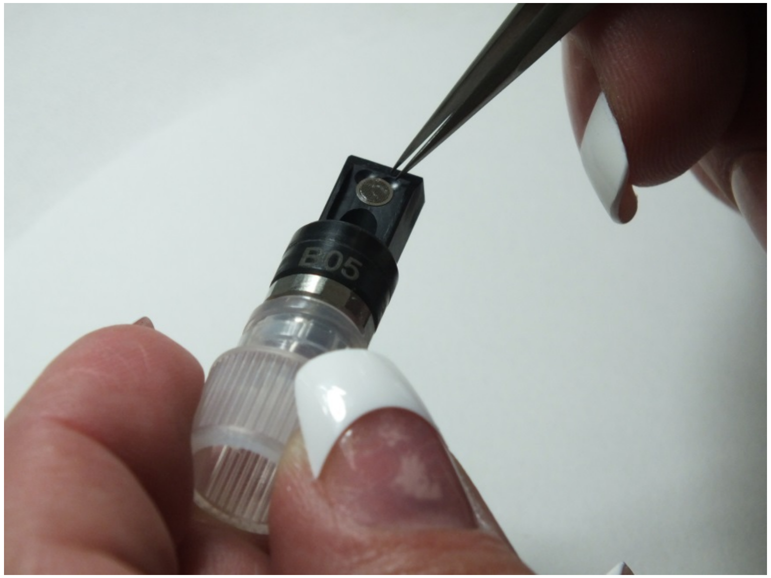


Cartridge ID

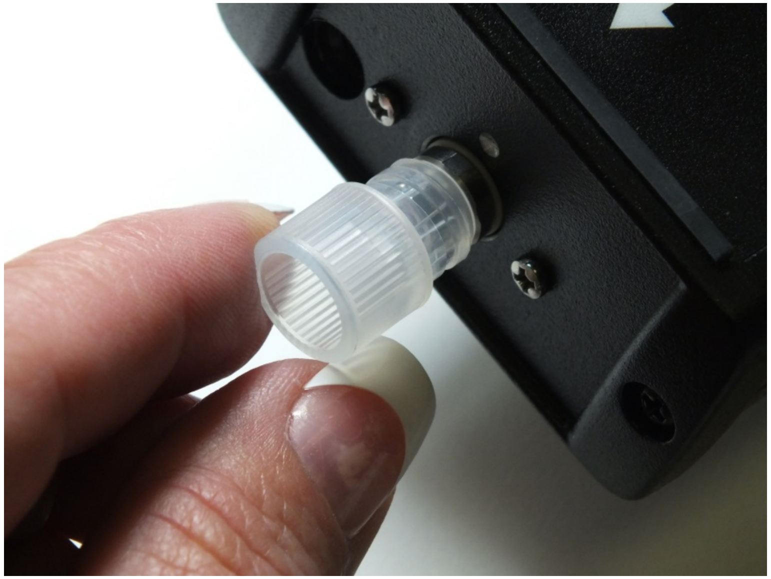
Magnet

Loading of an EM grid on the Cartridge





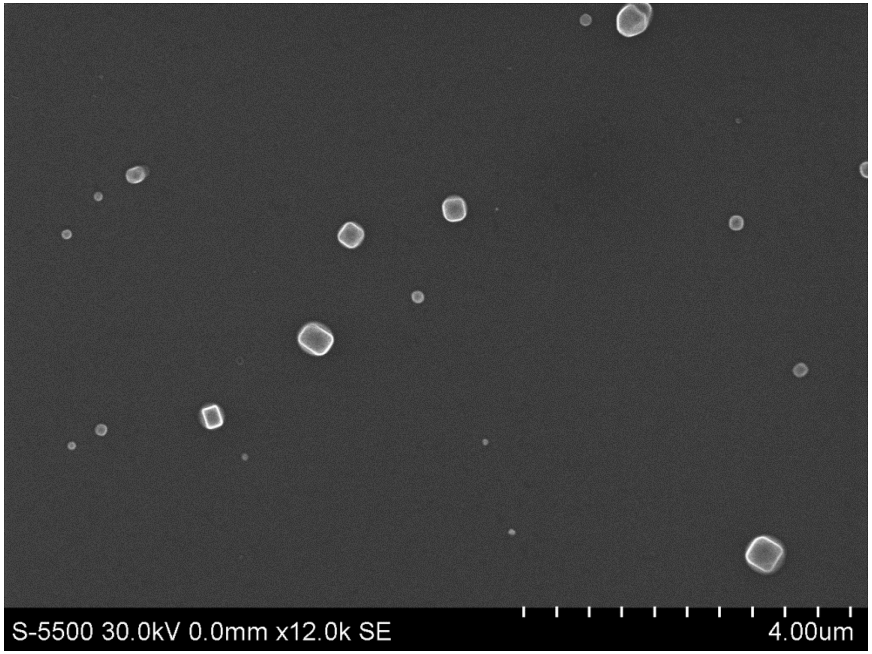
Loading of the Cartridge in the TPS100

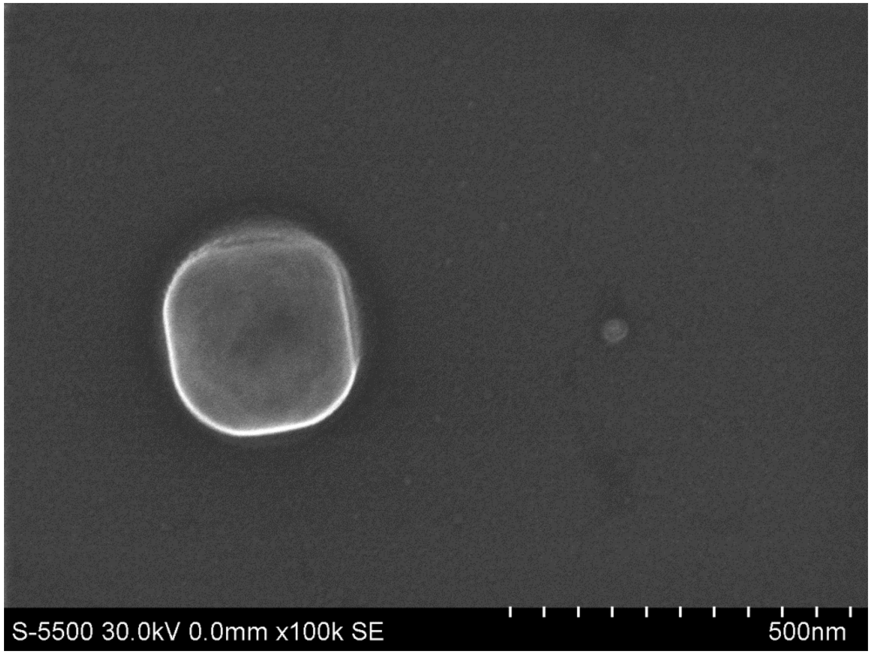


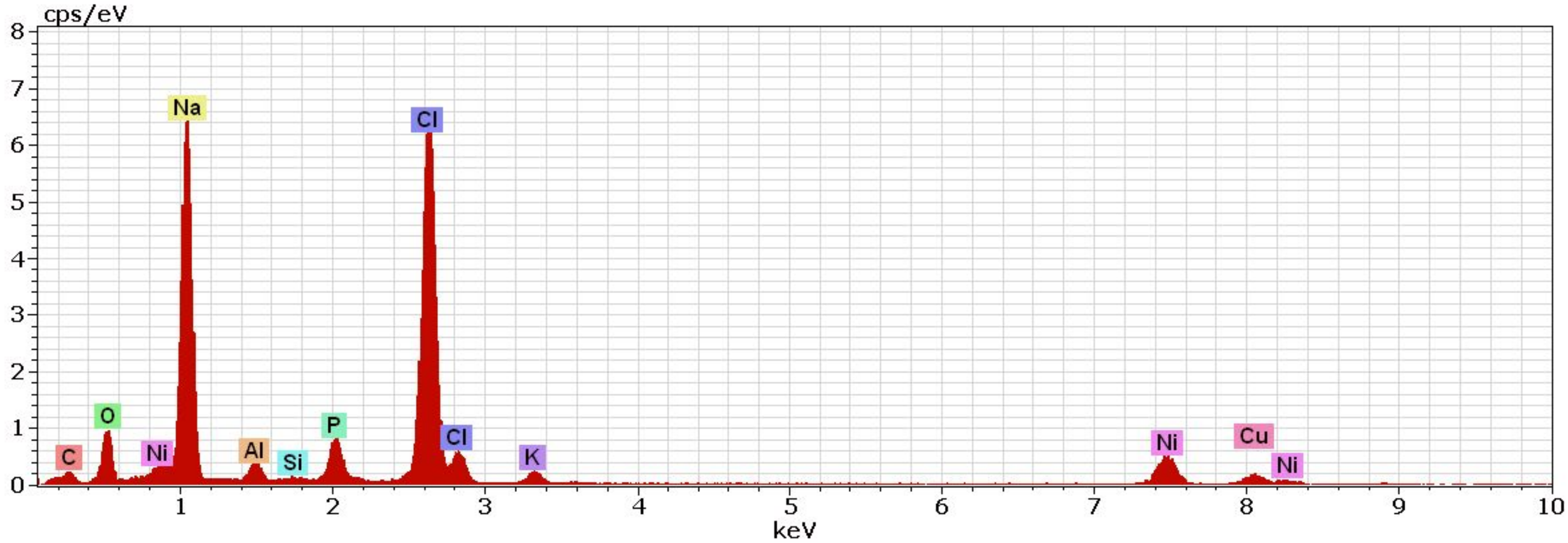
Laboratory Evaluation of the TPS100

- Salt particles (phosphate-buffered saline, PBS) were generated in a chamber using a collision nebulizer and an air pressure gauge
- The simultaneous measurement of particles was conducted with the TPS100 and scanning mobility particle sizer (SMPS)
- TPS100 samples were analyzed using EM and image analysis for particle size and count
- SMPS and TPS100 results were compared for particle concentration and size

PBS Particles Collected with the TPS100



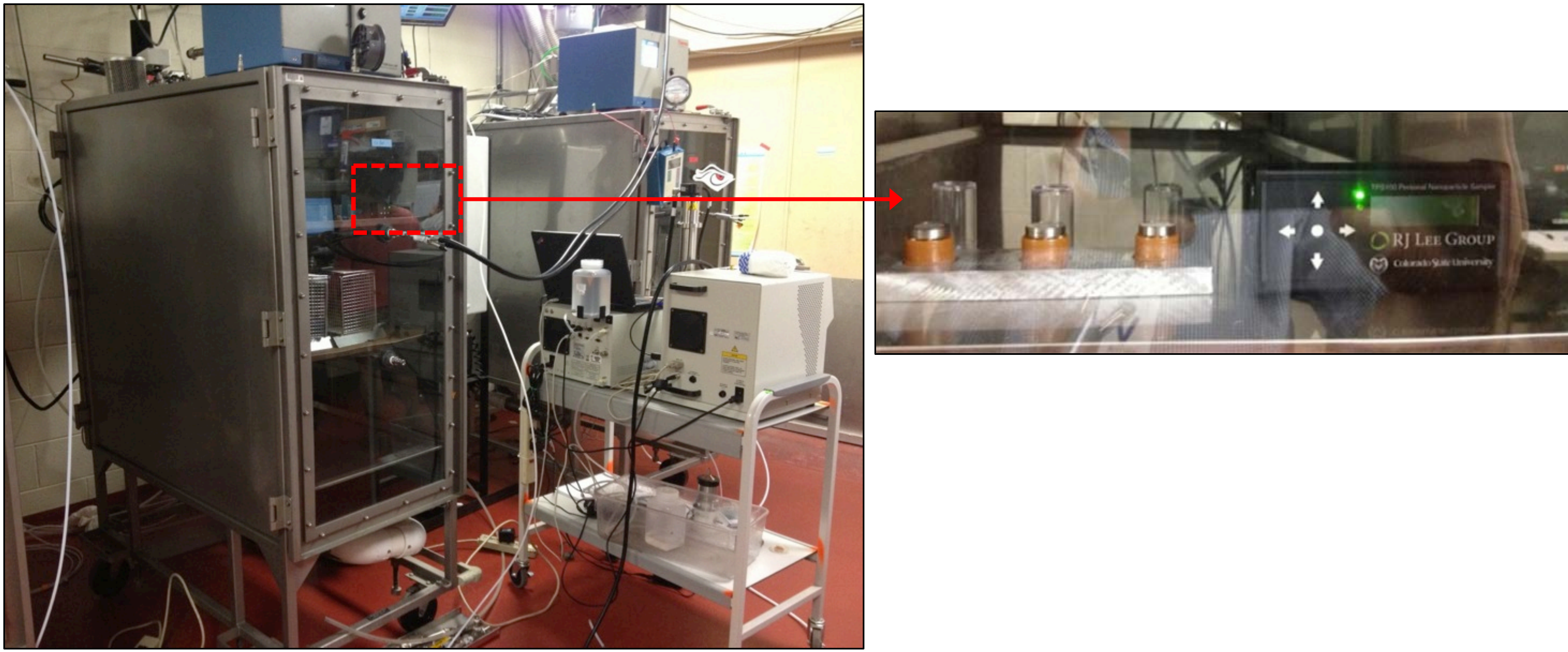




Field Testing of the TPS100

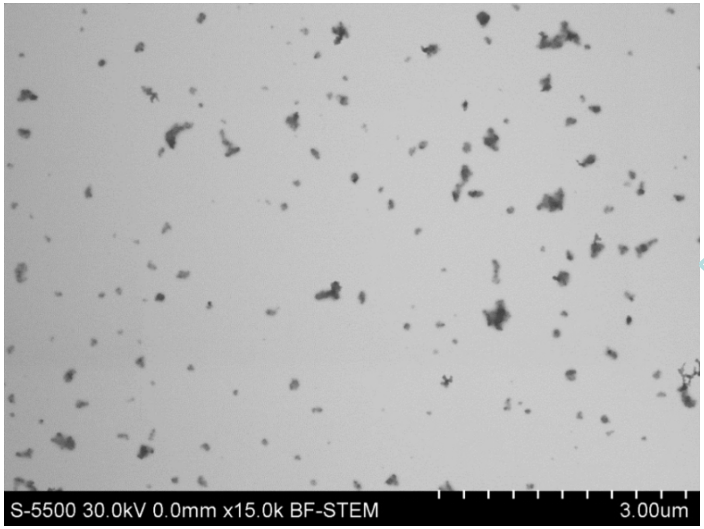
- Internal studies at RJLG and CSU
- U.S. EPA
- NIOSH
- Oak Ridge National Laboratory
- West Virginia University
- NASA
- Other groups
  - Germany
  - Canada
  - South Korea
  - China

Diesel Fuel Combustion Experiments (Cerium Oxide)
EPA Facility in RTP, NC



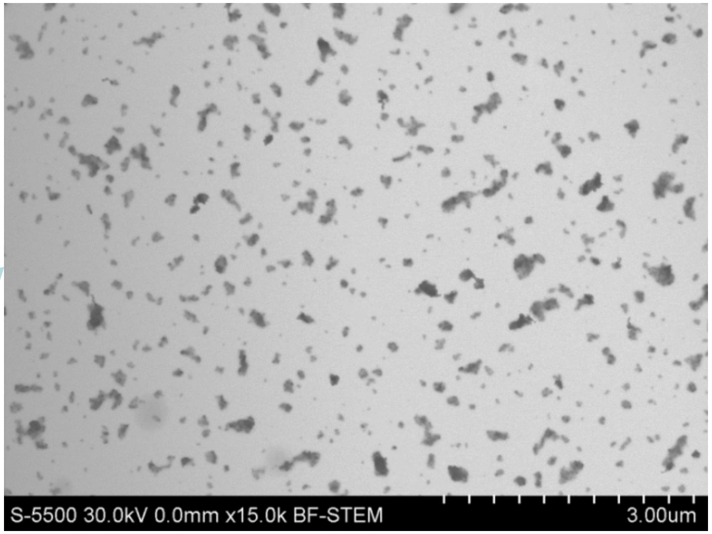
Evaluation of Particle Loading

27 min



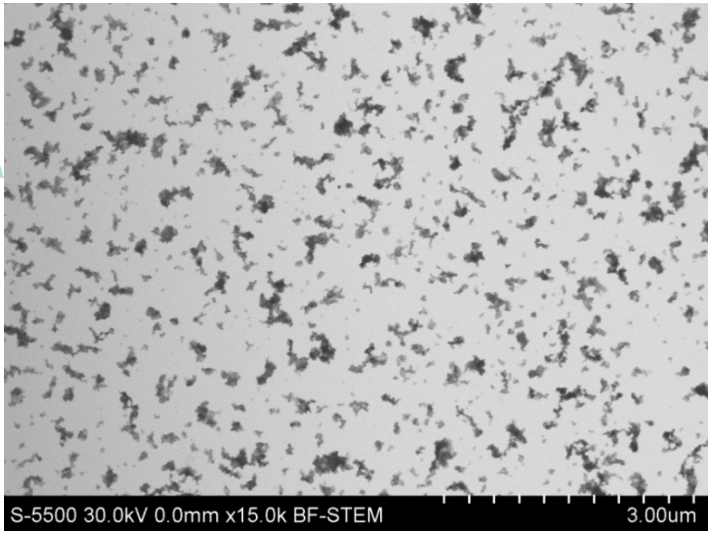
5x

135 min

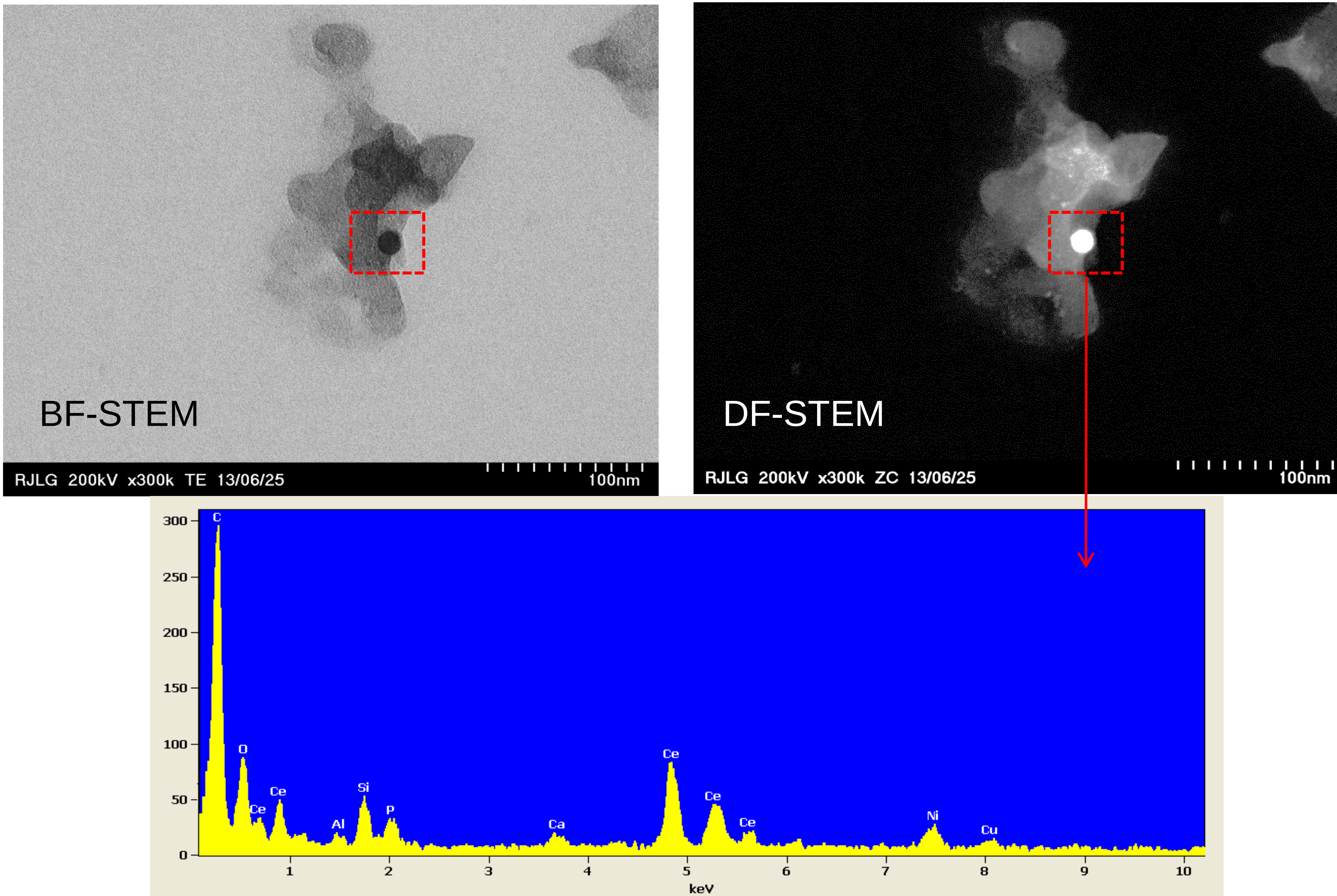


10x

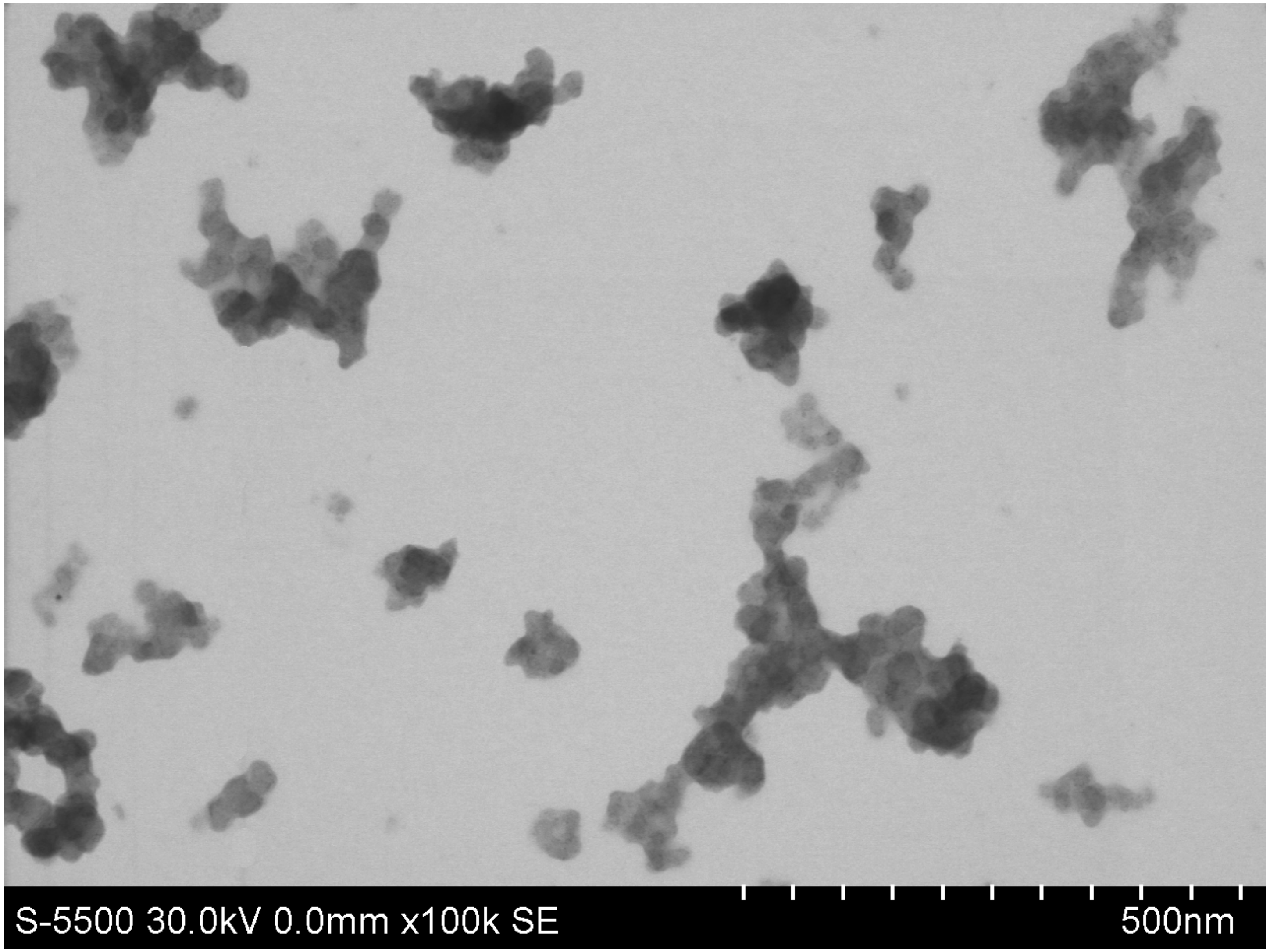
270 min



Cerium Particles Embedded in Soot



EM Analysis using STEM/ImageJ (Ce-Doped Diesel Exhaust)



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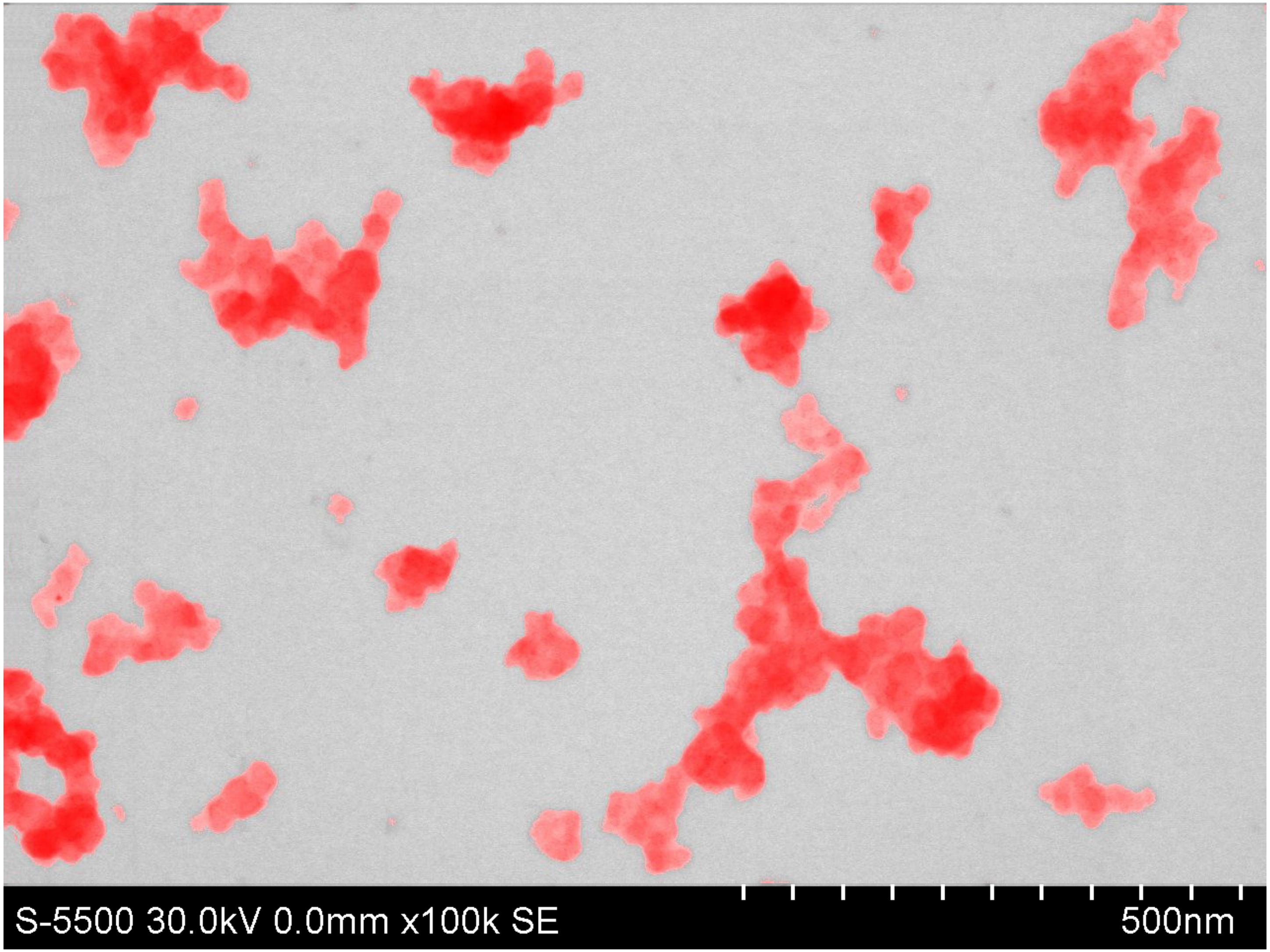
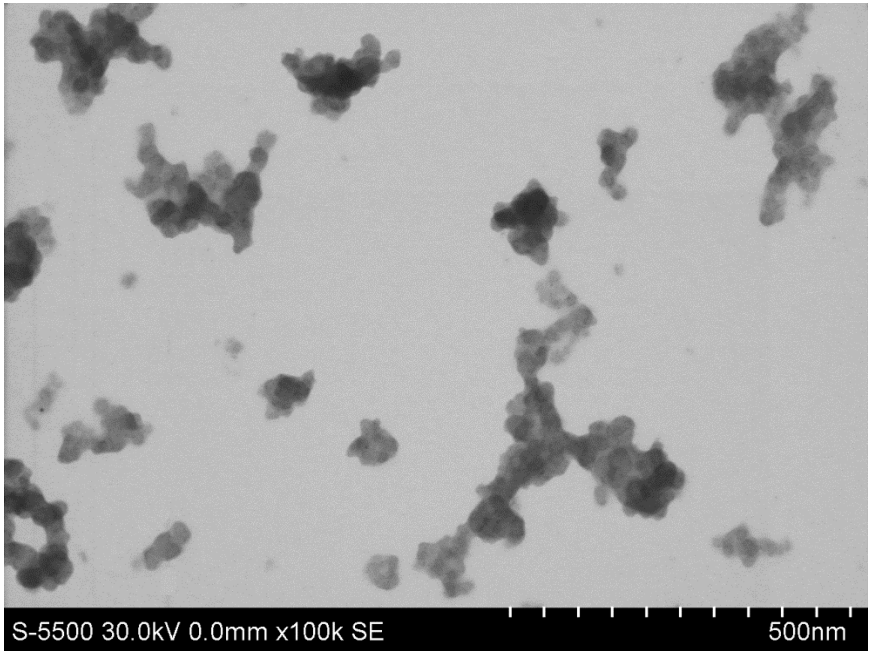
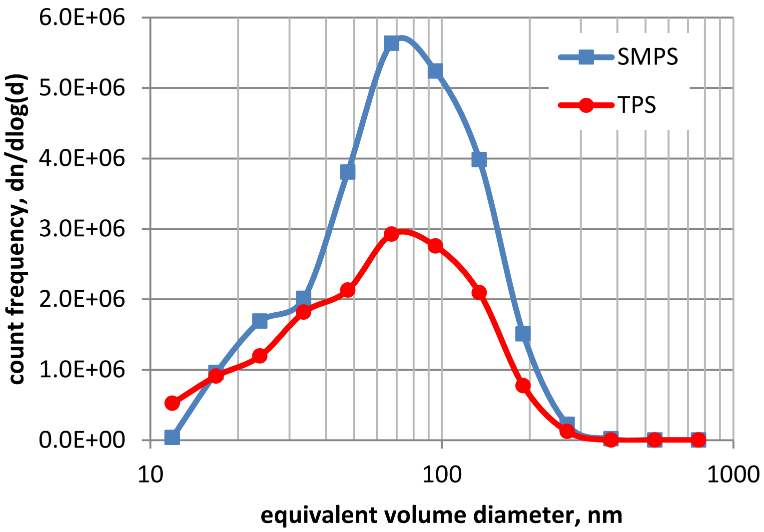


Comparison of SMPS and EM ImageJ Analysis Size Distribution and Particle Concentration EPA Diesel Emissions

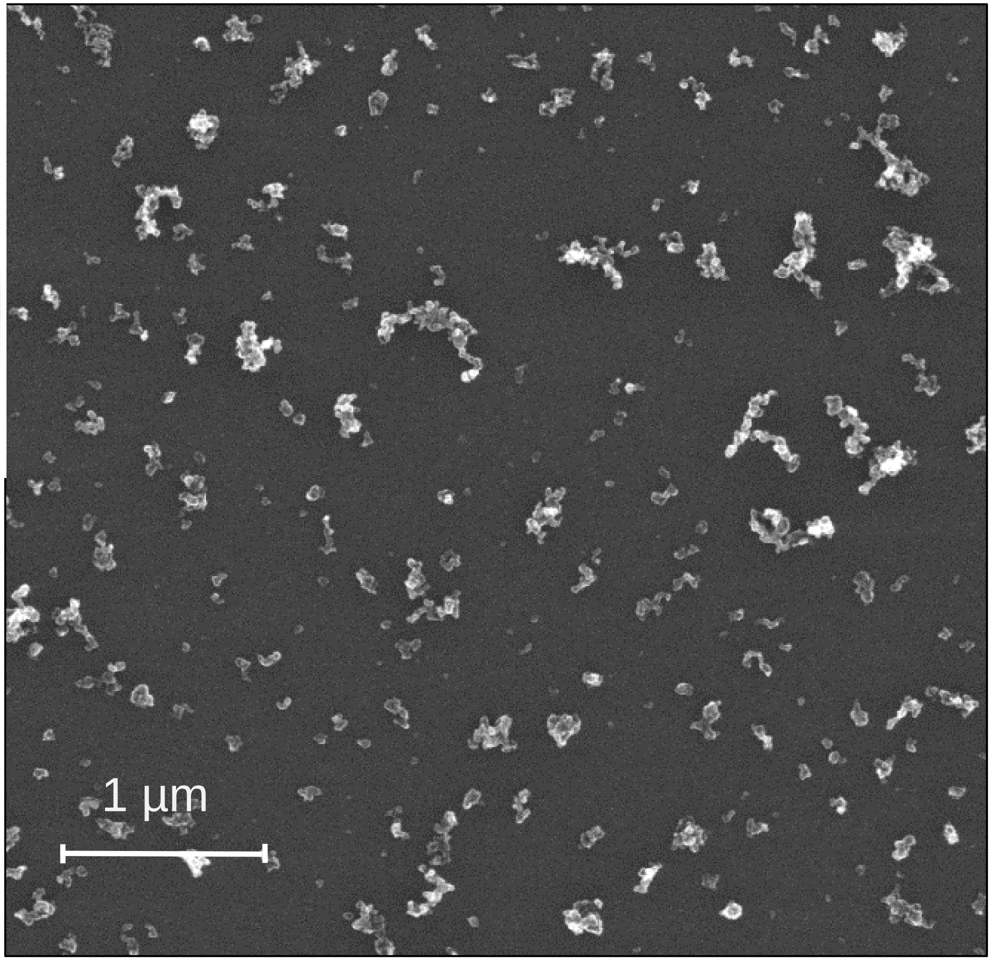




SMPS Particles/cc (Average)	
Test 1	Test 2
1.42E+06	1.10E+06

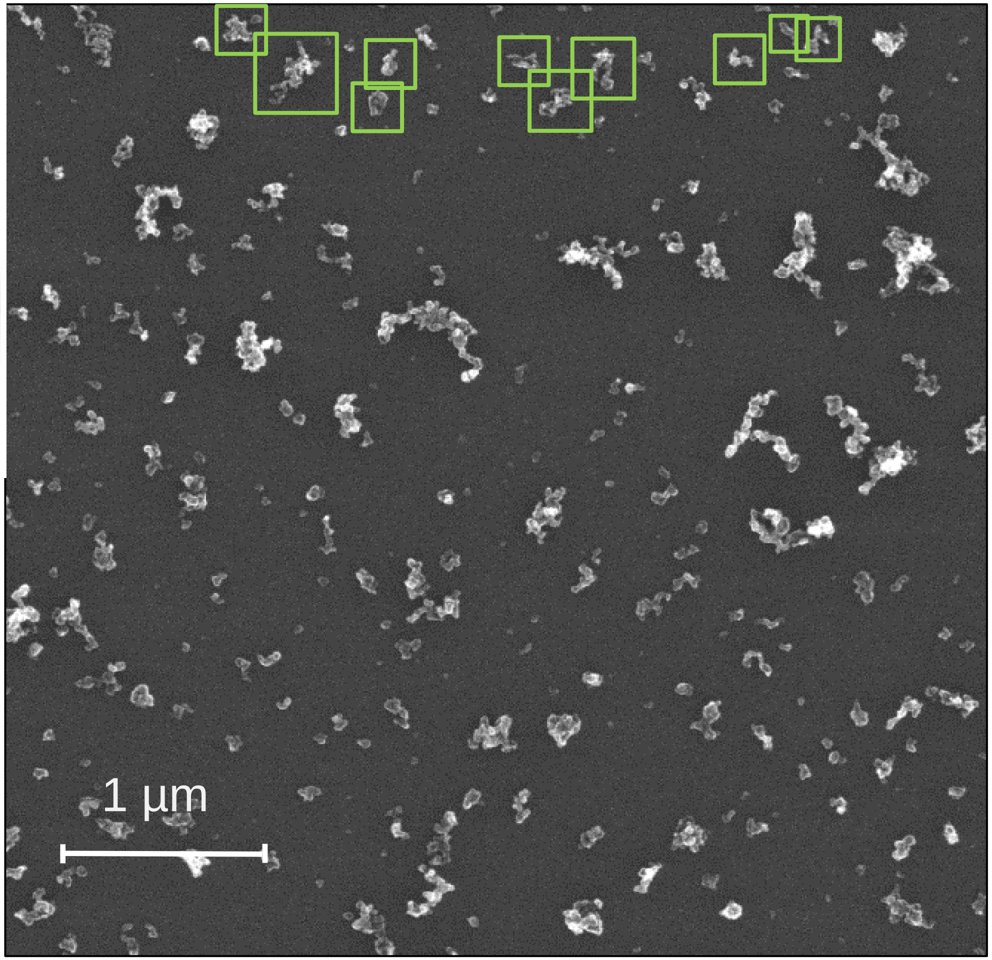
TPS correction factor developed in the PBS experiment applied

Automated Analysis of Diesel Nanoparticles with CCSEM Analysis of TPS Sample

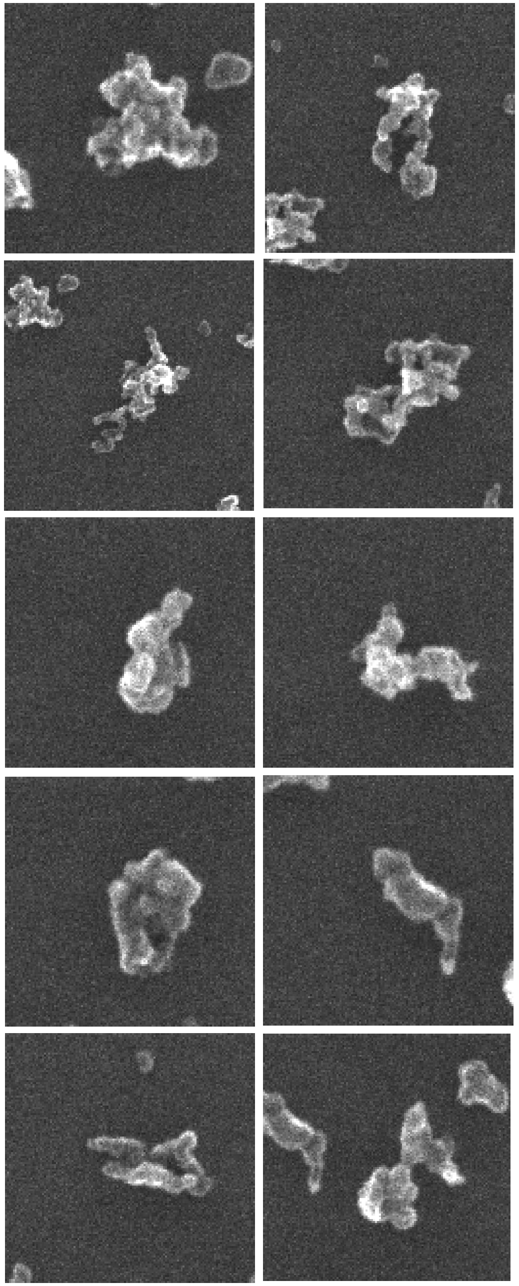


FESEM Field Image of Soot Structures

Automated Analysis of Diesel Nanoparticles with CCSEM Analysis of TPS Sample

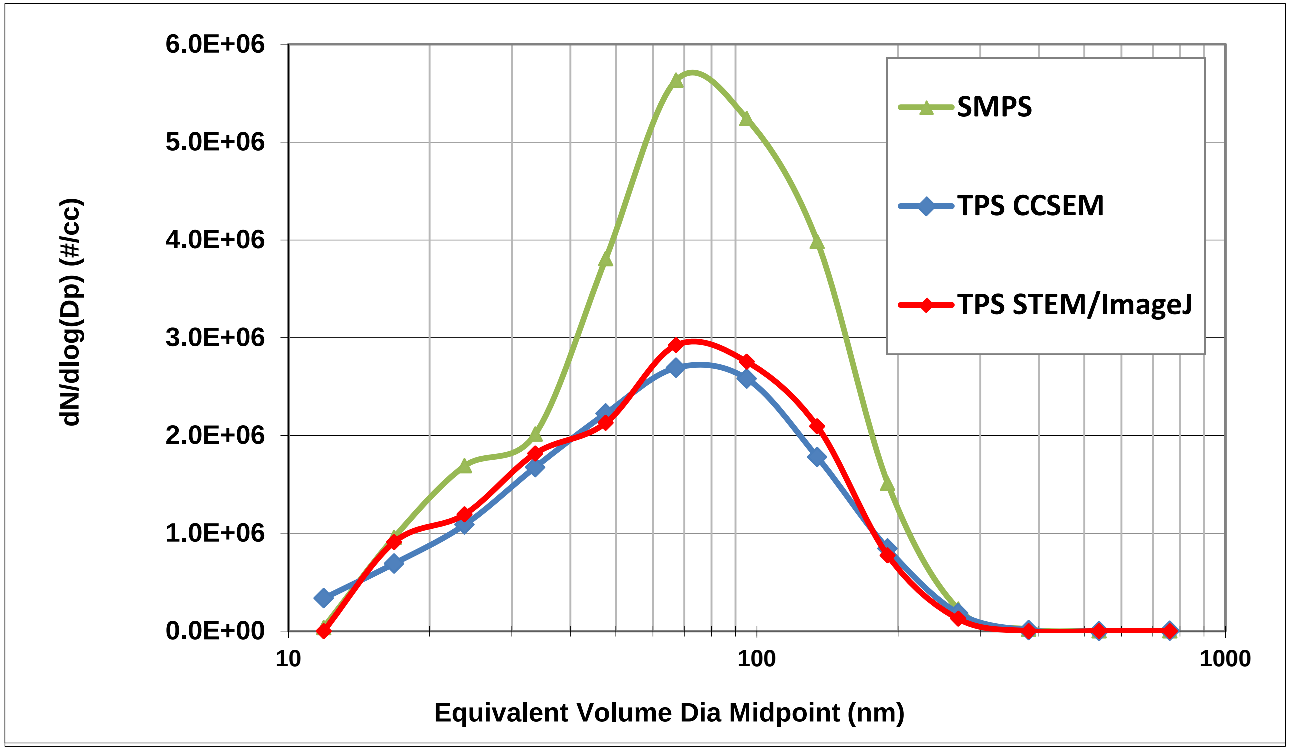


FESEM Field Image of Soot Structures



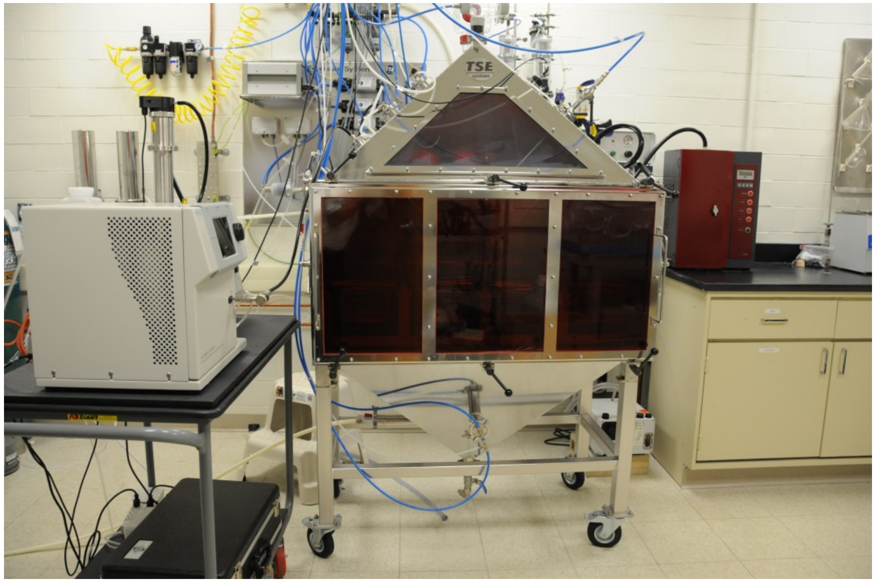
Comparison of Particle Size Distribution SMPS and TPS EPA Diesel Emissions

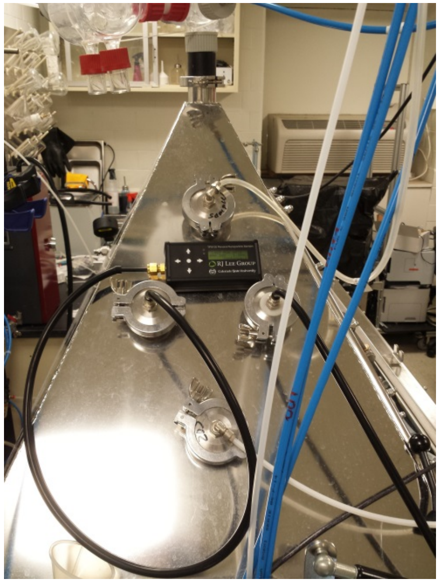
- SMPS
- TPS / STEM and ImageJ
- TPS / IntelliSEM CCSEM



TPS correction factor developed in the PBS experiment applied

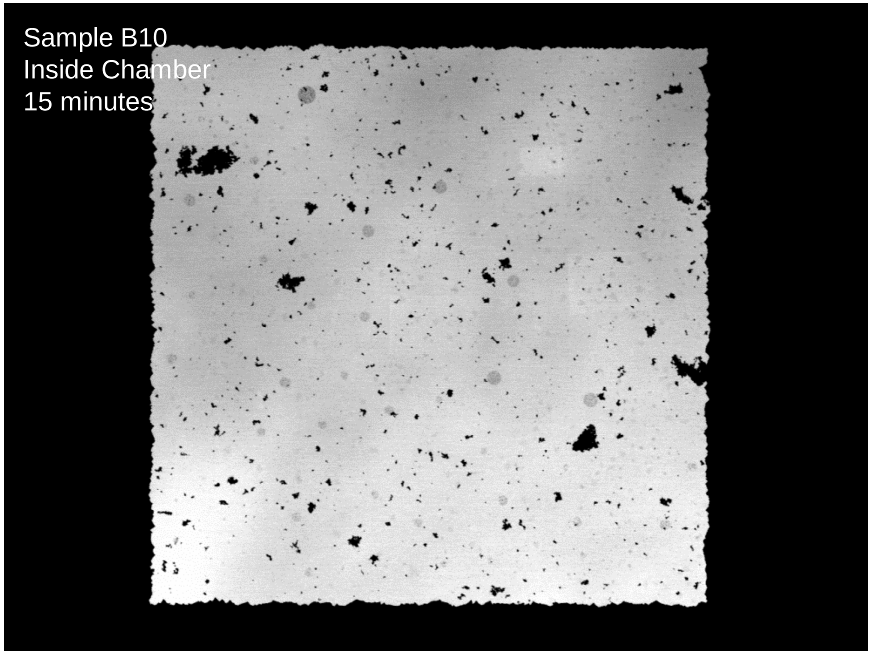
WVU Chamber Study: TiO_2 Sample Collection

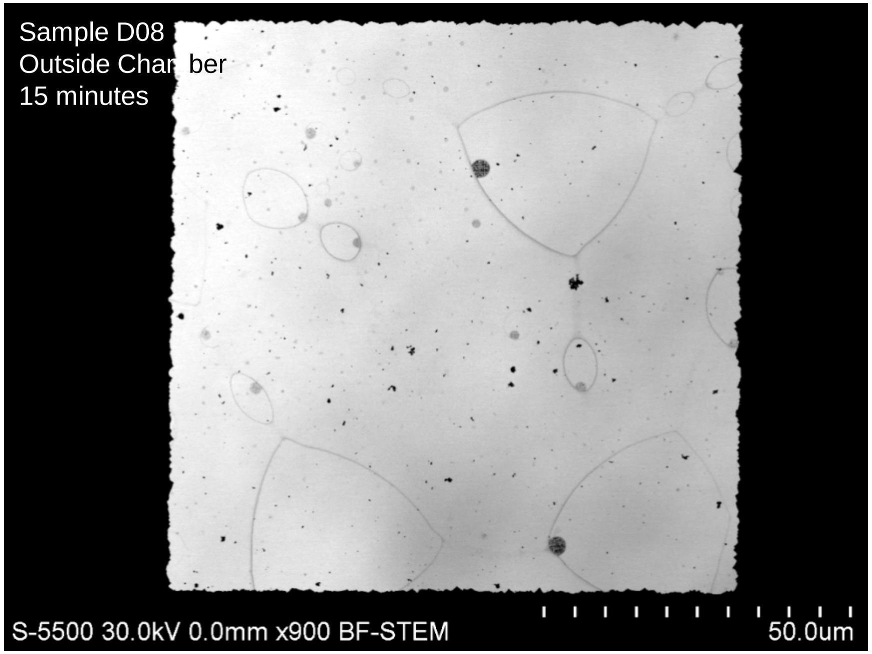


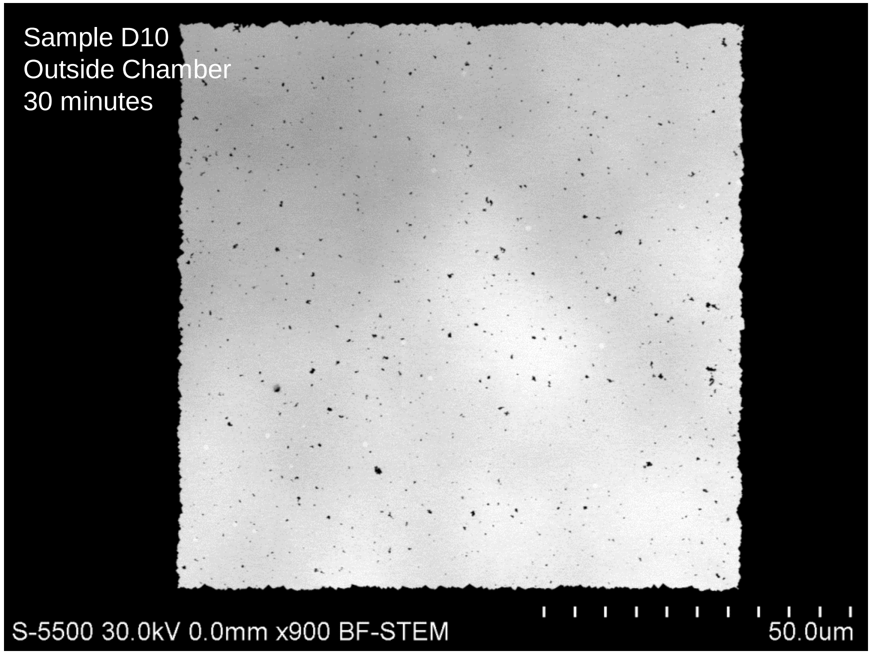


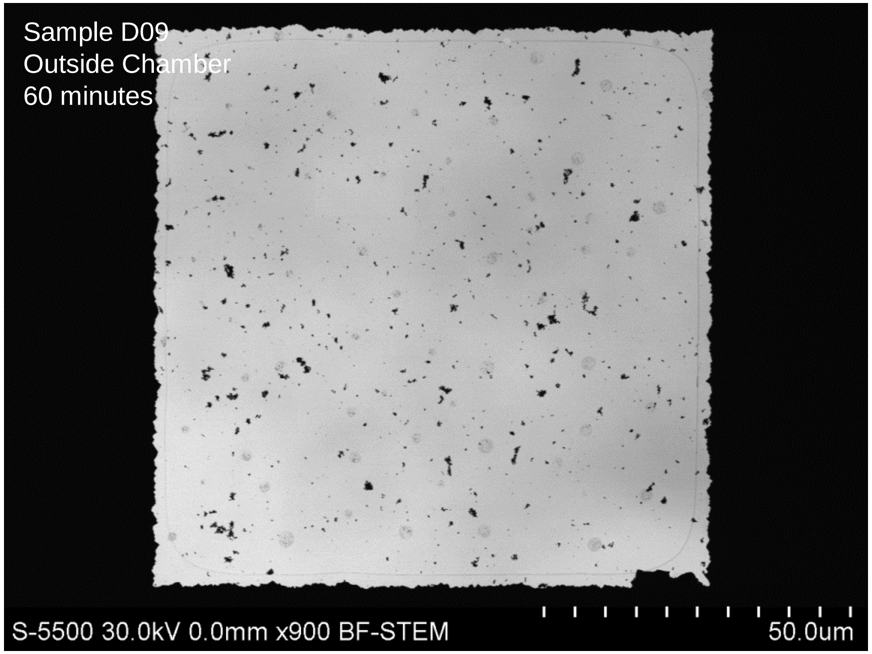
TPS ID	Sample ID	Description	Total Sample Time
V4-03	D-07	In-chamber sample	15 min.
V4-05	B-07	Out-side chamber	15 min.
V4-05	B-08	Out-side chamber	30 min.
V4-09	B-09	Out-side chamber	60 min.

Mass Concentration: 15.7 mg/m^3

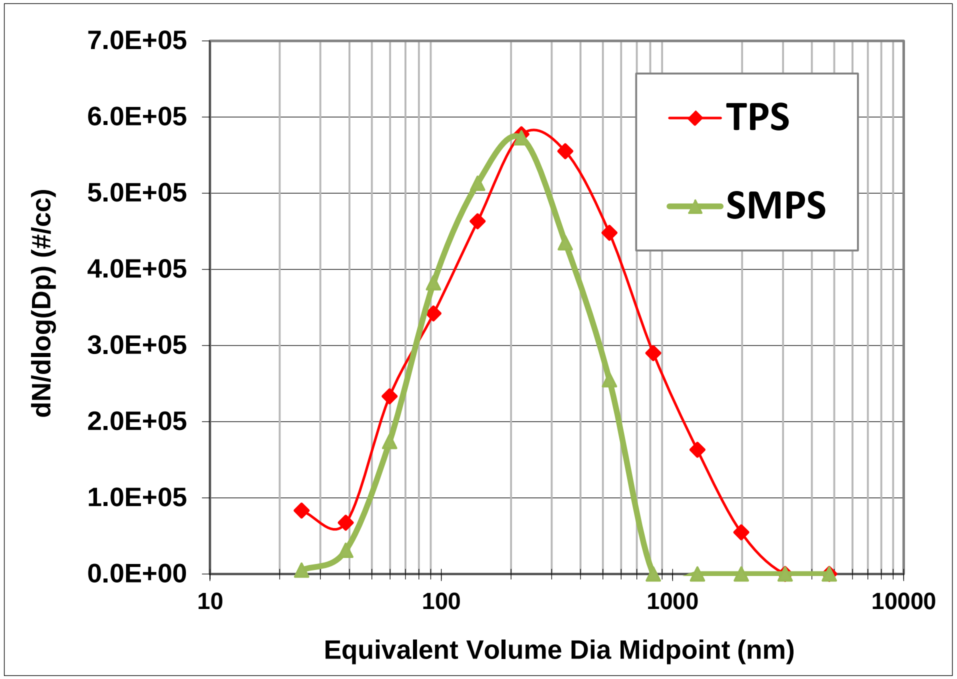

Sample B10
Inside Chamber
15 minutes


Sample D08
Outside Chamber
15 minutes
S-5500 30.0kV 0.0mm x900 BF-STEM
50.0um

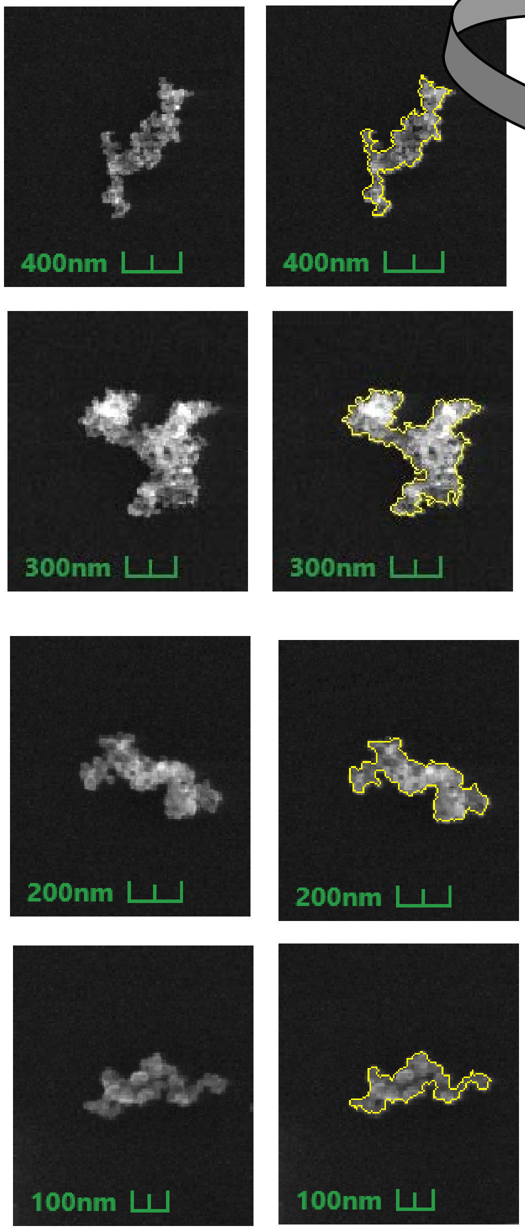

Sample D10
Outside Chamber
30 minutes
S-5500 30.0kV 0.0mm x900 BF-STEM
50.0um


Sample D09
Outside Chamber
60 minutes
S-5500 30.0kV 0.0mm x900 BF-STEM
50.0um

Comparison of SMPS and ImageJ Analysis of the TPS Sample Size Distribution and Particle Concentration

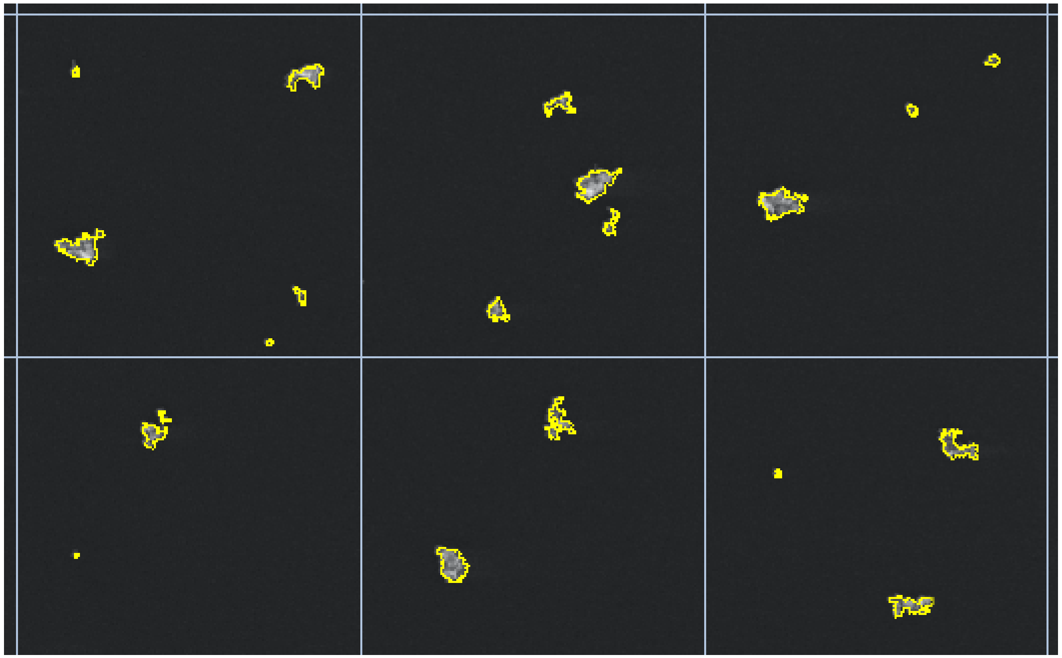


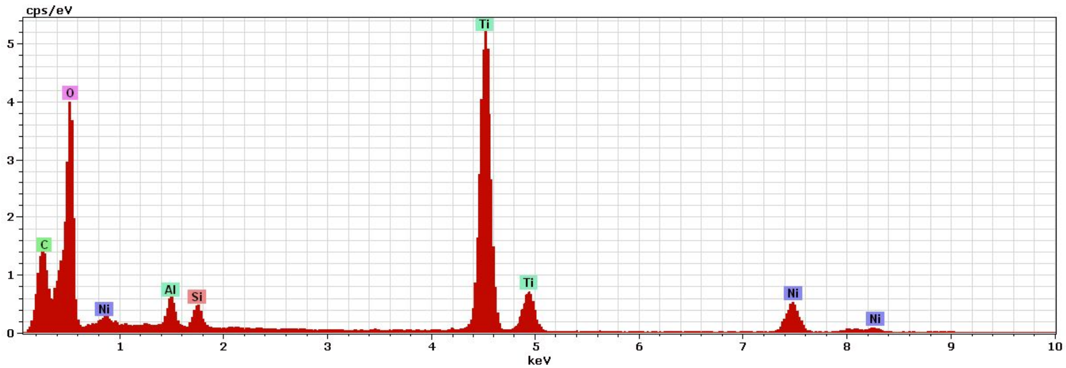
TPS correction factor developed in the PBS experiment applied



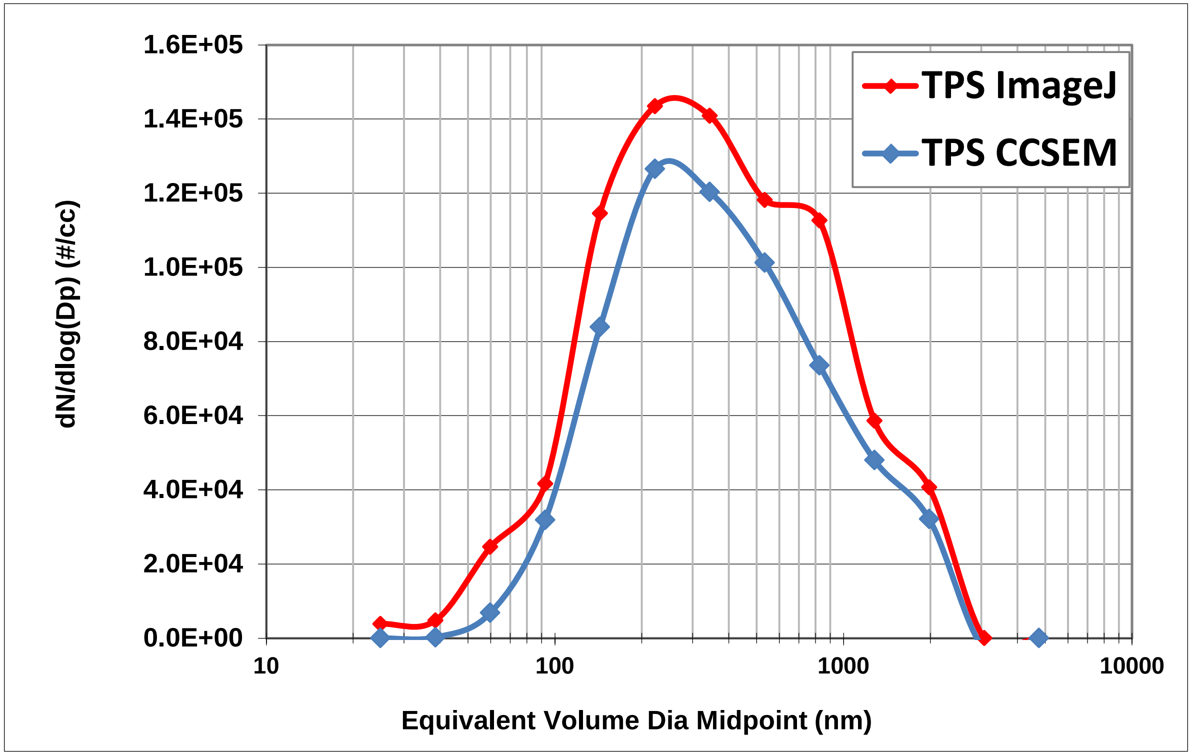
Detect Particle → Acquire Digital Image → Measure Diameters → Collect EDS

IntelliSEM Prospector





Comparison of CCSEM and Image Analysis Results for Sample #2 of the Initial WVU TiO_2 Study



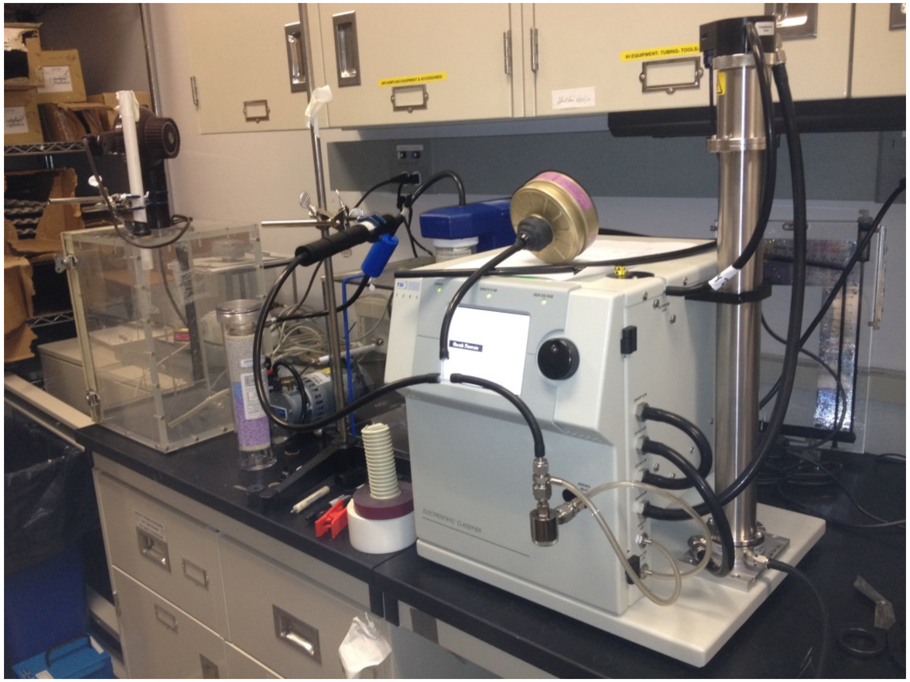
No. of Particles

CCSEM	Image Analysis
3495	443

Evaluation of Particles Generated by Small Electrical Motors

- Particle emissions from electric motors used in consumer products such as a hair dryer and hand held vacuum cleaner were collected using the TPS and SMPS
- Study performed as part of a student summer project
- TPS100 samples were collected in a test chamber
- SMPS and TPS results were compared for particle concentration and size

TPS100 Testing at ORNL



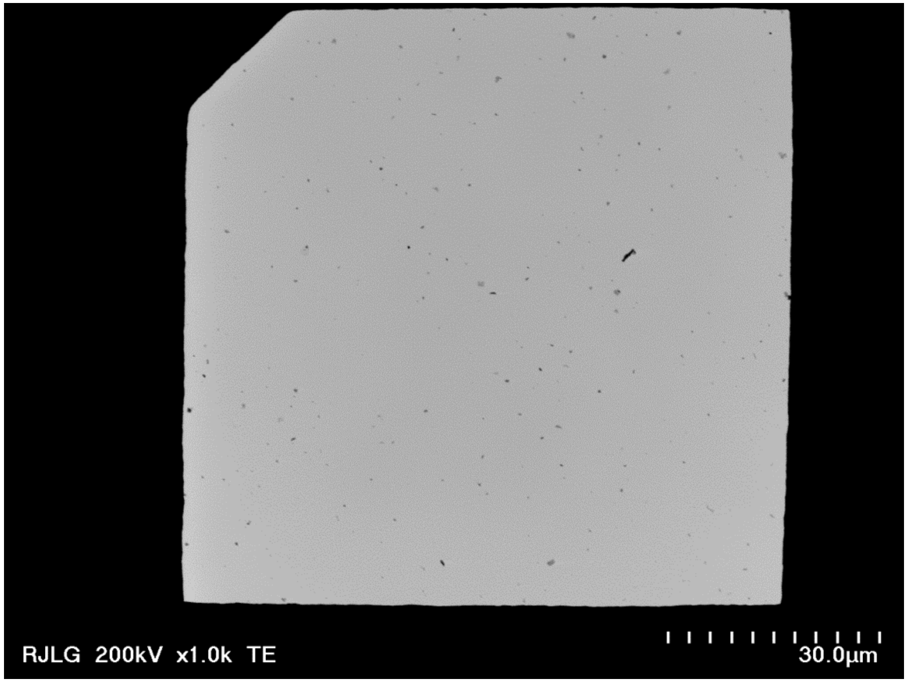
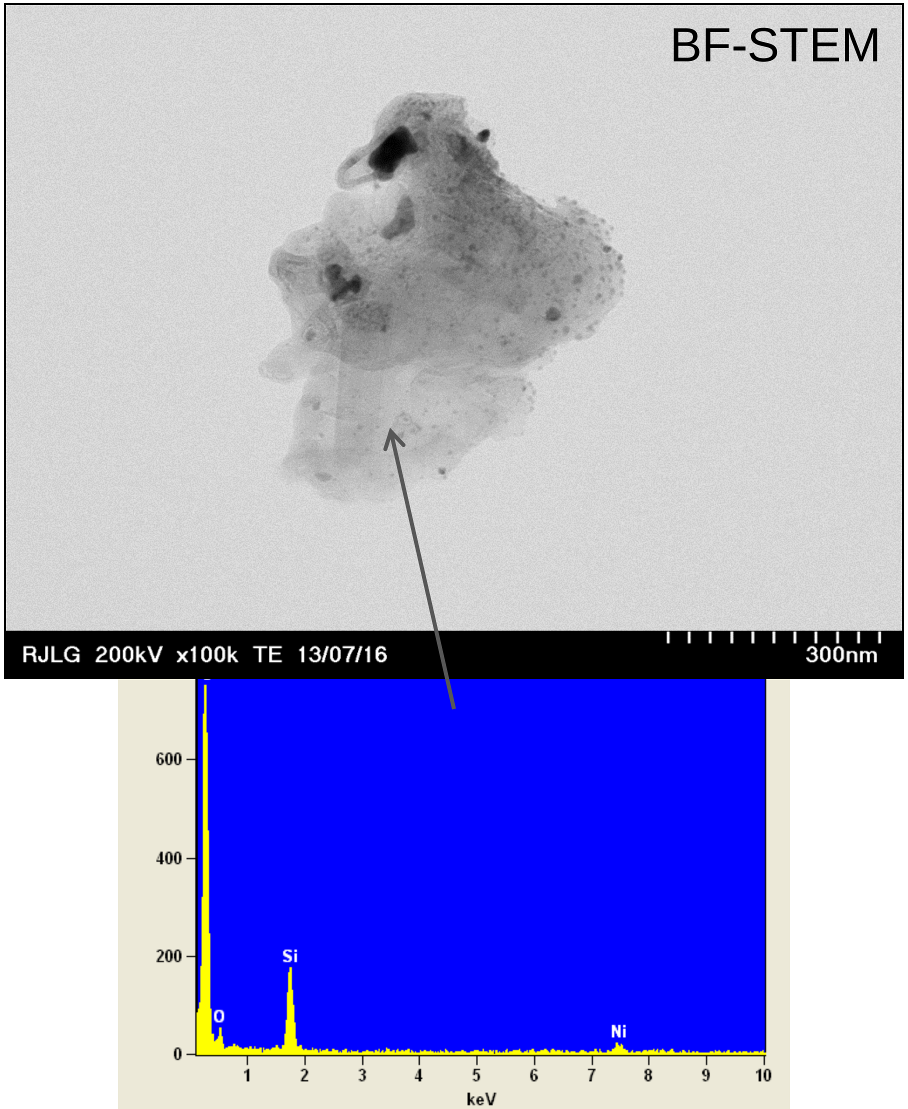
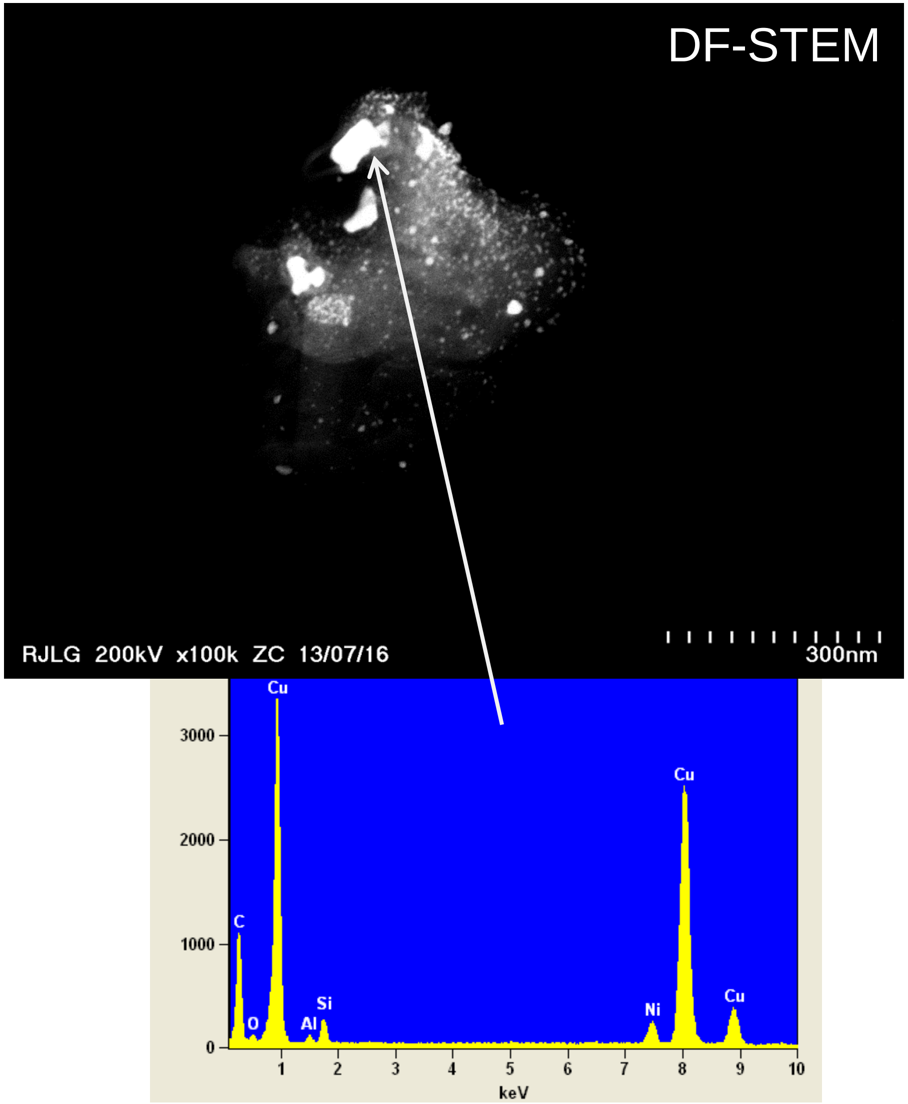


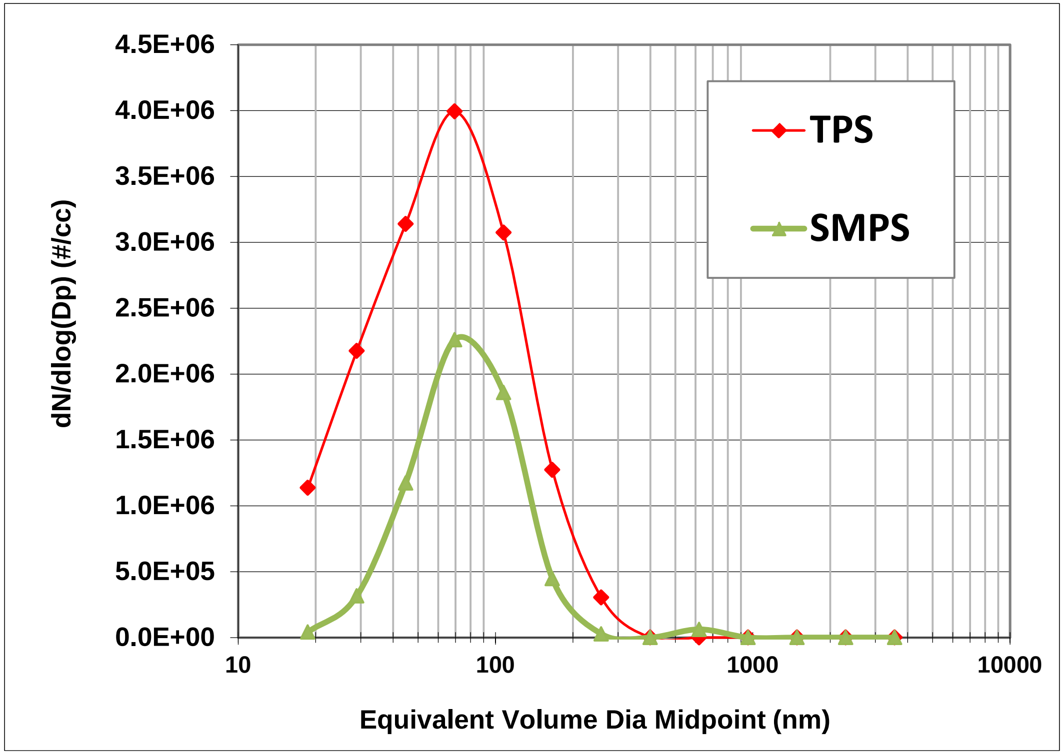
Illustration of test chamber (left) and low magnification image (1,000x) showing the distribution of particles on the TEM grid.

Example of Particle Produced by Small Electric Motor





Comparison of SMPS and EM Analysis ORNL Electric Motor Testing



TPS correction factor developed in the PBS experiment applied

On-going TPS100 Activities

- Laboratories studies
  - Evaluate collection of asbestos and CNTs
  - Continue to evaluate use of CCSEM to speciate nanoparticles
    - Potential for cost effective nanoparticle EM analysis?
  - Further evaluation of the transfer function
    - Comparison of CCSEM and SMPS data
- Continuation of Field Evaluation Studies
  - Real-world field studies w/simultaneous direct reading instrumentation
  - Comparison with filter based methods
- Evaluation of ambient ultrafine particulate
  - Secondary organic aerosols (SOA)
- TPS100 Commercialization

The TPS100


TPS100 Personal Nanoparticle Sampler
RJ Lee Group
Colorado State University


UNIVERSAL SMART CHARGER