

Aerosol Characterization, Interpretation, and Application of Data

NSRC Symposium

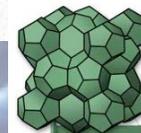
July 8, 2008

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Center for Nanophase Materials Sciences

OAK RIDGE NATIONAL LABORATORY

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**Center for Nanophase
Materials Sciences**

Aerosol Characterization, Interpretation, and Application of Data

Department of Energy (DOE) Nanoscale Science Research Centers (NSRC) developing *Approach to Nanomaterial ES&H*

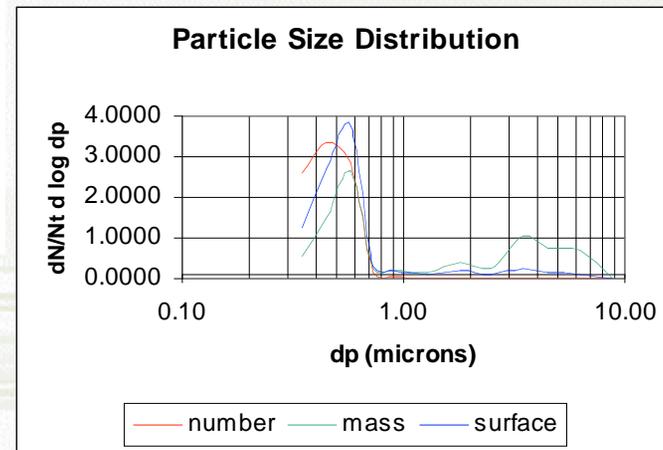
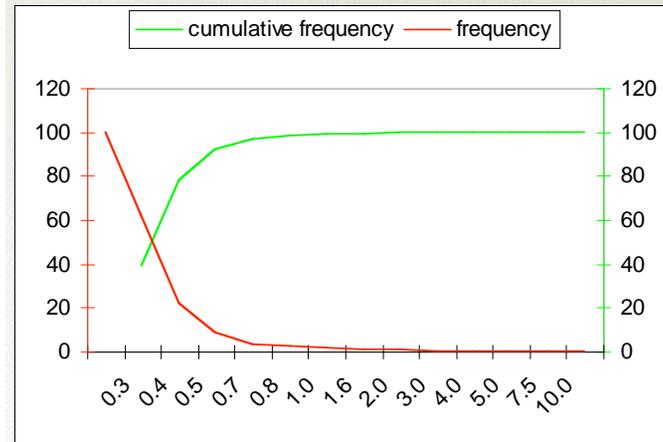
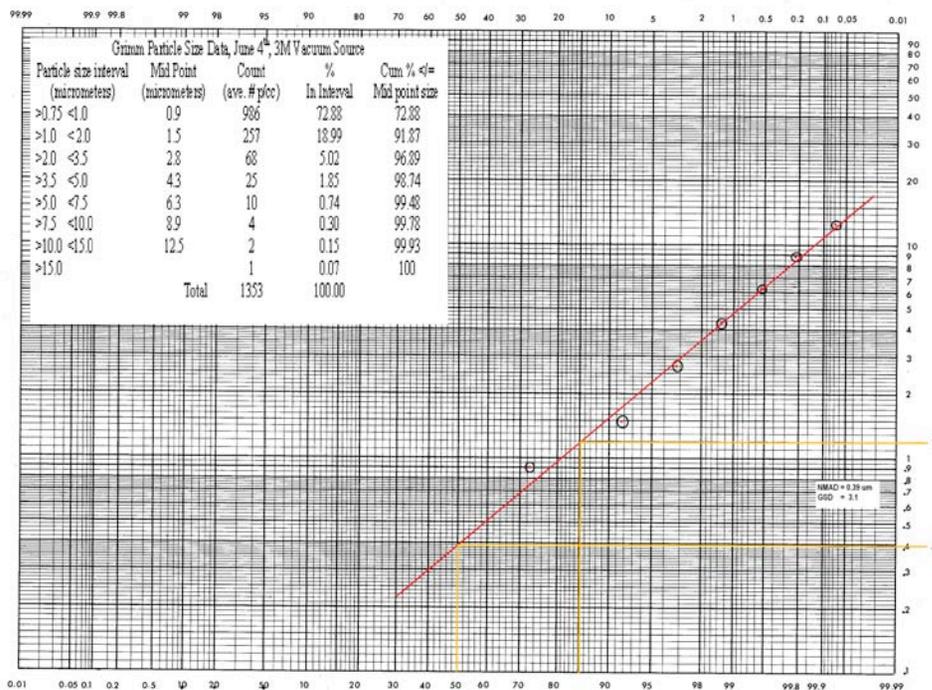
- *The CNMS Approach*

- *Establish Exposure Control Guideline (ECG)*
- *Characterize Aerosol*
- *Collect and interpret data*
- *Assign Process to a Control Band*

Aerosol Particle Characterization

- Size distribution (geometric mean and geometric standard deviation related to either mass, surface, or number)
 - Inertial impactor
 - Gravimetric
 - Direct reading
 - Microscopic
 - visible light, SEM, TEM
 - Direct reading
 - Photometer- Grimm
- Morphology (discrete particulate, agglomerate, flocculate, shape/aspect ratio)
 - Microscopic
 - visible light, SEM, TEM
- Concentration (mass, surface area, number)
 - Gravimetric - filtration for mass
 - Direct reading - CPC for number, AT 9000 for surface
- Chemical composition
 - Numerous analytical techniques
 - Product specifications

Particle Size Distribution



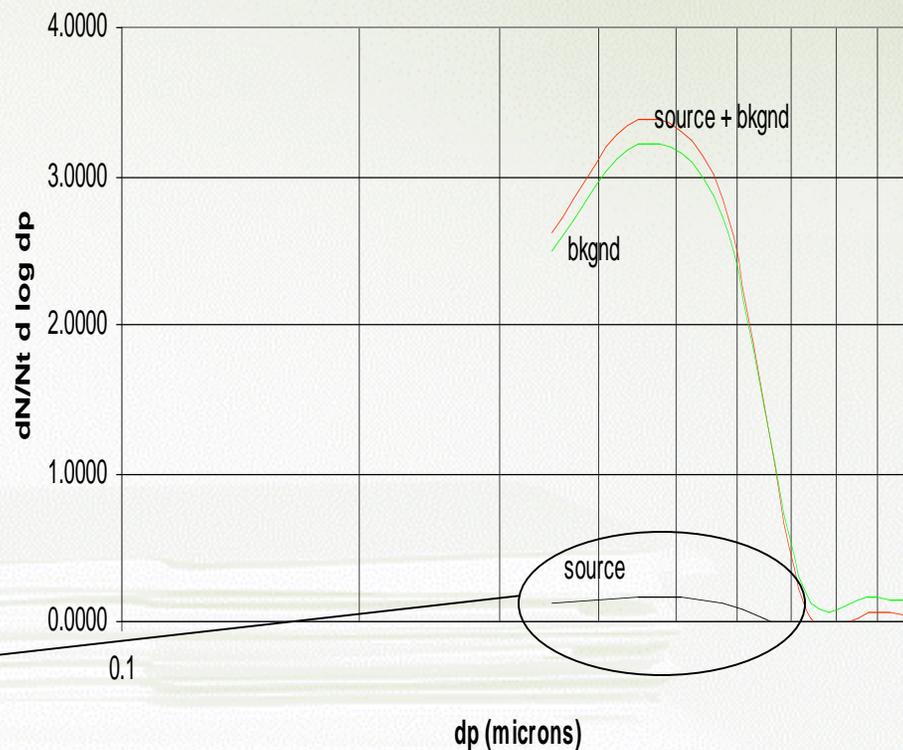
Particle Size Distribution

(background effects)

Laser Ablation 29 June 2007

Clean Room

mid point	bkgnd	source + bkgnd	source
0.35	2.4979	2.6166	0.1187
0.45	3.2178	3.3733	0.1556
0.575	2.7155	2.8479	0.1324
0.725	0.2231	0.1303	0.0927
0.9	0.1577	0.0566	0.1012
1.3	0.0618	0.0101	0.0517
1.8	0.0651	0.0121	0.0530
2.5	0.0225	0.0028	0.0196
3.5	0.0317	0.0040	0.0277
4.5	0.0206	0.0010	0.0196
6.25	0.0070	0.0003	0.0067
8.75	0.0060	0.0003	0.0057



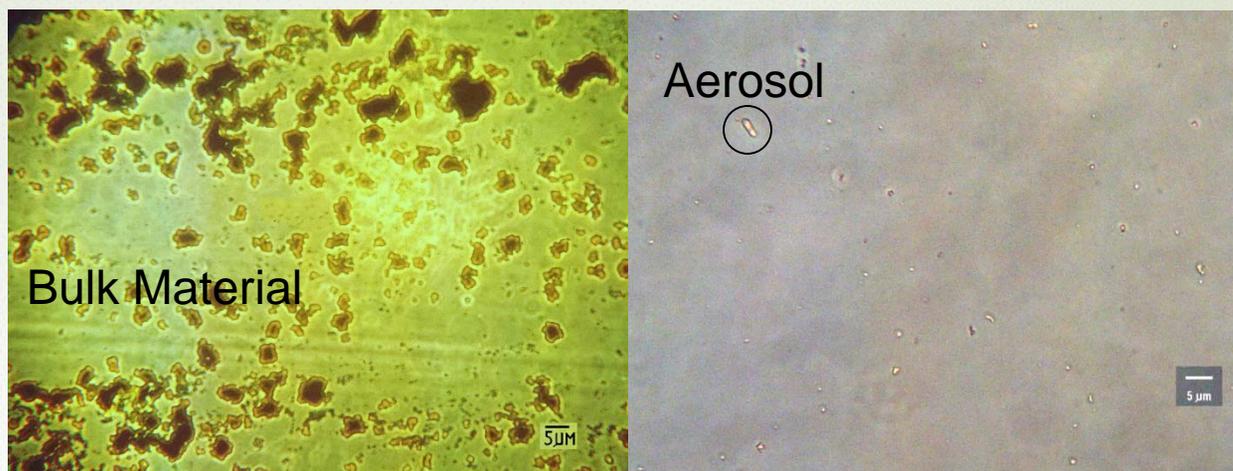
Particle Size Distribution
Laser Ablation Aerosol



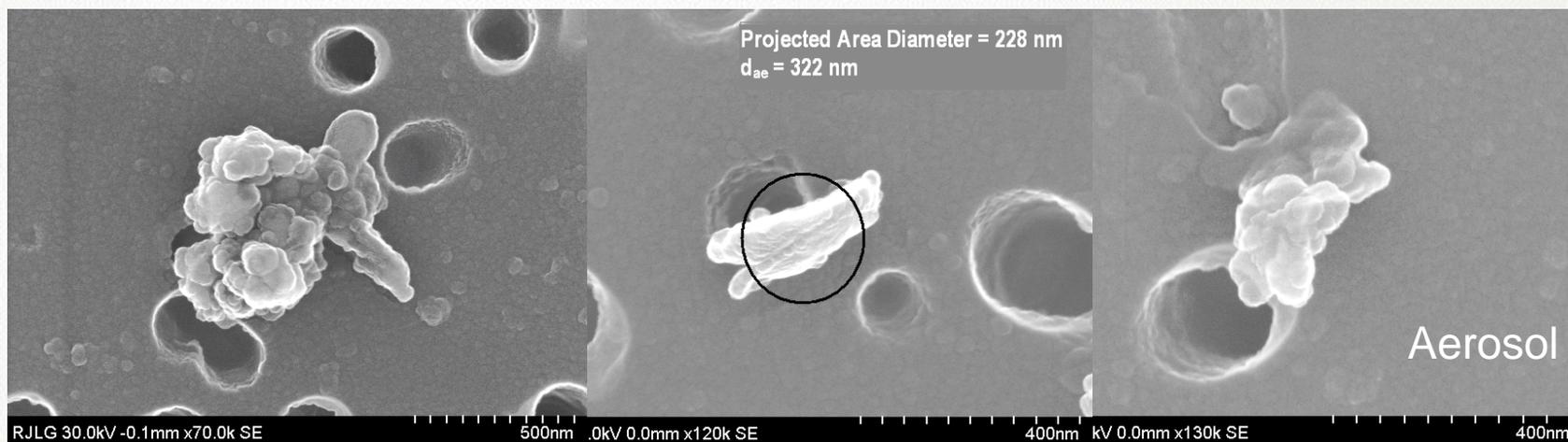
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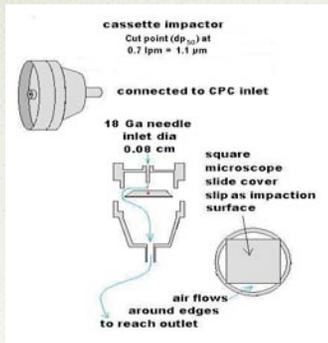
Particle Morphology from Light Microscopy



Particle Morphology from Transmission Electron Microscopy



3 Size Estimating Techniques



TSI-CPC 3007 concentration unchanged with impactor on and off indicates an aerosol predominantly below 1 µm

Could the At 9000 with cyclone and CPC with impactor provide an approximation of the average particle diameter of the aerosol below 1 µm?

AT 9000 CPC 3007

$$SA_{total} = \pi (d_{particle})^2 \times n_{particles} \Rightarrow d_{particle} = \sqrt{\frac{SA_{total}}{n_{particles}}} = \bar{d}_{particle}$$

GRIMM
Portable Aerosolspectrometer
 Model: 1.108

Specifications

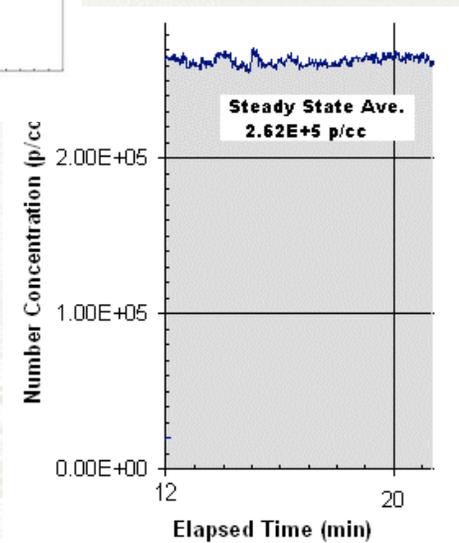
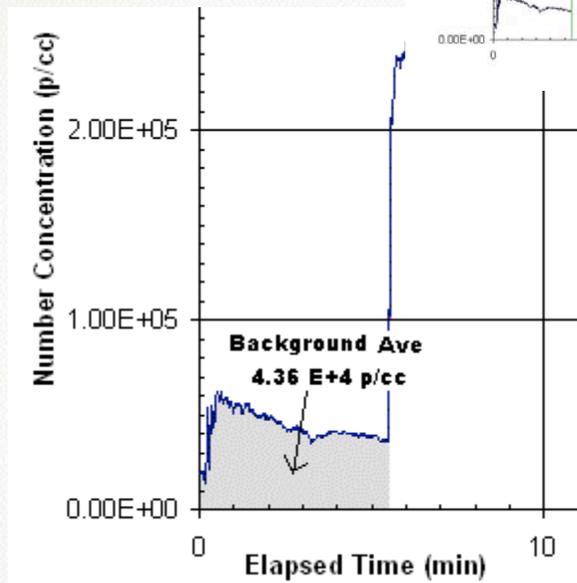
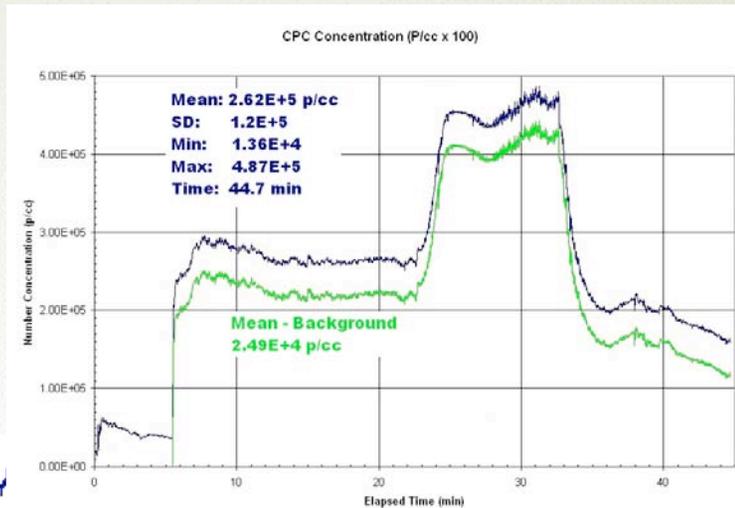
Model	#1.108
Dust range [µg/m³]	0.1...100.000
Size range [µm]	0.3...>20
Size channels [µm]	15 channels: 0.3/0.4/0.5/0.65/0.8/1/ 1.6/2/3/4/5/7.5/10/15/20
Sample air	1.2 l/min
Particle counting	up to 2.000.000 P/l
Battery duration	up to 8 h
Operating temp.	0...+40 °C (32...104 °F)
Dimension	24 x 12 x 6 cm
Weight (with battery)	2.4 kg (5.3 lb)
Application	work place, filter-, air-quality-, ventilation control

The Grimm 1.108 counts particles down to 0.3 µm, the CPC down to .01 µm. It has been presumed that the difference between a lower Grimm count and a CPC count represents particles below about 0.3 µm in size. We have not found this to be the case when particle concentrations are higher than the upper range specified for the photometer (2,000 p/cc). It did hold in one case where the concentration was on the order of 1000 p/cc.

Sometimes



Concentration



Composition

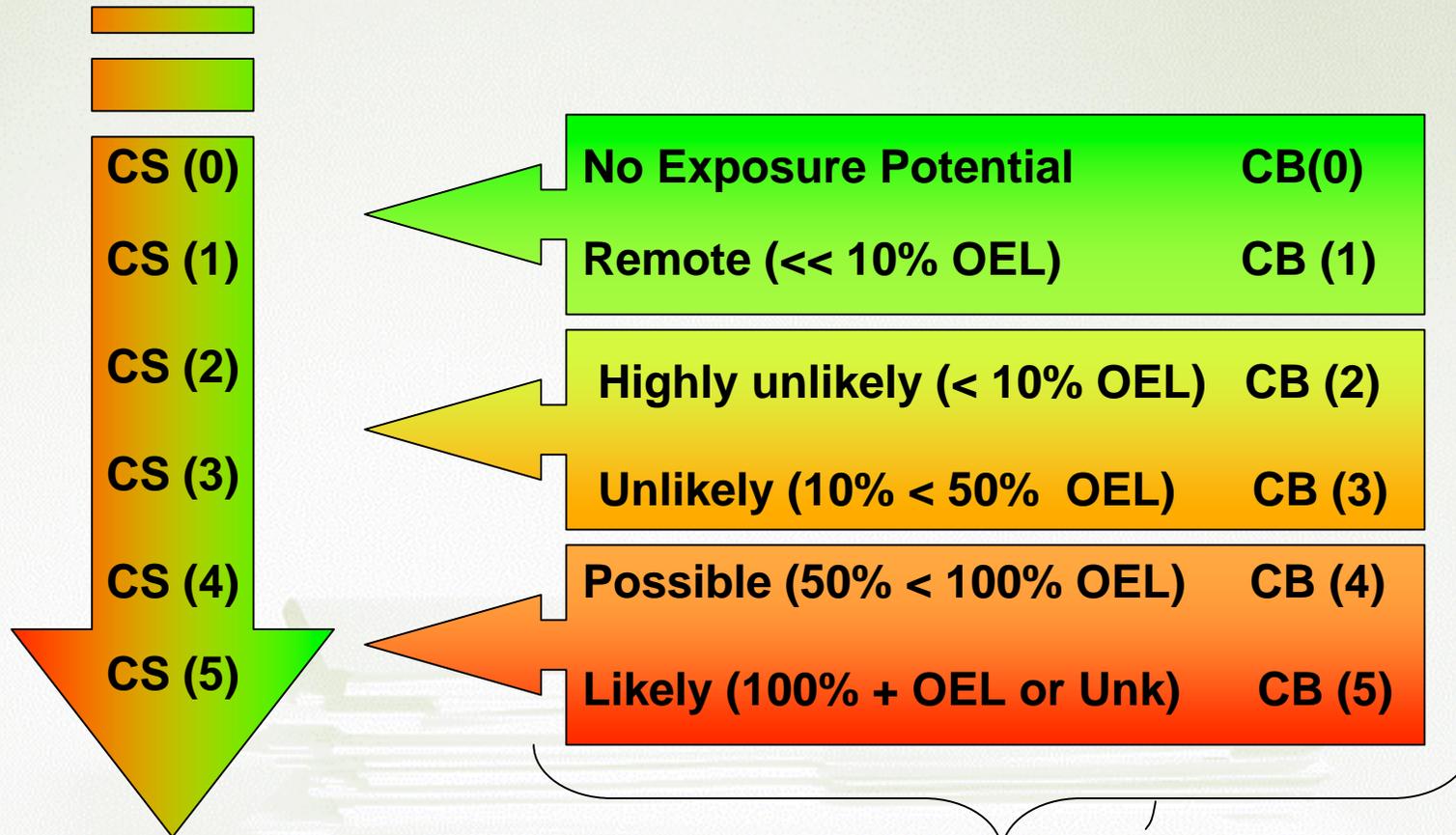
Graphites are for use in special applications requiring the low friction characteristics of these materials. When brushes must operate at very low current densities or very high peripheral speed a graphite grade should be used. Natural graphite can be abrasive due to its ash content.

Establish OEG based on the composition and particle size of the aerosol.

Number concentration	Mass concentration
$\leq 0.1 \mu\text{m}$ PSLT derived for specific size	$\leq 0.1 \mu\text{m}$ PSLT 100 $\mu\text{g}/\text{m}^3$
$\gg 0.1 \mu\text{m}$ OSHA OEL 530 p/cc	$\gg 0.1 \mu\text{m}$ ACGIH TLV 2 mg/m^3 (R)

Control Band Designations

A Control Band (CB) designation reflects a belief about the level of control for a particular process. Validation of the process's CB designation determines the actual control status (CS).



Validation as a CS of 3 or less permits continued operation of a process.

Assignment of a CB of 3 or less permits start-up and interim operation of a process under surveillance.

Control Banding

Control Band 2

Laser ablation nano particle generation and harvesting. Controls include Clean Room ventilation, HEPA vacuuming, glove bag and open handling within a lab hood.



Process is controlled using existing methods.

Inhalation hazard is low for agglomerated particulate

Operational exposure limit is protective and achievable

Monitoring results combined with professional judgment using Bayesian techniques confirm control band 2 is justified for operations whenever controls as specified are implemented.

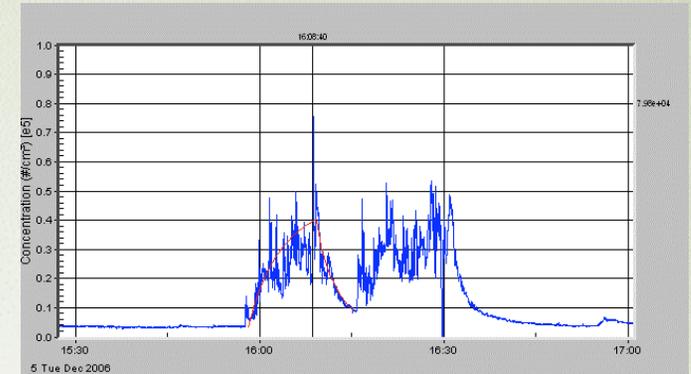
Resample in 12 – 24 months by performing a spot check (three BZ measurements). If median is less than or equal to 265 p/cc process is considered to continue as well controlled.

The Operational Exposure Guide is established by CNMS at 530 p/cc for work within enclosed systems as an average concentration above background.

Note: Unenclosed applications should not be allowed take place where short term exposures may exceed 10,000 p/cc without use of a respirator with a minimum protection factor of 50.

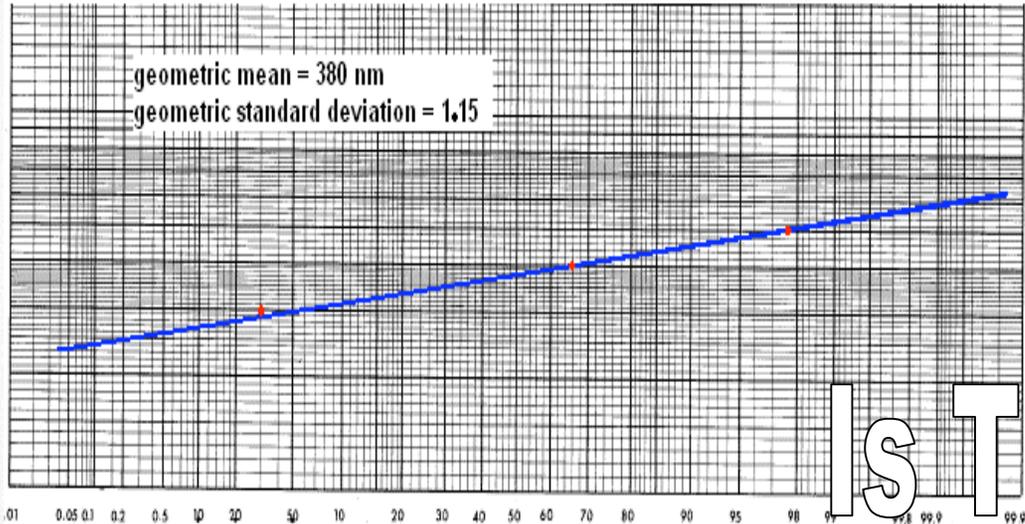
Characterization of friction stir welding of aluminum using the CPC and Grimm

The aerosol concentration over time depicted in the figure to the right represents a mean concentration of 12,000 p/cc with a maximum of 80,000 p/cc measured in the sample. The particle generation rate is approximately 10 -15 thousand particles /cc/ min, and the aerosol half life is approximately 2 to 3 minutes.



The aerosol particle size distribution is almost monodisperse (GSD = 1.15). The geometric mean particle size of the aerosol by number is 380 nanometers. Extrapolating below the last data point suggests that the nano-size fraction (< 100 nm) makes up much less than 0.01 percent of the aerosol.

$$p / cc_{nano} = \left(\frac{< 0,01\%_{nano}}{100} \right) (12,000 p / cc_{ave}) < 1.2 p / cc_{nano}$$



Conclusion: process does not produce a nano size particle exposure. Apply the AL fume TLV (5 mg/m³) and assess gravimetrically

Is This Credible?

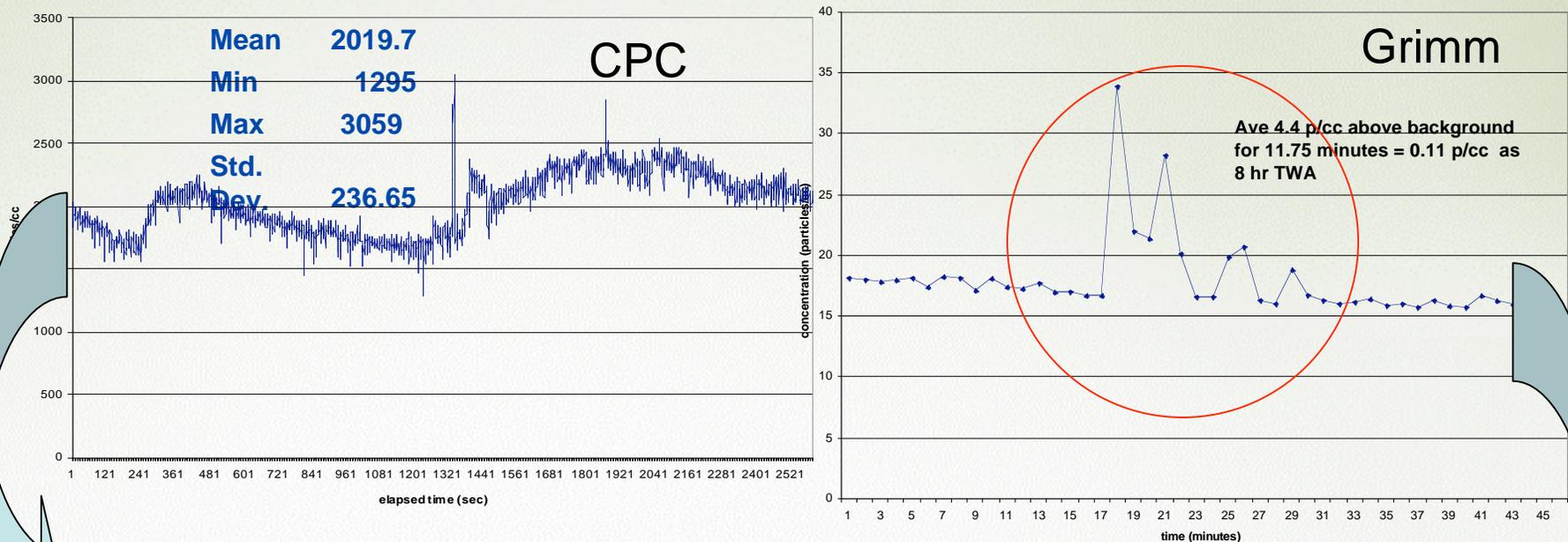


Characterization of silicon based nano fiber transfer activity

(Wrong method of analysis? TEM/PCM fiber count may be more appropriate Failure to decide on appropriate exposure limit prior to sampling. Incomplete analysis, background not ascertained and particle size not determined.)

Silicon Nano Fiber Transfer Process

Total particles (0.3 - 20 microns) measured by GRIMM

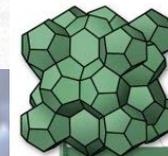


The particle count for the CPCs is much higher than the Grimm - this could be valid for number counts if there is a very large portion of the aerosol below the resolution limit of the Grimm (300 nm). There is a difficulty in determining if that smaller fraction is all background or has been added to by the process. In the graph above, there is no discernable background and **no background data was taken**.

The Grimm data shows a clear background. The average increase is about 4.4p/cc as an 11.75 minute average. The 8 hour TWA for the increase above background is approximately 0.11 p/cc. If the OEG was taken as the asbestos limit of 0.1 f/cc as a TWA and 1 f/cc as a Ceiling, **and the particles were assumed to be fibers of the appropriate length and width**, one might conclude that there is the potential for overexposure???. **A decision cannot be made on the basis of this data!**

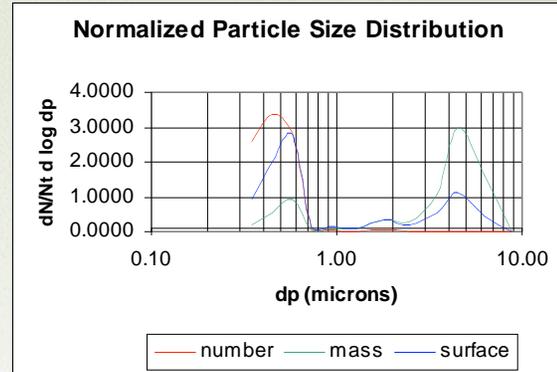
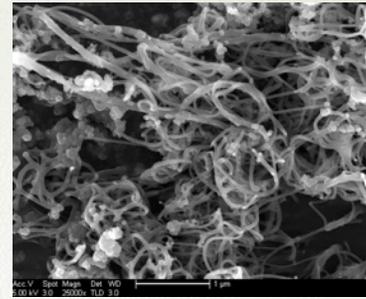
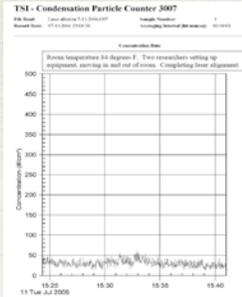
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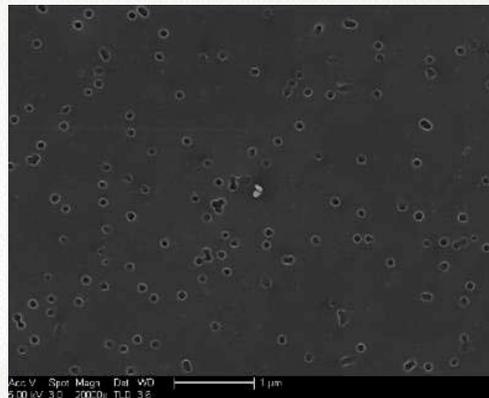
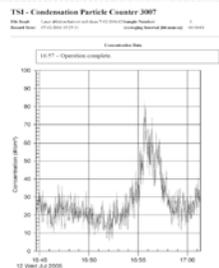


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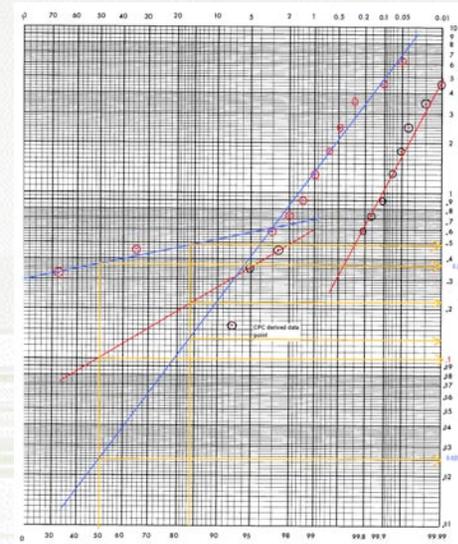
Carbon nano fiber harvesting



Background measured with TSI condensation particle counter prior to operation.



Particle size measured with Grimm



Exposures measured with TSI condensation particle counter near breathing zone of staff performing nano-material harvesting.

Conclusions:

- At the point of operation, no nanoscale particles observed.
- The aerosol source was not measured; therefore we cannot recommend suspending or confirming the need for the controls in place.

My Thoughts on Instrumentation and Microscopy

- CPC or Grimm w/o TEM of limited value unless there is process knowledge of aerosol size.
- CPC with impactor seems useful. However still can't rule nano size particles in or out.
- CPC better than Grimm for particle concentration if aerosol concentration in excess of 2,000 p/cc.
- If p/cc > 2,000 and CPC count is > Grimm count, can't say that difference is due to particles less than lowest Grimm channel (0.3 μm). Have one good example in low concentrations (< 1000 p/cc) where lower Grimm count was due to particle size distribution.
- PCM – quick and less costly, provides suggestive info, but can't rule out nano size particles.
- TEM – Definitive for nano size material. Makes other measurements (CPC and Grimm, as well as others) meaningful.