Assessment of Nanoparticle Measurement Instruments

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A typical industrial hygiene analysis of workplace dust exposure does not include instrumentation to detect particles in the nanometer size range. One of the goals of this research project is to compare a suite of aerosol measurement instruments for the purpose of demonstrating their differences and similarities to more effectively evaluate workplaces that may have a nanoparticle aerosol. The instruments analyzed include a scanning mobility particle sizer, portable condensation particle counter, surface area monitor, photometer, and optical particle counter. The measurements made by these instruments were compared to mass concentration measurements made by gravimetric analysis, and count concentration and size distribution made by transmission electron microscopy. All instruments are connected via ports attached to a 20 L sealed chamber acting as a plenum through which dilution air flowed at 25-L/min. Prior to this work, an assessment of various methods for aerosolizing nanoparticles from the bulk powder were compared. These methods included both dry powder dispersers and nebulization of a liquid suspension and involved powders consisting of titanium dioxide, iron oxide, silicon dioxide, and single-walled carbon nanotubes. Polystyrene latex spheres with diameters less than 100 nm also were tested as a control for particles with known geometry and size distribution. Multiple trials of each dust type were conducted, and t-tests were used to perform pair-wise comparisons of instrument output for instruments that were directly comparable. Conversions were made to some measurements to compare, for example, count measurements with surface area measurements. The results indicate a need to apply a shape factor to make direct correlations between instruments, especially when comparing between instruments with different units—count, surface area, or mass concentrations. This information will be useful for comparing results obtained by different instruments and for choosing an appropriate instrument for evaluation of nanoparticles in the workplace.

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Assessment Methods for Nanoparticles in the Workplace

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Overall Research Objectives

1. Identify and evaluate methods to measure airborne nanoparticle concentrations.
2. Characterize nanoparticles to assess their surface and bulk physical and chemical properties.
3. Determine the collection efficiency of commonly-used respirator filters when challenged with nanoparticles.

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Instrument Comparison

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Comparison Apparatus

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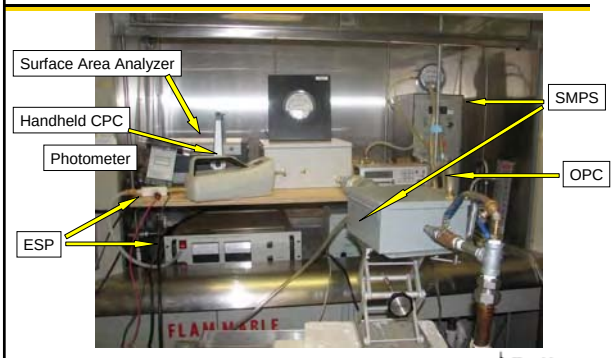
Instruments Compared



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Instrument Specifications

Instrument	Model	Application	Measured Unit	Limits	Particle Size Range, nm
TSI Handheld CPC	3007	Count	#/cm^3	0 - 10^5	10 -1000
TSI CPC	3010	Count	#/cm^3	10^{-4} - 10^4	10 – 3000
TSI DMA	3071	Count/Diam	#/cm^3	NA	5 – 1000
GRIMM OPC	1.108	Count	#/1000 cm^3	0 – 2x10^6	300 – 20,000
Matter Inst. SAA	LQ1-DC	Surface Area	μm^2/cm^3	0 - 2000	10 - 80

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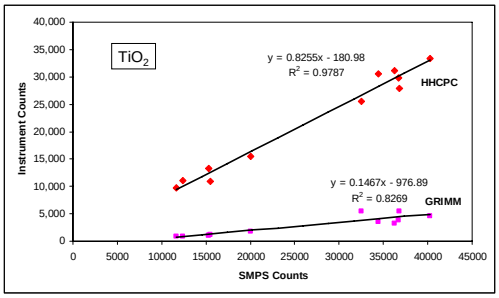
Powder Types Analyzed

- Iron Oxides:
  - High Concentration
  - Medium Concentration
- Titanium Dioxides
  - High Concentration
  - Medium Concentration
  - Low Concentration
- Single Walled Carbon Nanotubes

TiO_2 Comparison

Trial Sets	Geometric Mean (nm)	GSD	SMPS Average Count (#/cm³)	GRIMM Average Count (#/cm³)	CPC Average Count (#/cm³)	LQ1 (μm²/cm³)	Average SMPS Surface Area (μm²/cm³)
AVG I	89.2	2.5	13,120	915	11,363	264	930
AVG II	118.3	2.1	17,735	1,500	13,197	450	1,782
AVG III	129.1	1.9	35,571	3,754	30,197	1,205	3,171
AVG IV	151.4	1.6	34,624	5,480	26,696	1,556	3,548
AVG V	104.7	2.4	38,252	3,925	32,282	604	3,157

Count Correlations



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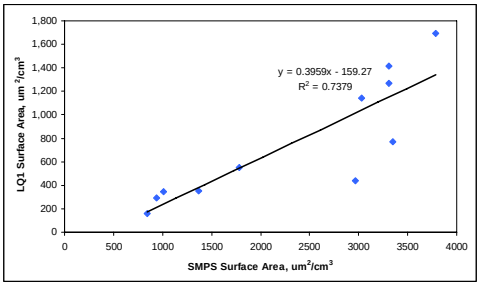
Surface Area Correlations



Aerosol Generation

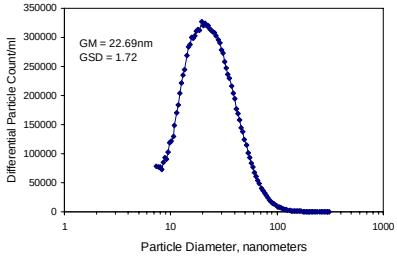
Collison Nebulizer

Added bulk powder to filtered water
Nebulized at 20 psi

Instrument Comparison

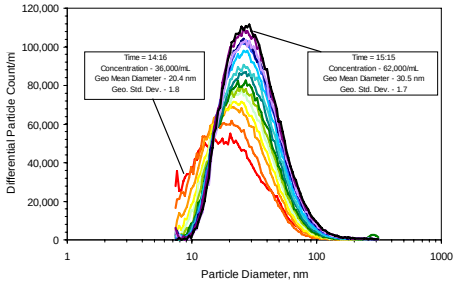
Water Contamination

Typical Water Only Results

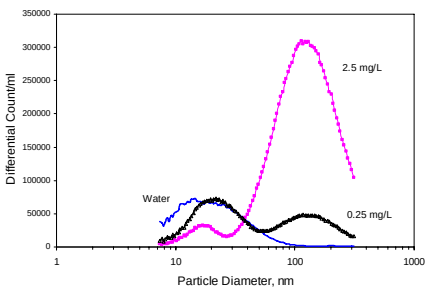


6-jet Collison Nebulizer
Ultrapure Water from Lab System

Water Output over Time

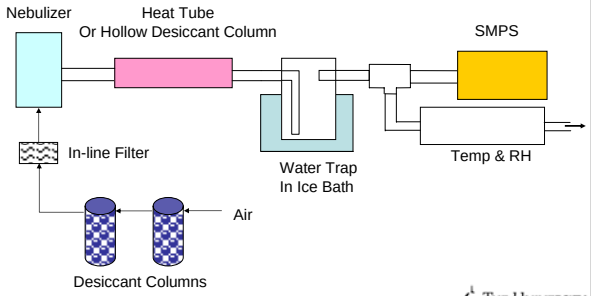


Nebulizer Output with Powder

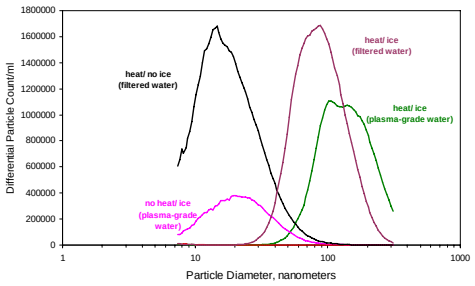


6-jet Collison Nebulizer
Ultrapure Water from Lab System
20-nm TiO2 Added and ultra-sonicated

Water Trials



Water Trials



Park Work\SMPS Files\Dec 15 Water Setup Tests\comparison

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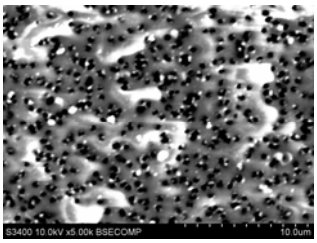
SEM of Water



Park Work\SEM-EDS Jonas Results\PC membrane_filtration

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SEM-EDS

Spectrum: 2hr_Cfilter 1

El	AN	Series	unn. C [wt.-%]	norm. C [wt.-%]	Atom. C [at.-%]	Error [%]
N	7	K-series	21.95	21.95	30.31	9.0
Cu	29	L-series	19.79	19.79	6.02	8.2
Na	11	K-series	5.54	5.54	4.66	0.5
Cl	17	K-series	2.39	2.39	1.31	0.1
P	15	K-series	1.97	1.97	1.23	0.1
K	19	K-series	1.37	1.37	0.68	0.1
Mg	12	K-series	1.34	1.34	1.07	0.1
Si	14	K-series	0.88	0.88	0.61	0.1
O	8	K-series	44.77	44.77	54.12	15.2
		Total:	100.00	100.00	100.00	

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Instrument Issues

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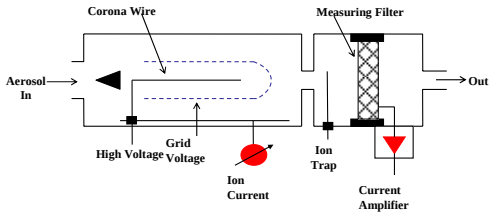
Surface Area Analyzer



- Particles are charged by unipolar diffusion of ions from the corona charger.
- A filter downstream from the charger measures the current of the particles via an electrometer.
- Active surface area (not individual particle surface area) is calculated from the measured current.

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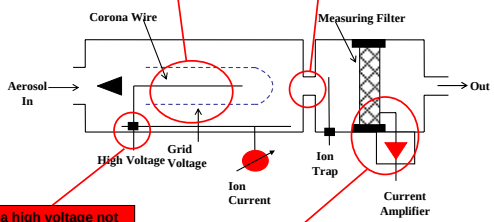
Areas of Degradation

Deposition of material on wire increases wire diameter. Voltage increases and eventually results in an incorrect display reading. Replaced part.

Connection between charger and filter became brittle. Replaced part.



Corona high voltage not constant due to a defective electronic part. Causes wrong or instable display reading. Replaced part.

Measuring filter – lack of sensitivity. Caused by deposition of material in the glass/metal feedthrough and changing humidity. Replaced part.

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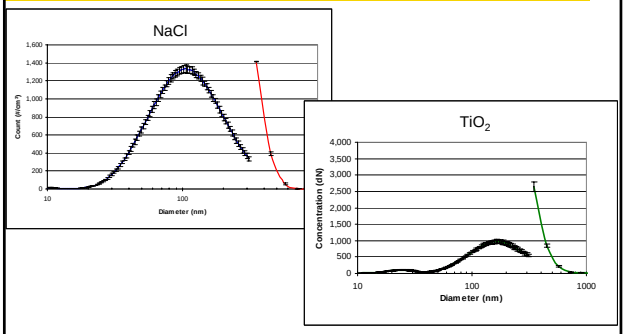
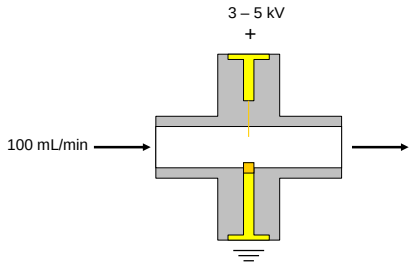
SMPS and GRIMM Size Distributions



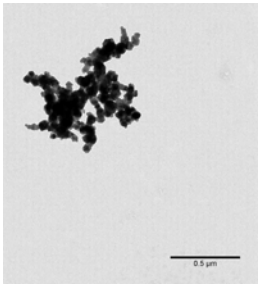
Microscopic Sizing

ESP

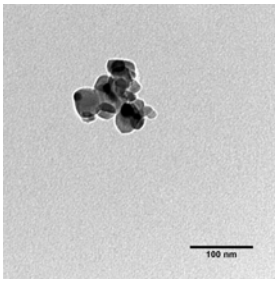


TEM Imaging/Counting

Large Fe_2O_3 Agglomerate

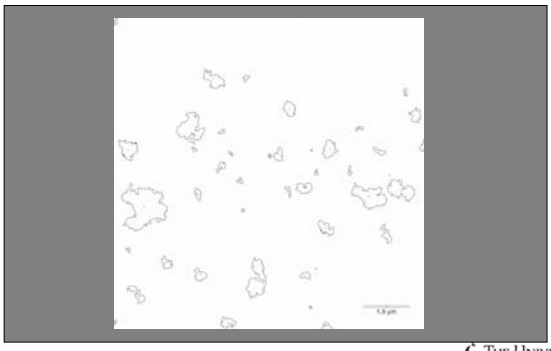


Small TiO_2 Agglomerate



Captured on TEM grid via ESP collector

TEM Imaging/Counting



Park Work\TEM Images\Summary\Fe2O3\..s files

Particle Characterization

Characterization Techniques

Technique	Information
XPS	Elemental Composition
XRD*	Crystallinity
SEM TEM	Shape, homogeneity, tube size, size distribution, and surface morphology
BET	Surface area
Raman spectroscopy	Tube diameter, conductivity, purity
AFM*	Tube length, diameter

* Future work

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TiO_2 Analysis

Crystalline or Amorphous	Crystalline
Phase	Anatase
Primary Particle Diameter (nm)	4 ± 1
BET Surface Area (m^2/g)	266 ± 3
Surface Functionalization	O, O-H, and H_2O
Aerosol Aggregate Size	100 ± 50 nm

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Carbon Nanotube Analysis

	SWNT	DWNT
Average Diameter (nm)	4.5 ± 3	2.8 ± 2
Surface Area (m^2/g)	457 ± 4	575 ± 10
Catalyst Contamination	Co < 0.2%	Not detectable
Conductivity	Semiconducting	Semiconducting

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Field Sampling

Nano-structured Lithium Titanate Facility

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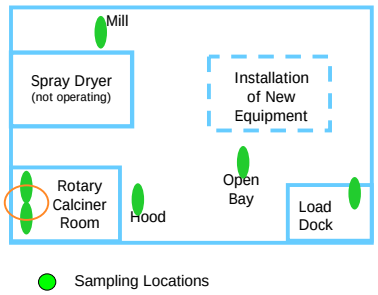
Facility Schematic



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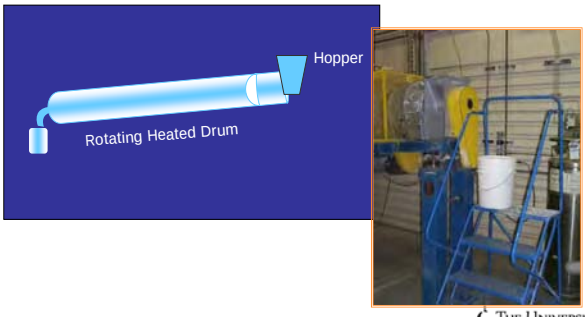
Rotary Calciner



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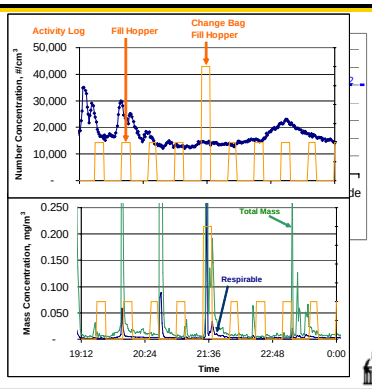
Real-time Measurements



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Conclusions

- Material handling of lithium titanate disperses large particles (>1 μm)
- Ultrafine particles likely associated with forklifts, welding, grinding

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  - Particle Characterization

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  - Filtration Studies
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  - Particle Characterization
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  - Water Contamination & TEM/SEM
- Ron Johnson – MS
  - Field Sampling

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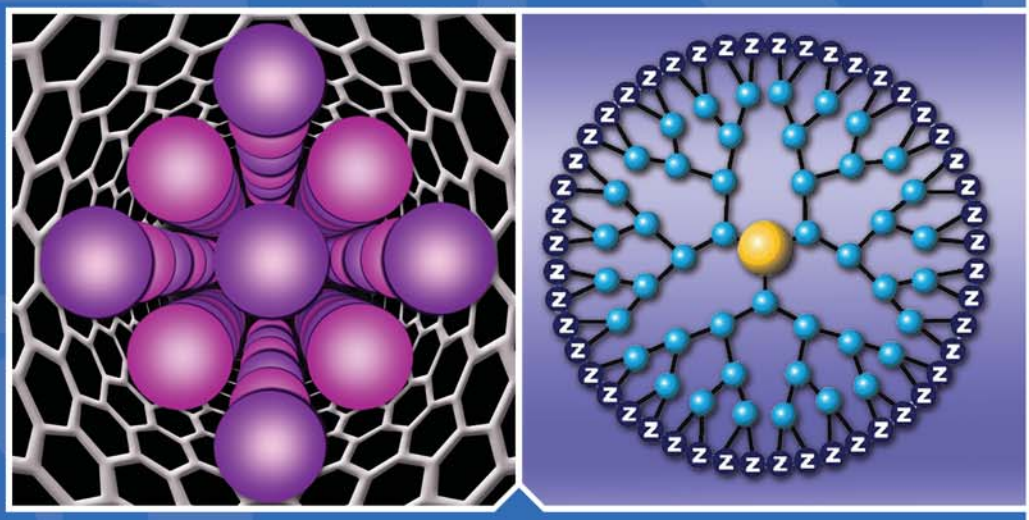

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