HORIBA Scientific

Particle Characterization

Exploiting Fluorescence for Enhanced Nanoparticle Tracking Analysis of CMP Slurries

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“Sensitivity in nm range….”

Background – SEMI Standards

Semi standards do not list FCS or NTA on the list of techniques for particle size…
However, they do acknowledge the needs for improved particle metrology as semiconductor technology advances.

SEMI C98-1219

GUIDE FOR CHEMICAL MECHANICAL PLANARIZATION (CMP) PARTICLE SIZE DISTRIBUTION (PSD) MEASUREMENT AND REPORTING USED IN SEMICONDUCTOR MANUFACTURING

“Response to Semiconductor Technology Advances

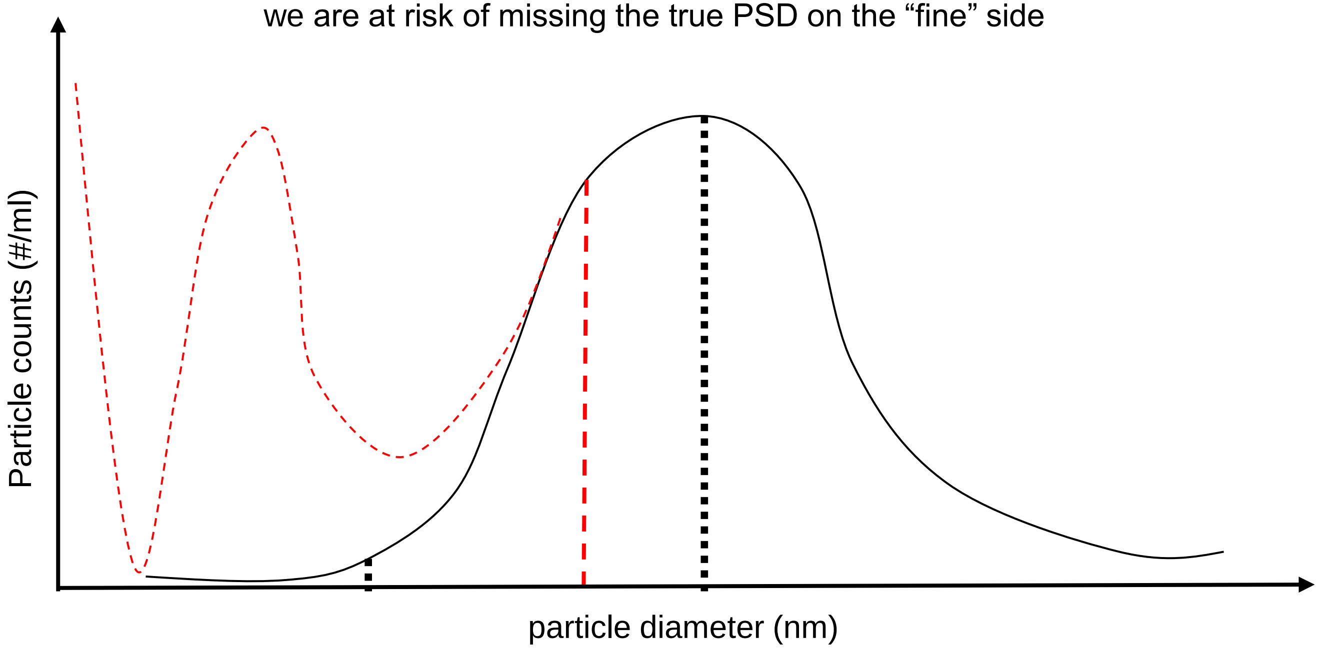
- As node sizes continue to decrease, new requirements for CMP PSD are becoming increasingly important.
- *As CMP slurries move towards smaller particle sizes more nano-size sensitive PSD metrologies are needed.*
- More PSD information is needed at smaller particle sizes (i.e., more particle size bins in the nanometer size range).
- Metrologies capable of differentiating the nature of the measured particles are needed….”

Next gen PSD requires: “Sensitivity in the nm range….Smaller bins in the nm range”

The Problem

What happens when mean particle size approaches the limit of resolution?

As our mean particle size approaches our resolution limit, we are at risk of missing the true PSD on the "fine" side

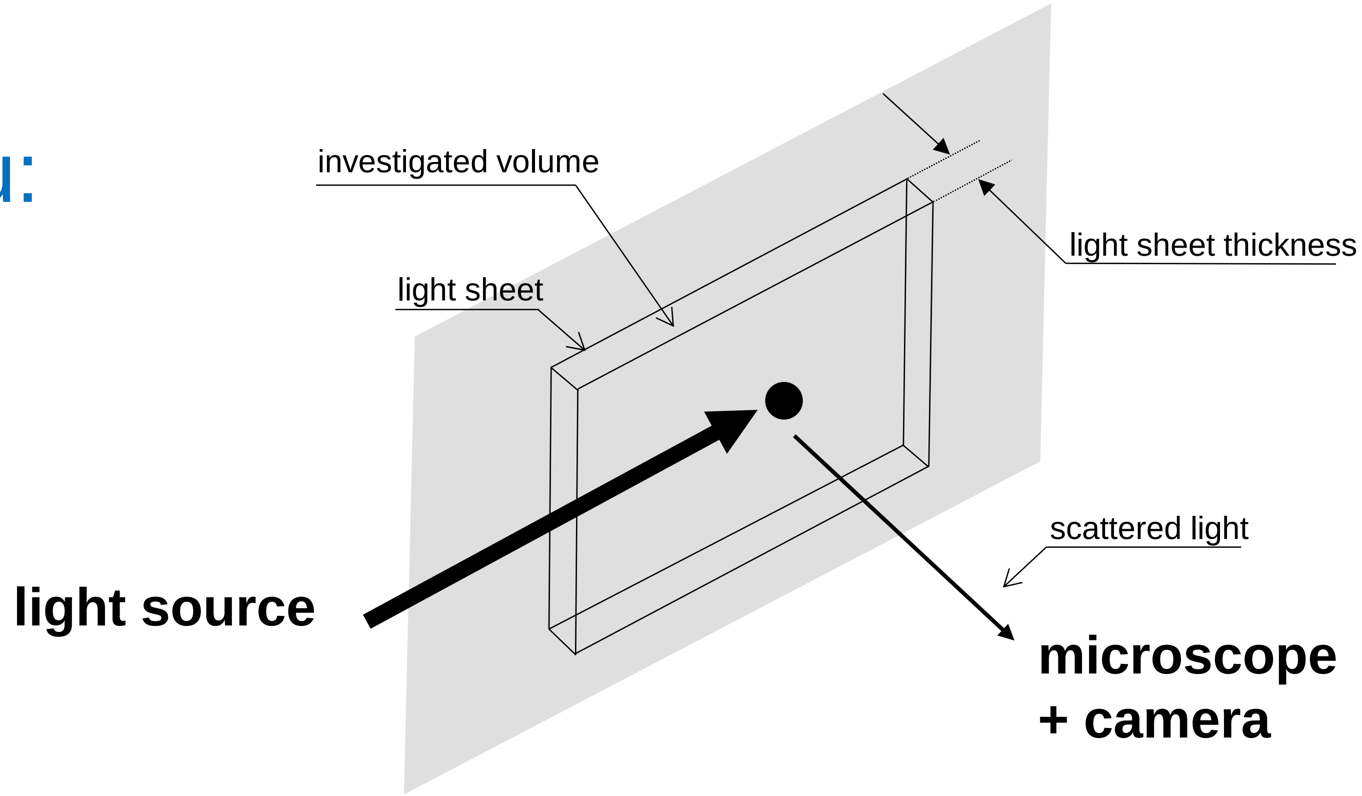


Improve Process Control and meet Roadmap Challenges:
Improve the resolution of fine particles

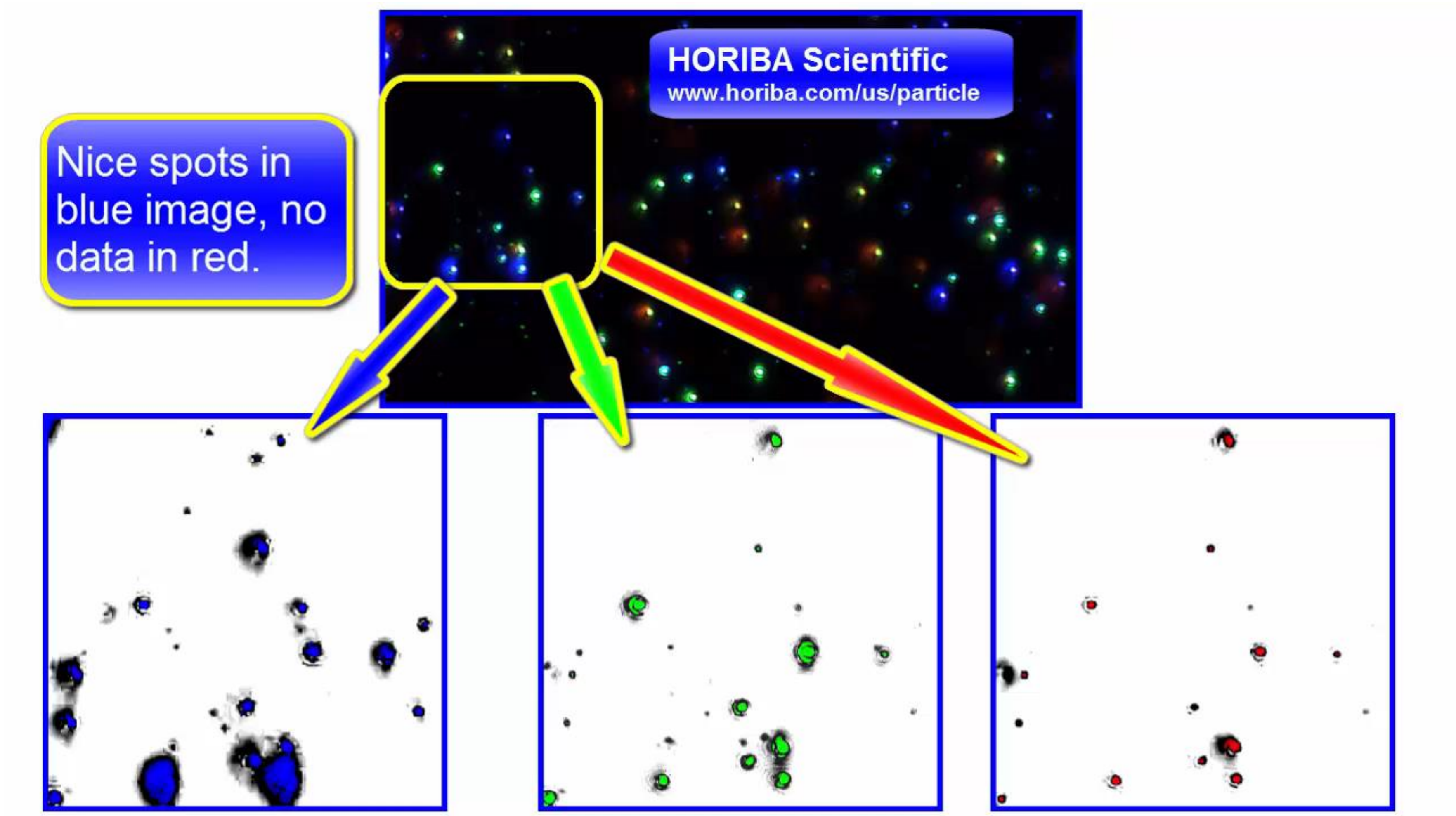
Nanoparticle Tracking (NTA)

Particle by particle gives you:

- Detailed Distribution
- Particle Concentration



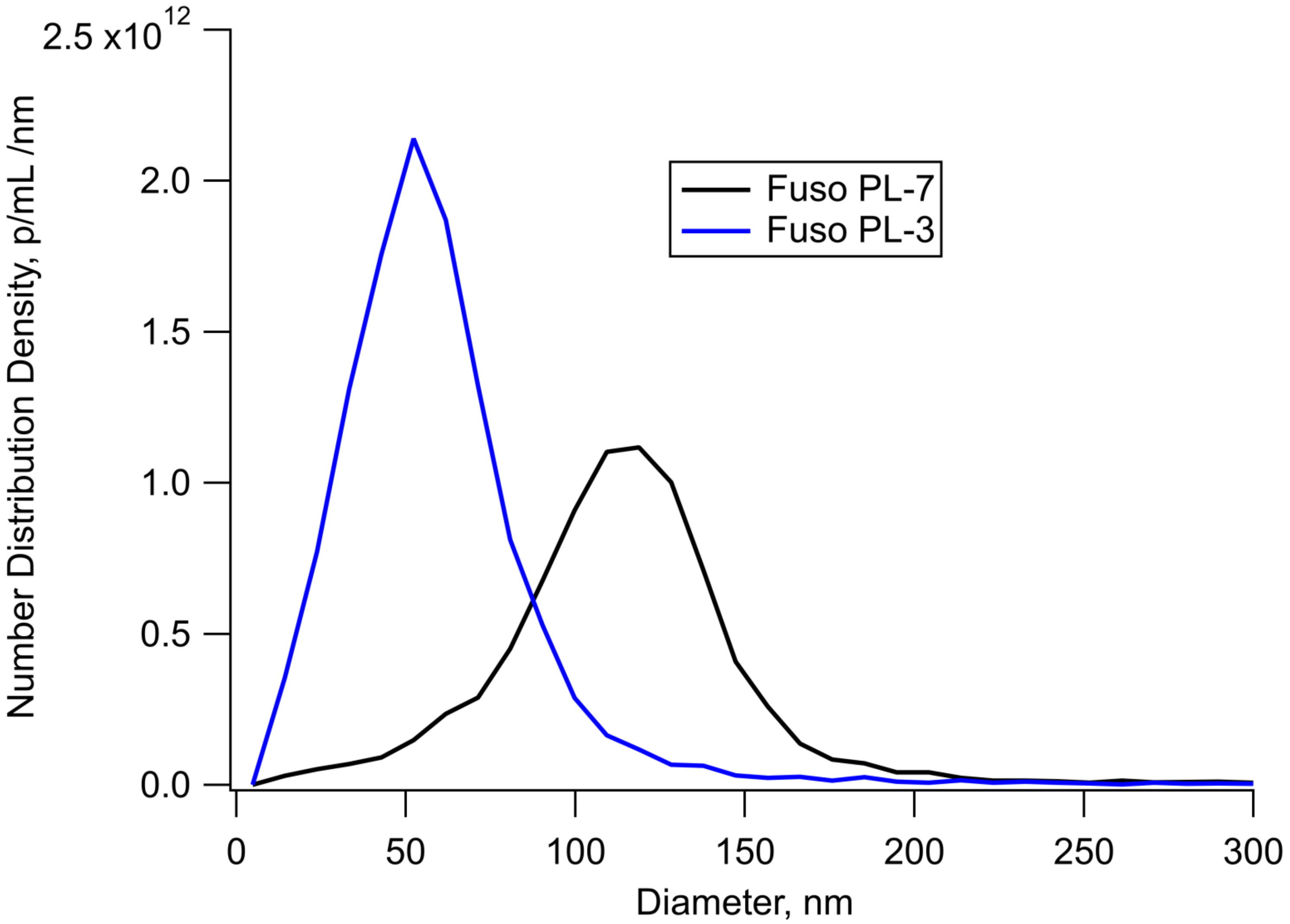
Why three colors?



Silica Particles by NTA

Number, not volume based distribution.

Particle concentration!



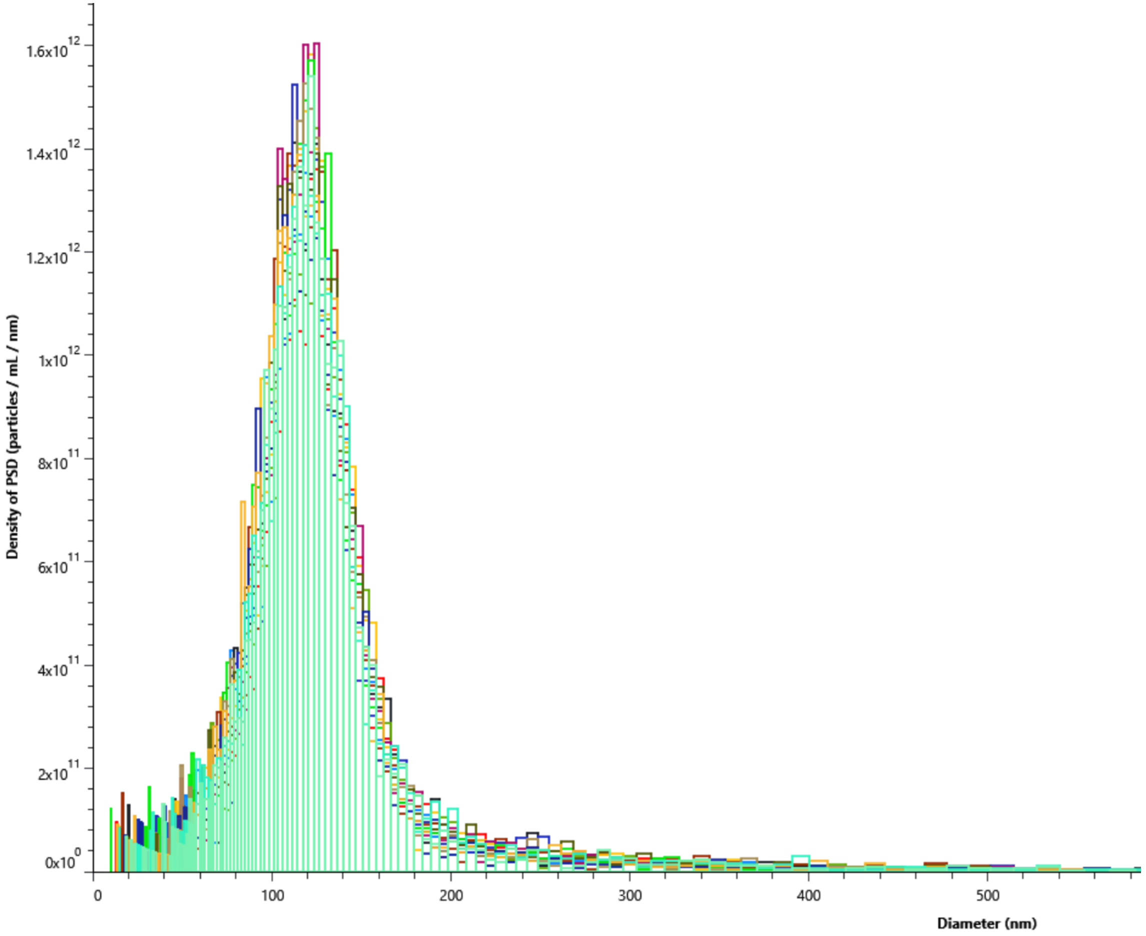
Repeatability

Dilute and run PL-7 15 times

Concentration: 8.48E+13 p/mL
CoV (SD/mean): 3.54%

Median Size: 120.93 nm
CoV (SD/mean): 1.04%

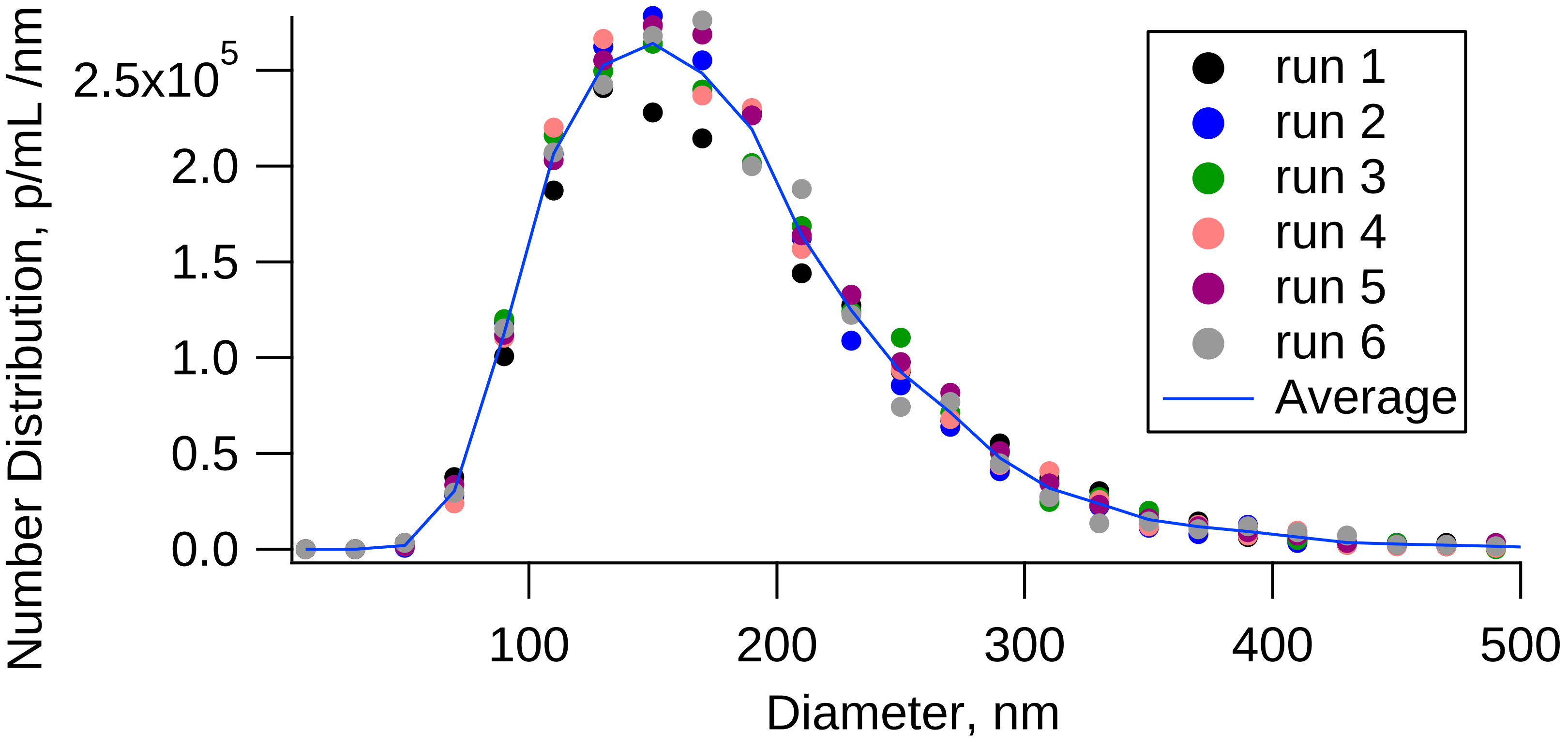
What is driving repeatability?



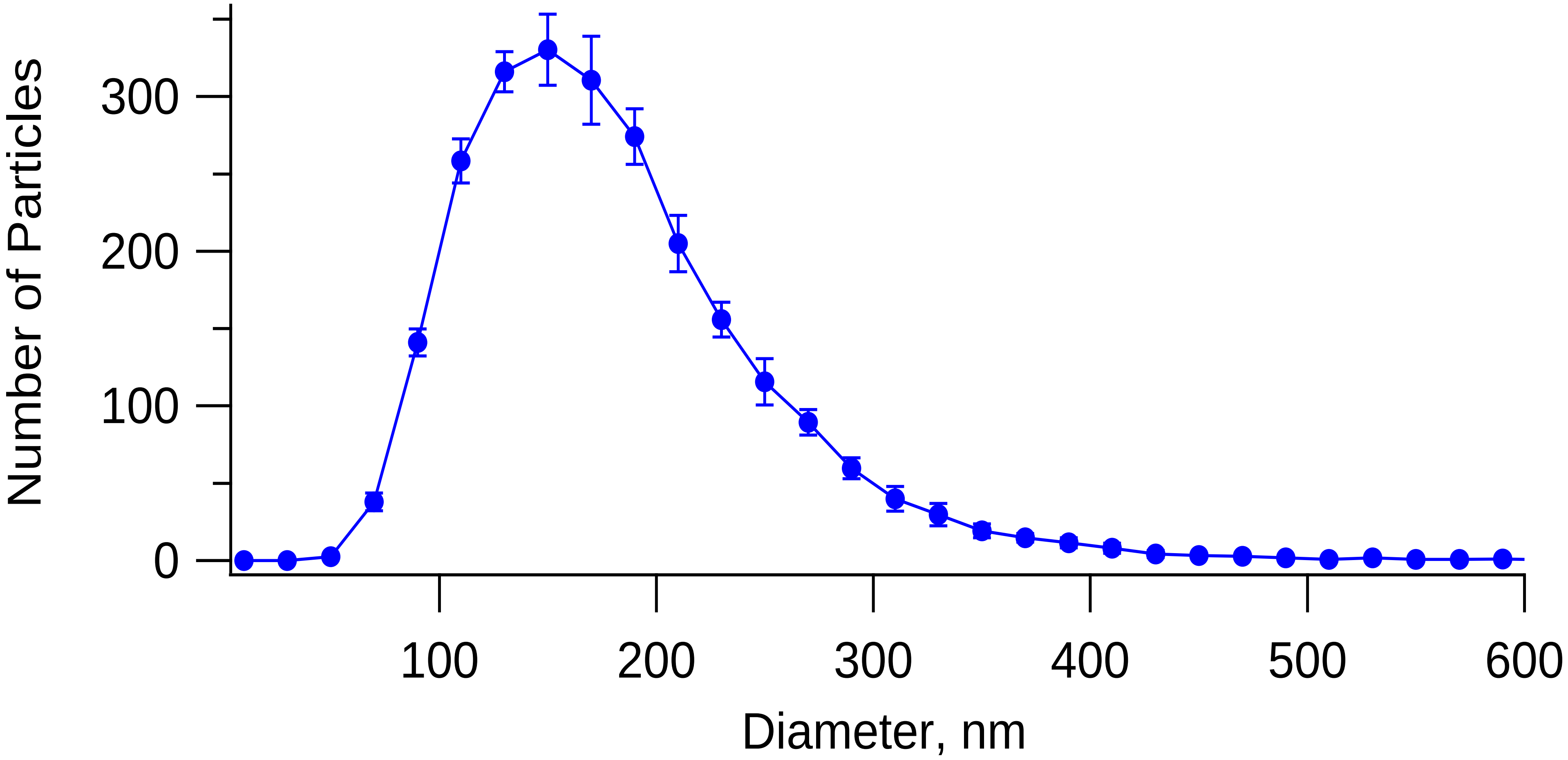
Statistics

Do we follow counting (Poisson Statistics)?

Zirconia, run six times as repeats



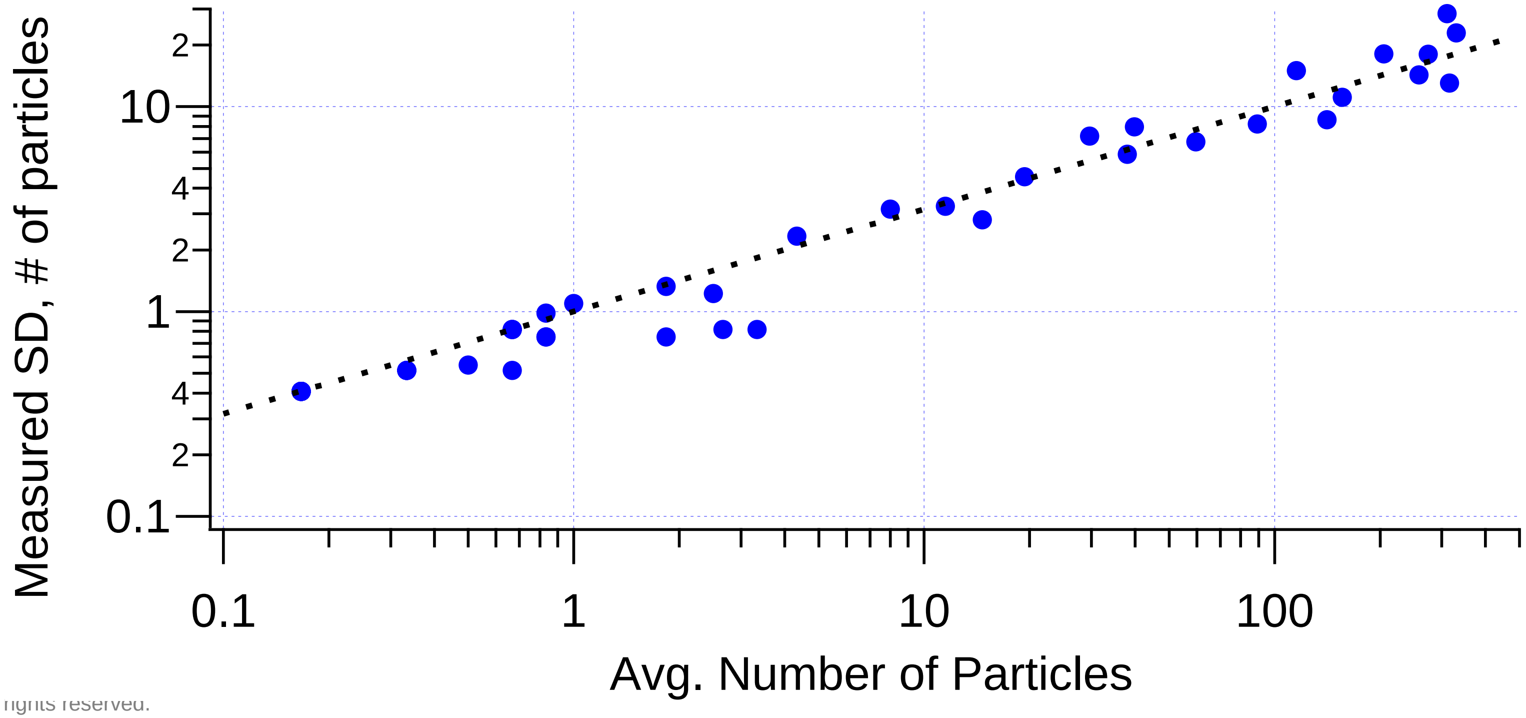
Error bar is standard deviation of 6 repeats



Yes

Plot standard deviation as a function of number of particles in each bin.
Dashed line is sqrt(num particles) and theoretical.
This means

1) mixing is correct (random sampling)
2) uncertainty can be estimated by looking at particle count.

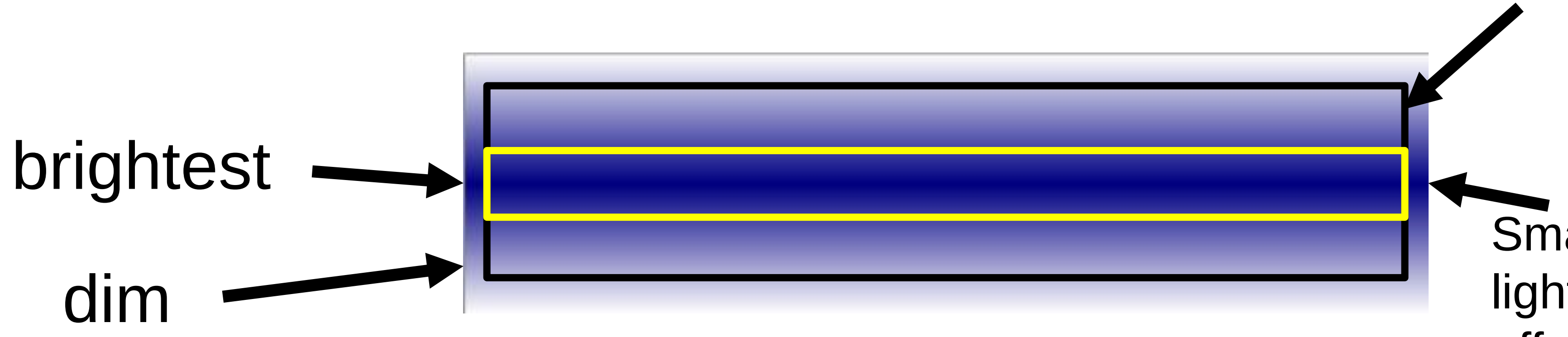


Volume normalization

Light sheet is squeezed and not uniform:

Top view of scattering volume

Large particles get enough light to be detected in larger volume.

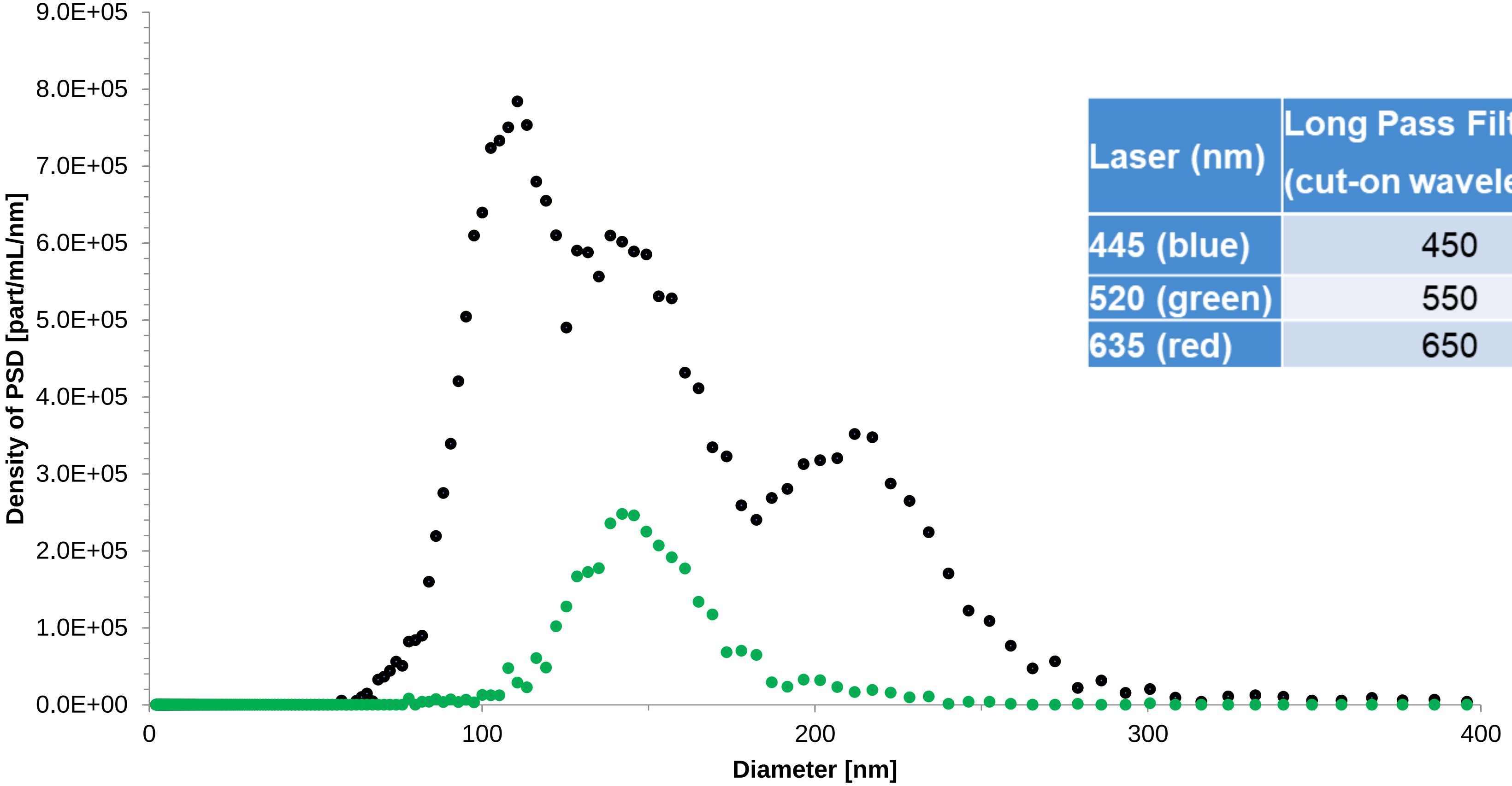


Small particles need more light and have a smaller effective volume

Effective volume goes down as particle size goes down.

This is in surmountable…but noise (uncertainty due to fewer particles) is not.

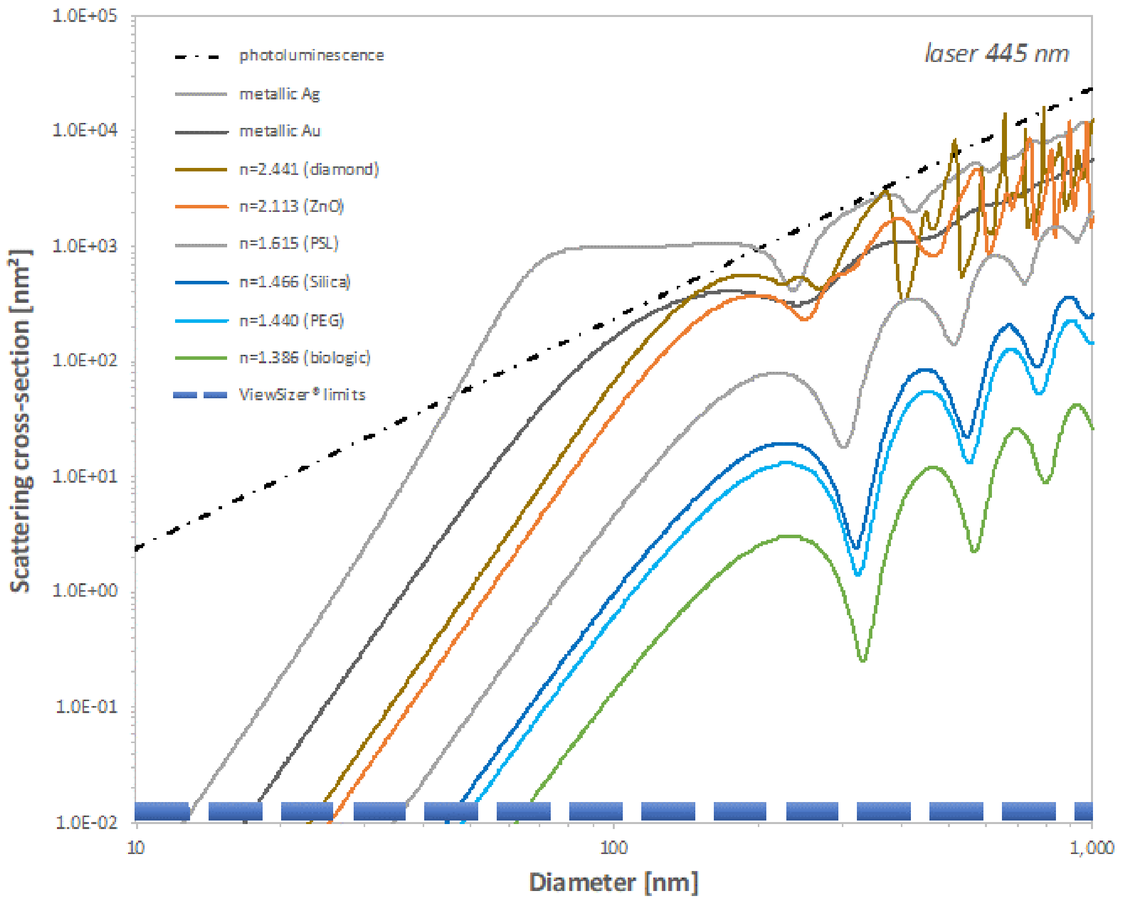
Look to fluorescence to help



Laser (nm)	Long Pass Filter (cut-on wavelength)
445 (blue)	450
520 (green)	550
635 (red)	650

Scatter and fluorescence measured orthogonally.
With 3 laser excitation sources, we have many options of fluorophores to selectively identify mixed particles systems.
Long pass and short pass filters allow for isolation of fluorescent particles.

Detection limits



in water (n=1.337), laser 445 nm wavelength, polarized, objective NA=0.28, 80°÷100° integration

Rayleigh Scattering

$$I = I_0 \left(\frac{1+\cos^2\theta}{2R^2}\right)\left(\frac{2\pi}{\lambda}\right)^4\left(\frac{n^2-1}{n^2+2}\right)^2\left(\frac{d}{2}\right)^6$$

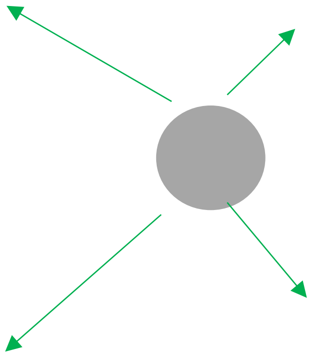
I	=	scattered intensity
Theta	=	viewing angle
R	=	viewing distance
lamda	=	wavelength of light
n	=	particle refractive index
d	=	particle diameter

Rayleigh scattering diminishes quickly ~ d^6

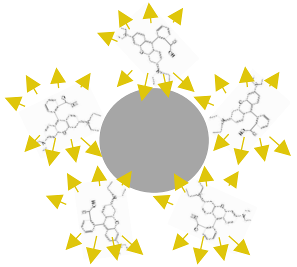
Calculated limit for detecting scatter in silica is ~ 40 nm.

Fluorescent particle emission signal diminishes less rapidly, ~ d^2

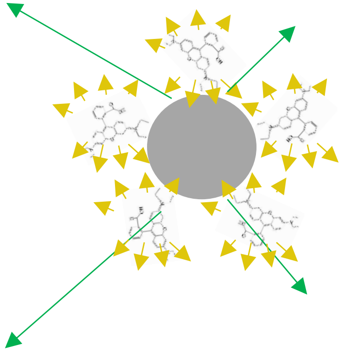
Enhancing detection limits



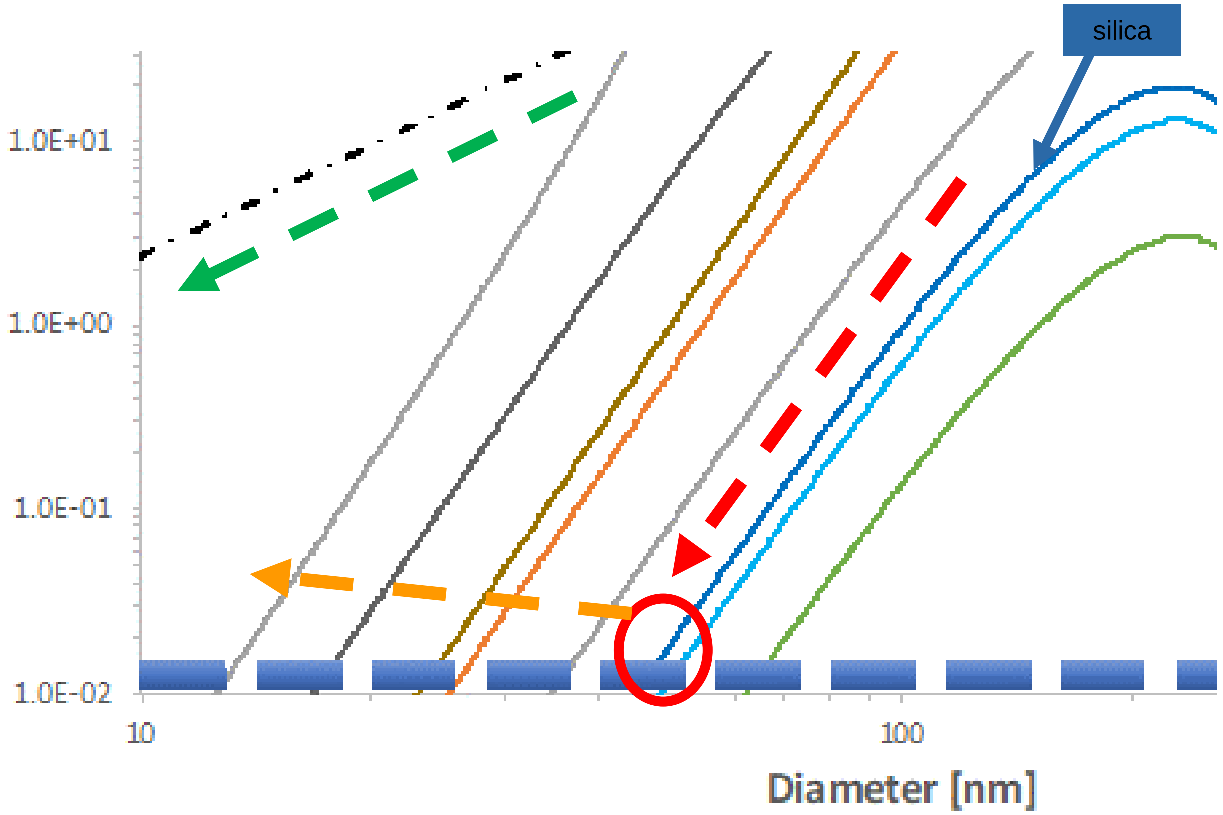
Scattered signal
Rayleigh scattering degrades ~ d^6



Fluorescent emission
Fluorescence signal degrades ~ d^2

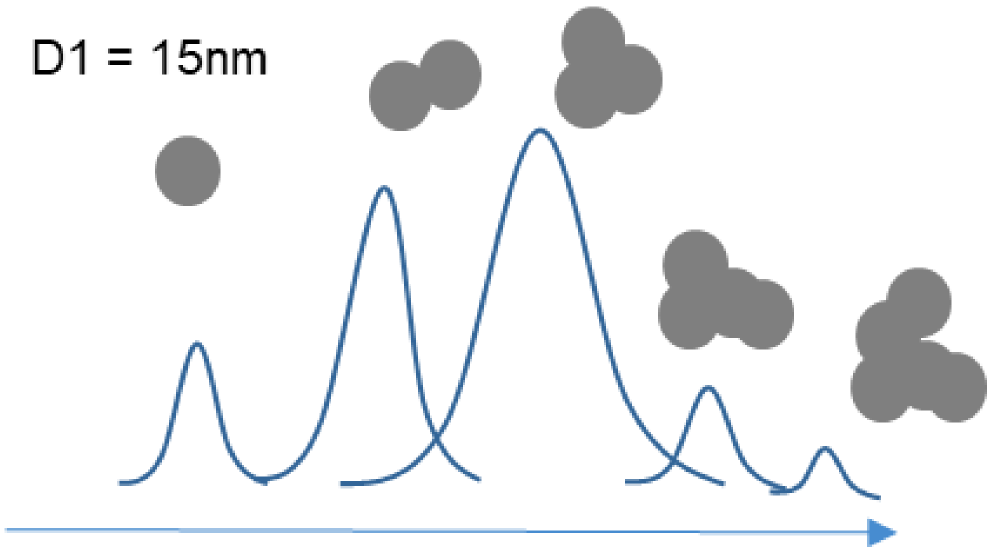


Detection may improve with added fluorescence



Can we enhance our signal by tagging the silica with an adsorbed dye; combine the scattered signal with fluorescent emission

Test the Concept: A Challenging Colloidal Silica



ULTRA HIGH PURITY COLLOIDAL SILICA

クォートロン® Quartron®

FUSO

PLシリーズ

超高純度コロイダルシリカ

Ultra high purity Colloidal Silica

超高純度アルキルシリケートを原料に、ゾルゲル法で合成した純度99.9999%の超高純度コロイダルシリカです。合成因子などを操作することで粒子径や会合度を自由にコントロールすることが可能です。

FUSO's ultra high purity colloidal silica is produced by sol-gel synthesis from ultra high purity alkyl silicate. The particle size and aggregate ratio can be controlled by adjusting parameters.

特徴 Characteristics

- ゾルゲル法で合成した超高純度コロイダルシリカ Ultra high purity colloidal silica by a sol-gel synthesis
- 粒子径や会合度を自由にコントロール Various particle size and particle shape
- 粒子は単分散で、粒度分布がシャープ Uniform dispersibility and sharp particle size distribution
- pHが中性~アルカリ性で極めて安定分散 Stable at neutral and basic pH
- ロット間のバラツキが少ない Less lot to lot variation
- 凝集・沈降しにくい Less sedimentation

主用途 Applications

様々な分野への応用が期待されています
Applicable to a wide range of fields

- 各種ウエハー用研磨材 Wafer polishing
- CMPスラリー CMP slurry
- 各種コーティング材 Coatings
- クロマトグラフィ用充填材 Chromatography carrier
- セラミックバインダー Ceramic binder
- インクジェット用紙 Ink-jet paper
- 触媒担体 Catalyst carrier

PL-1 PL-3 PL-7 PL-10H

特性 Typical Properties

下記代表グレード以外にも粒子径、粒子形状の異なる製品を多数取り揃えております。

項目 Items		単位 Unit	PL-1	PL-3	PL-7	PL-10H
一般物性 General properties	外観 Appearance	–	透明性乳白色 slightly opal	透明性乳白色 slightly opal	乳白色 milky	乳白色 milky
	比重 (20/4℃) Specific gravity	–	1.07	1.12	1.14	1.14
	pH	–	7.3	7.3	7.3	7.3
	シリカ濃度 Silica content	%	12	20	23	23
粒子径 Particle size	一次粒子径 Primary size (D1)	nm	15	35	75	90
	二次粒子径 Secondary size (D2)	nm	40	70	125	220
	会合度 Aggregate ratio	–	2.7	2.0	1.7	2.4
純度 Impurities	アルカリ金属 Alkali metals	ppb	300以下 below 300			
	重金属 Heavy metals	ppb	100以下 below 100			

扶桑化学工業株式会社

電子材料事業部

With a ~ 40nm mean particle size and a wide range of aggregate sizes, Fuso PL-1 is a good challenge for the resolution of the Viewsizer 3000.

https://fusokk.co.jp/eng/wp/wp-content/uploads/2019/05/5d5d380df5aea451f62d038624cb8cb5.pdf

Test the Concept: An Efficient Dye

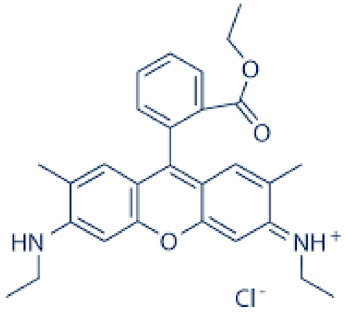
Cationic dye can interact electrostatically with the negative surface charge colloidal silica

- Very efficient adsorption in the literature

Surface modification of colloidal silica particles using cationic surfactant and the resulting adsorption of dyes
Asad M. Khan
Journal of Molecular Liquids, Volume 274, 15 January 2019

Selective adsorption of organic dyes by porous hydrophilic silica aerogels from aqueous system *Wei Wei*
Water Science & Technology | 78.2 | 2018

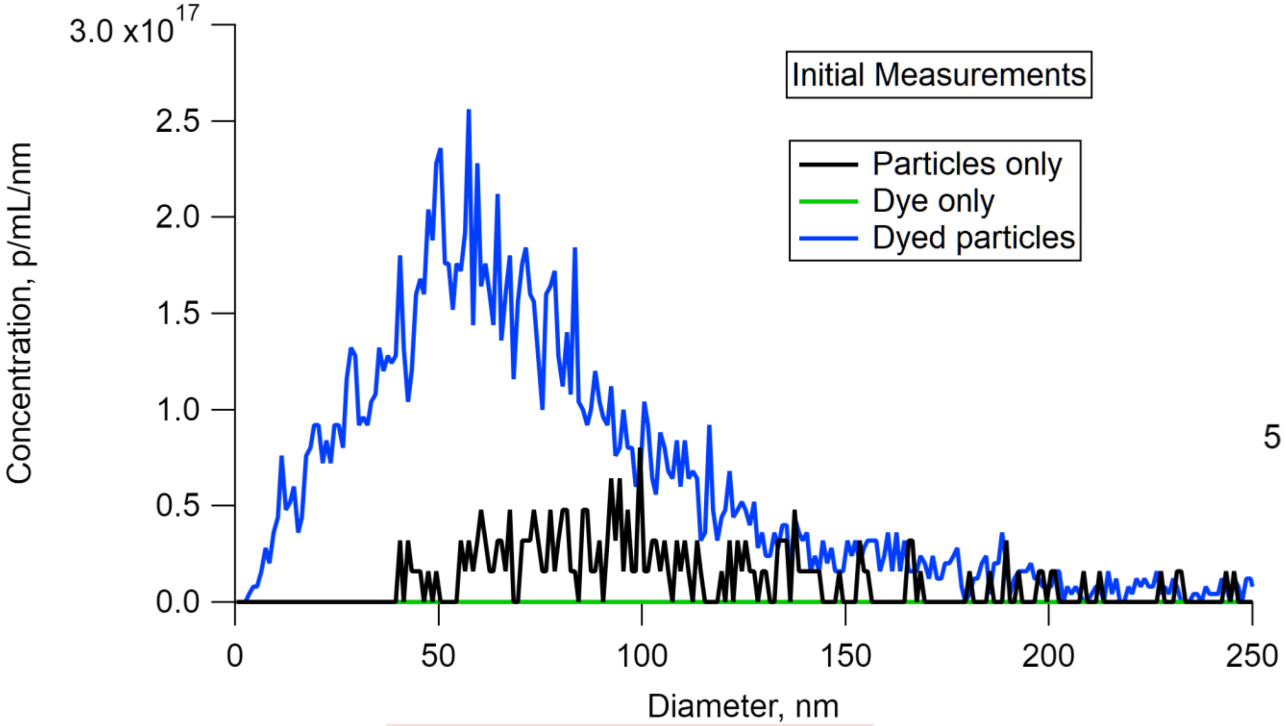
Adsorptive removal of methylene blue from aqueous solution using coal fly ash-derived mesoporous silica material *Ning Yuan*
Adsorption Science & Technology 2019, Vol. 37(3–4) 333–348



Rhodamine 6G (R6G)
λ_{ex} = 530 nm, λ_{em} = 565 nm

Based on Prof. Remsen's results and literature supporting cationic dye adsorption on SiO2, and good fluorescence alignment with our green laser
We chose a high purity colloidal silica **and Rhodamine 6G**

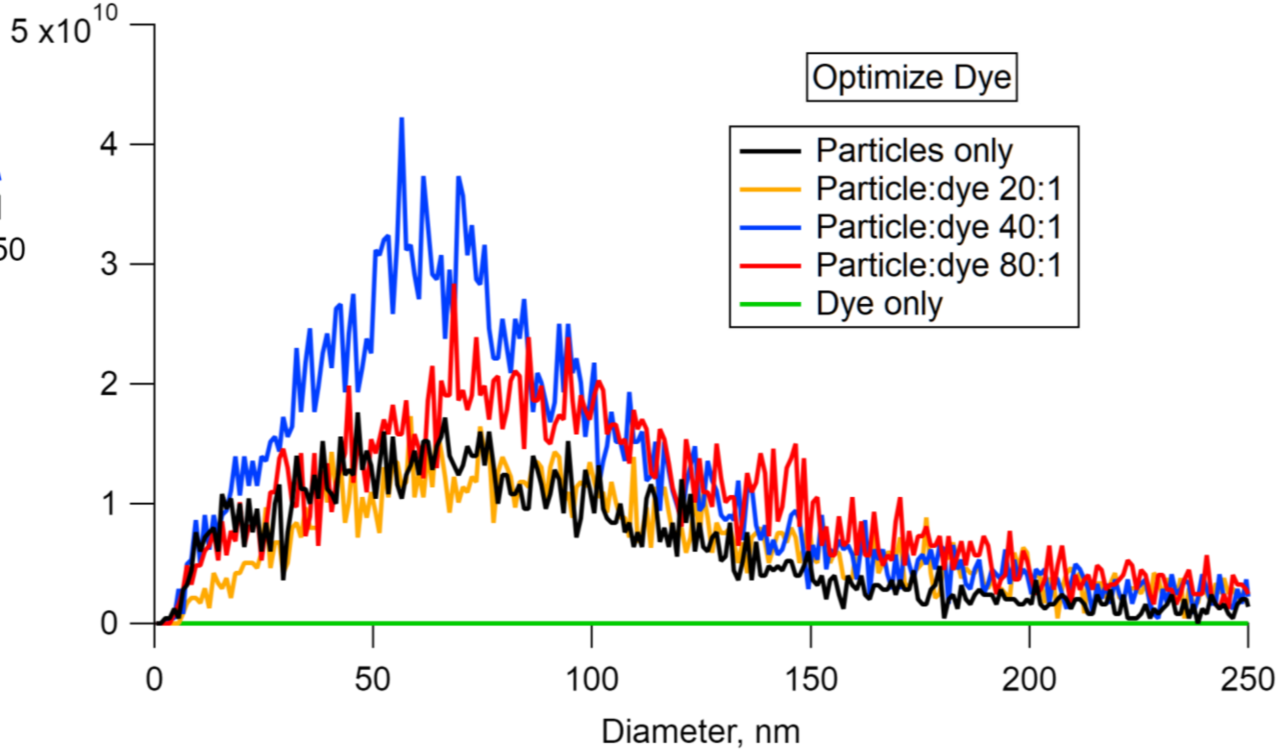
Test the Concept: Series of Experiments



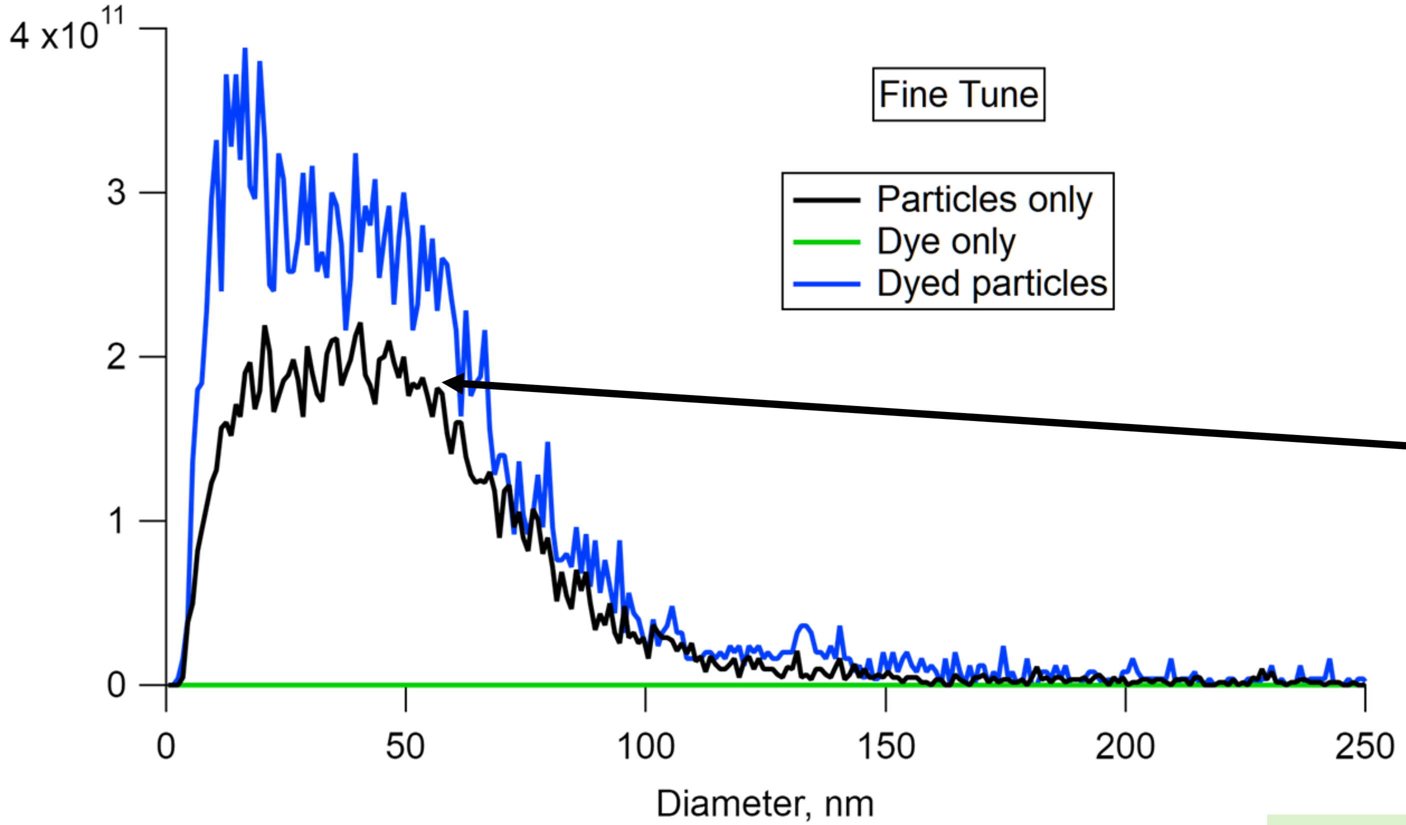
Proof of concept

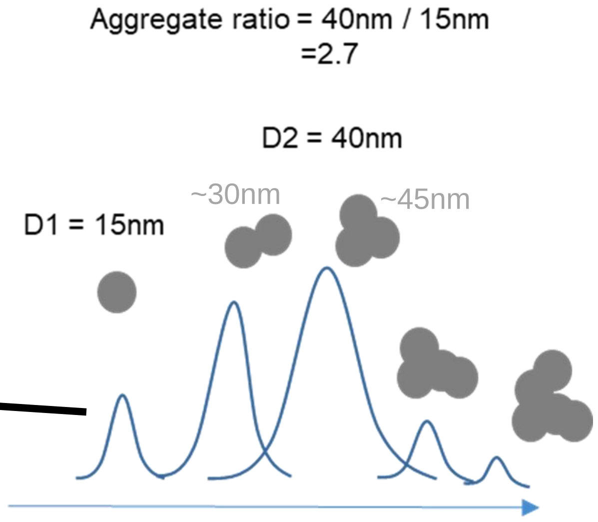
- “standard settings”
- increased counts
- detected finer particles

Optimized dye: silica ratio
Proportions to boost detection



Optimized Conditions



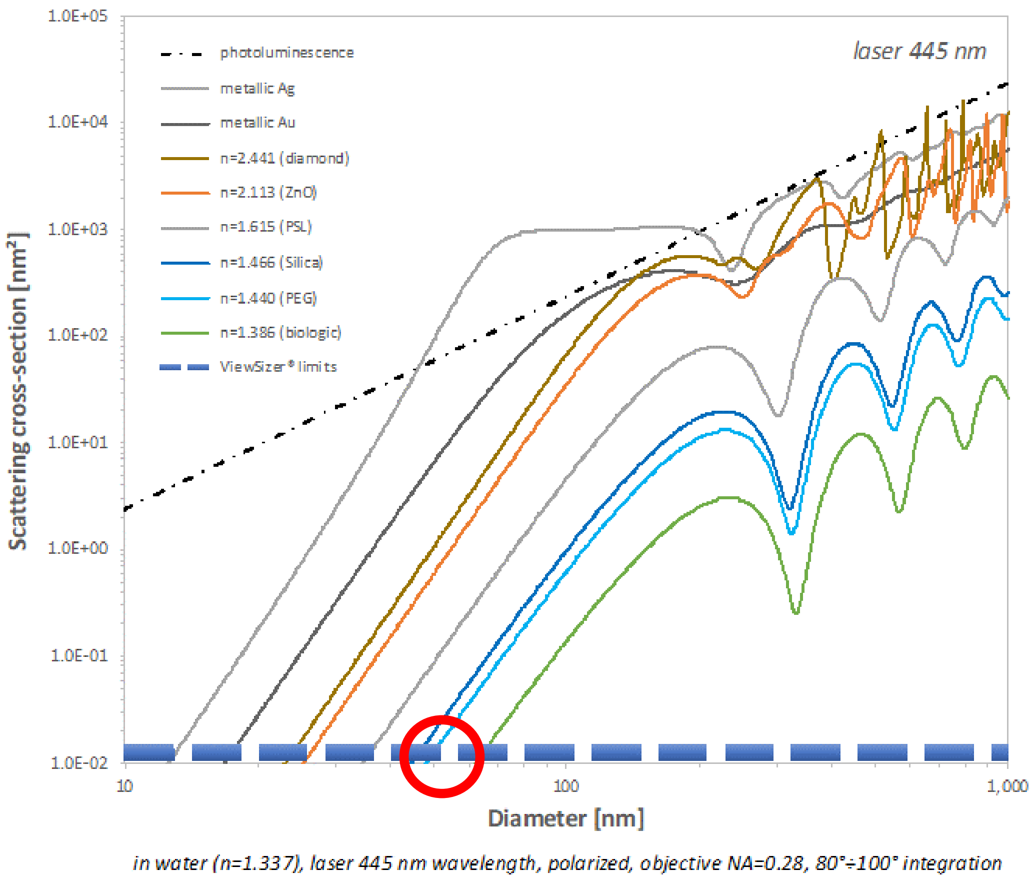


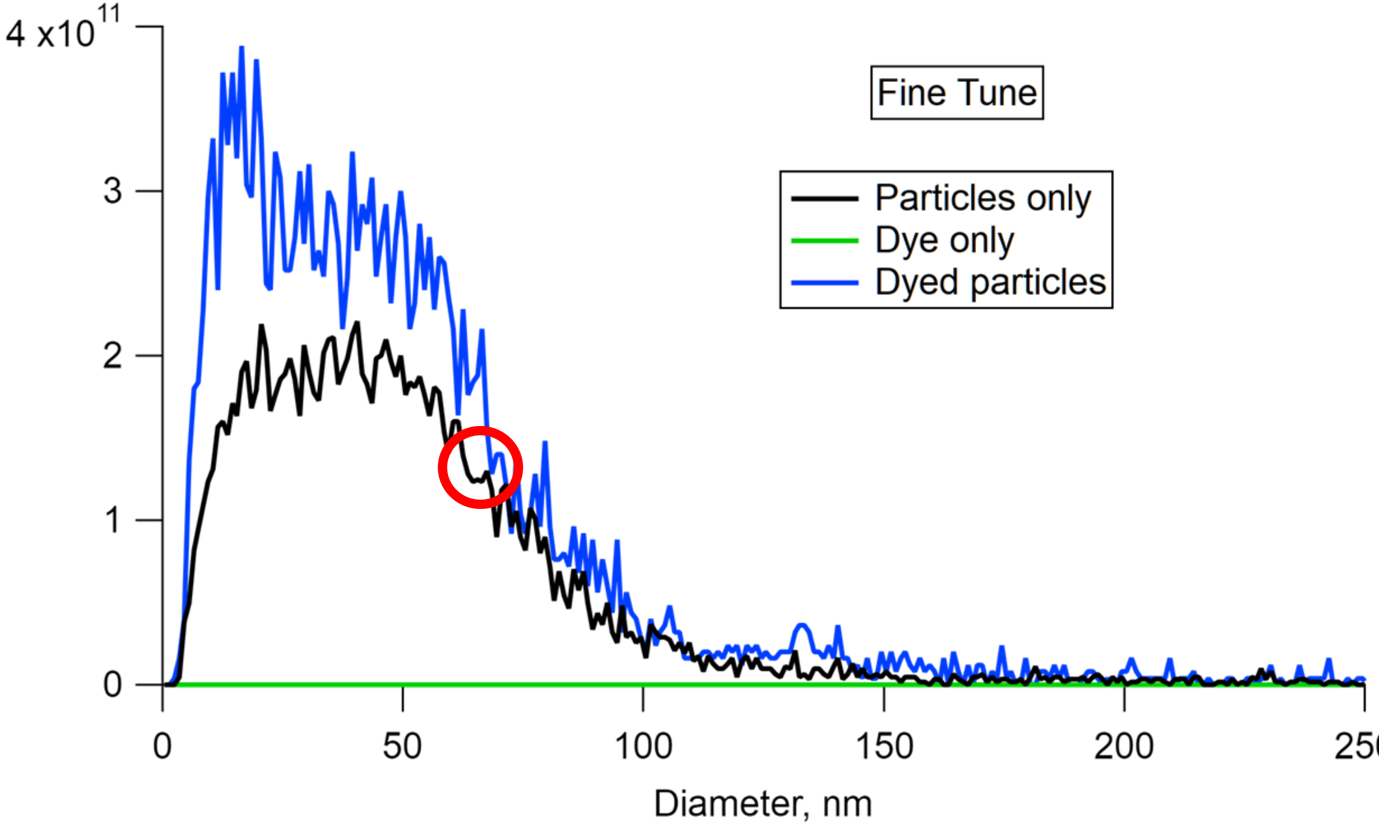
Optimizing the trends seen in the previous experiments;

- dye : silica,
- optimal dilution
- optical settings (higher gain)

Undyed PSD is close to expected MPS
Clear enhancement of fines when we add dye

Series of Experiments





Comparing the calculated limit of scattering detection for the Viewsizer and the enhanced signal of the dyed particles, The improved detection is pronounced at sizes smaller than ~ 65nm.

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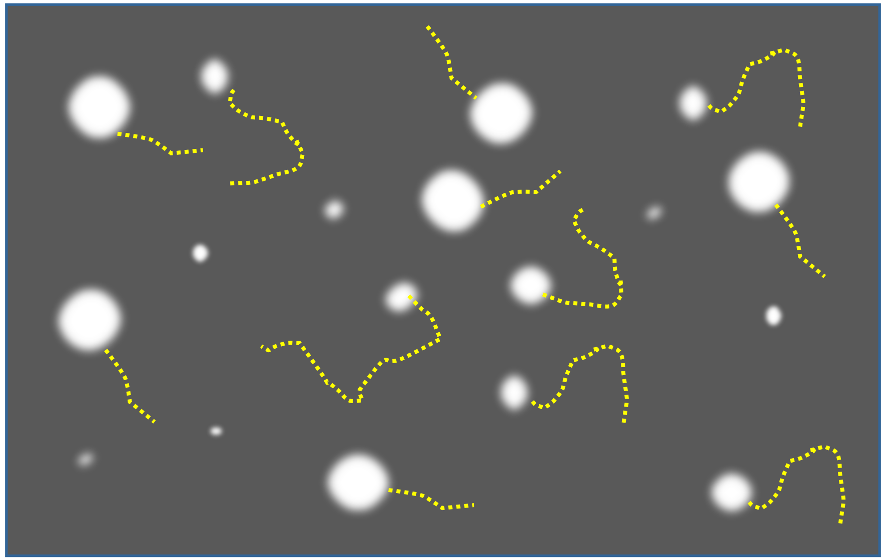
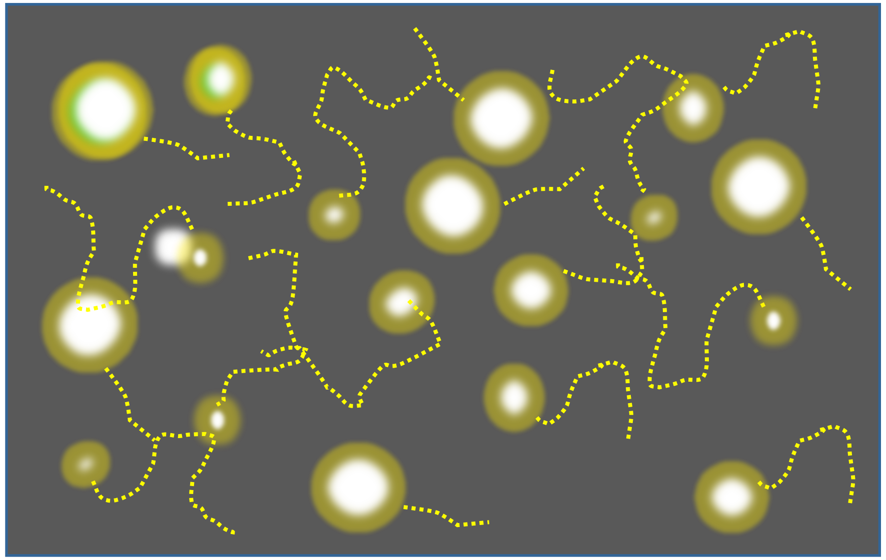
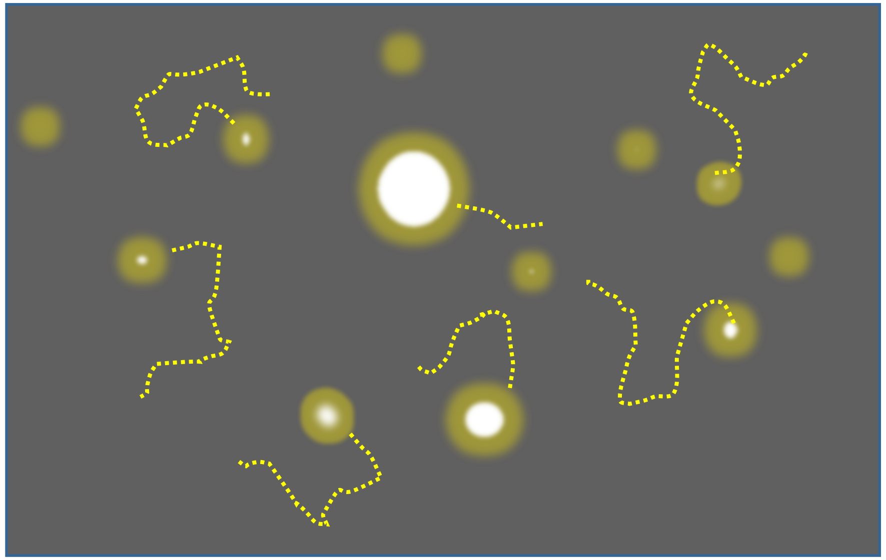
Illustration of the Experiments



Standard process
Fines poorly detected



Dyed particles increase counts
Need dilution to count all particles



Dyed and diluted, we can optimize the optical settings to improve detection of fines

Summary of Results

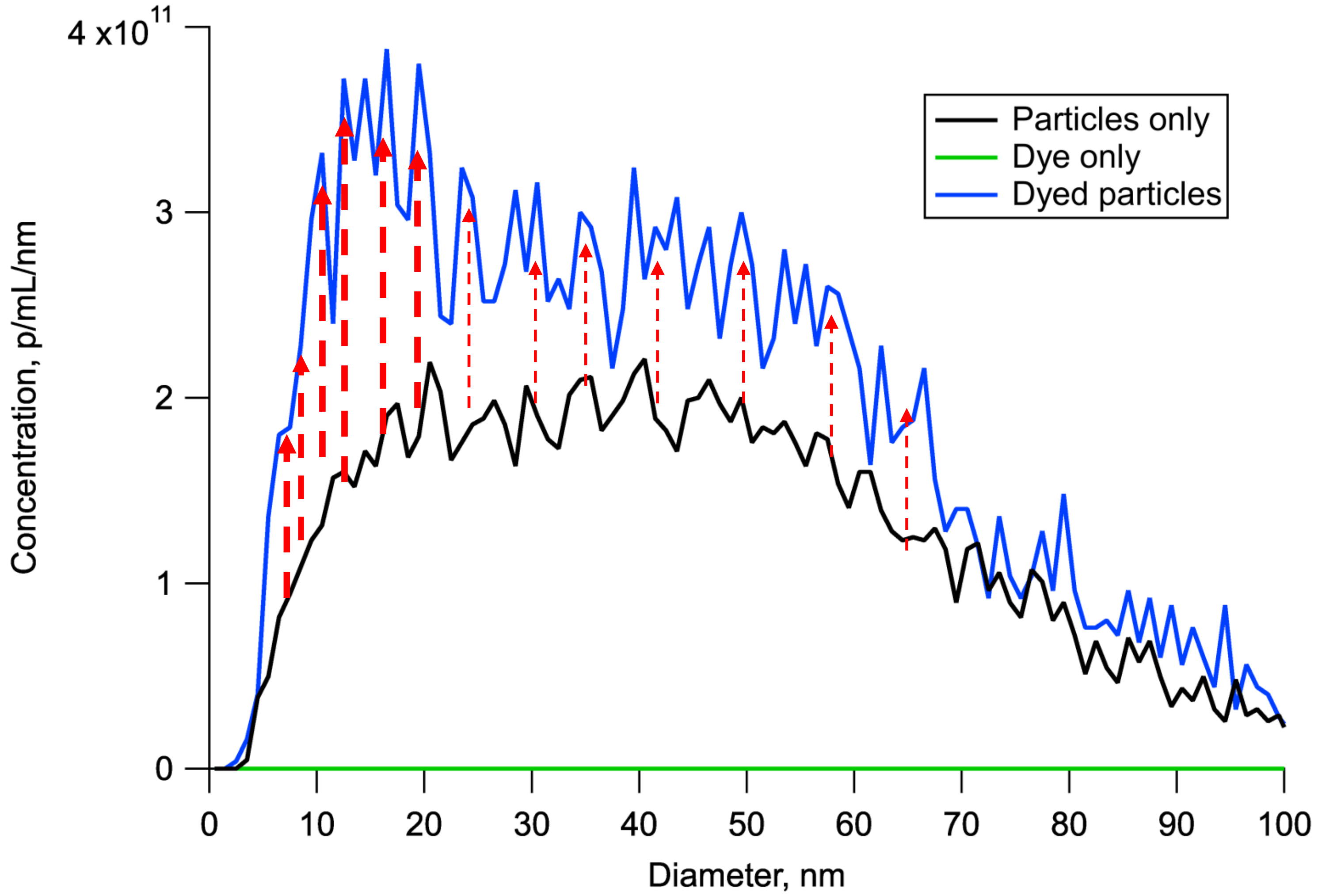
Addition of Rhodamine 6G to Fuso PL-1:

- Consistently increases the counts
- Detection of finer particles upon optimal dilution

More counts->better statistics

Opportunities for follow-up

- More efficient dyes
  - blue and red
- Lot-to-lot (good vs. bad)
- Dyes for other particle types
- Process for complex slurry formulations (interfering additives)




Omoshiro-okashiku
Joy and Fun
おもしろおかしく
நன்றி
Terima kasih
Tack ska du ha
Gracias
谢谢
Danke
Σας ευχαριστώ πάρα πολύ
धन्यवाद
Grazie
THANK YOU
شكرًا
ขอบคุณครับ
Obrigado
Большое спасибо
ありがとうございました
Cảm ơn
Merci
감사합니다
Dziękuję