Fine Particle Characterization in Chemical Mechanical Planarization (CMP) Slurries with Fluorescence Correlation Spectroscopy

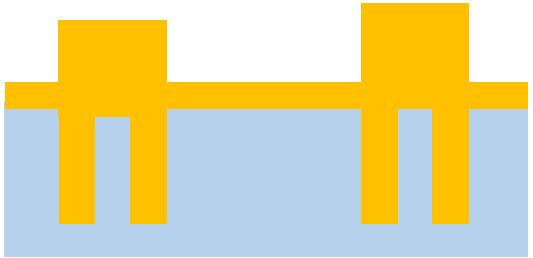
June 8th, 2021

HORIBA Semiconductor

Presentation Content

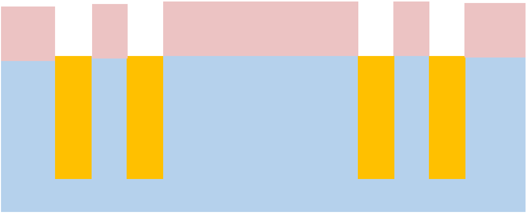
1. Brief CMP description
    1. Particle size variation
    2. Simplified abrasion model
2. Motivation and scope
    1. Process variation
    2. Roadmap Fine Particle Focus
        1. IRDS
        2. SEMI Standard
3. 2 methods using fluorescence
    1. FCS
    2. NTA

Basic Description of CMP

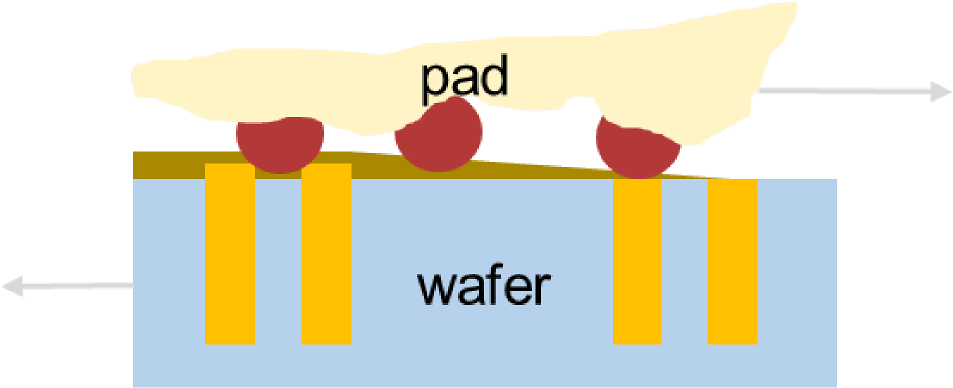


Material overburden

Chemical Mechanical Polishing



Continue the process flow

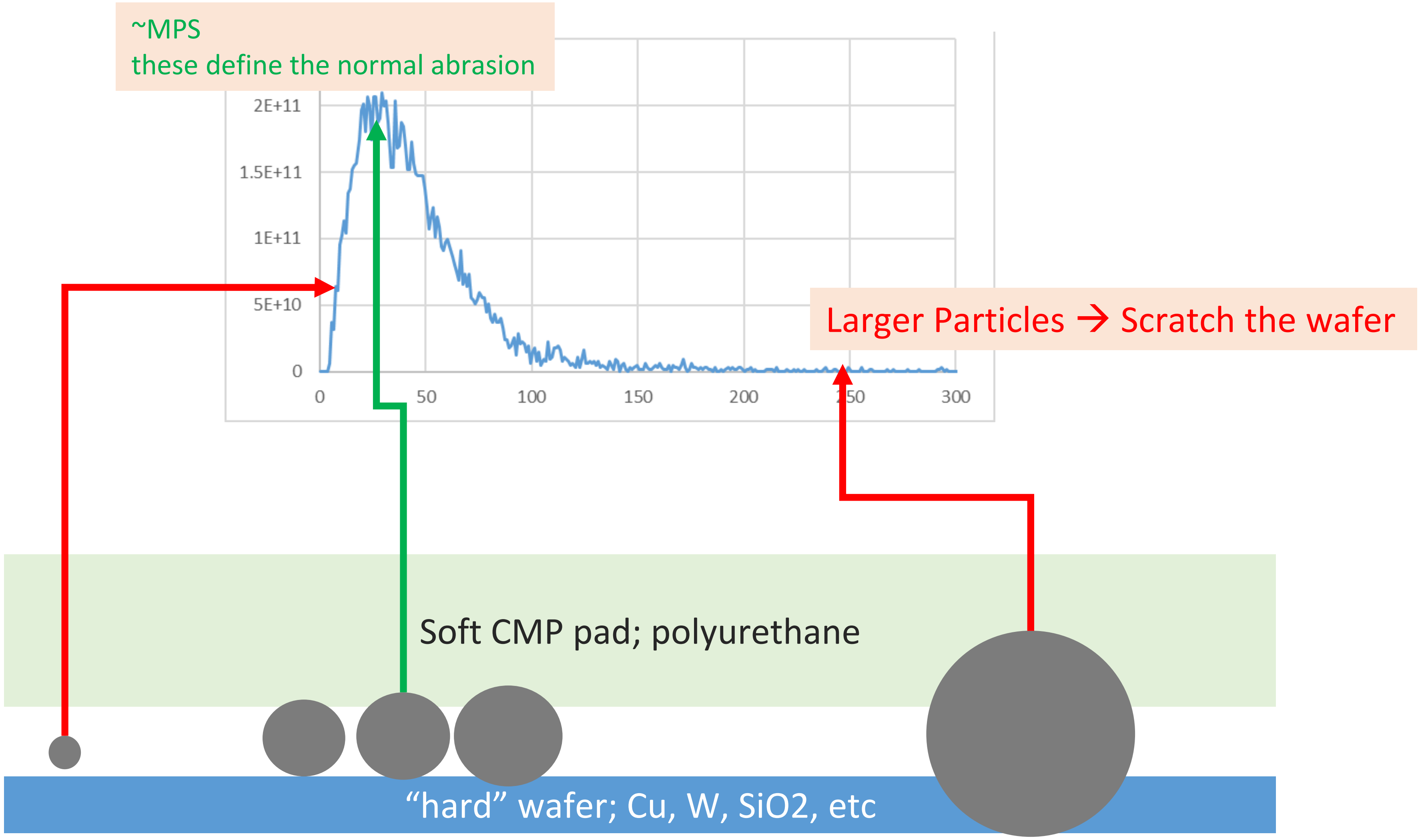


- Slurry: Liquid, additives, particles
    - Chemically modify surface
    - Mechanical abrasion of modified surface
- Compliant pad
- Wafer

Dynamic process…focus on particle metrology

Simplified Mechanical Abrasion Model

- ~D20 and less
- ***<u>Difficult to measure</u>***
- These can be useless filler if too high
- Essentially depleting the active abrasives near MPS
- Can remain on the wafer as post CMP defects
- High surface area may react with other additives uncontrollably



Motivation and Scope

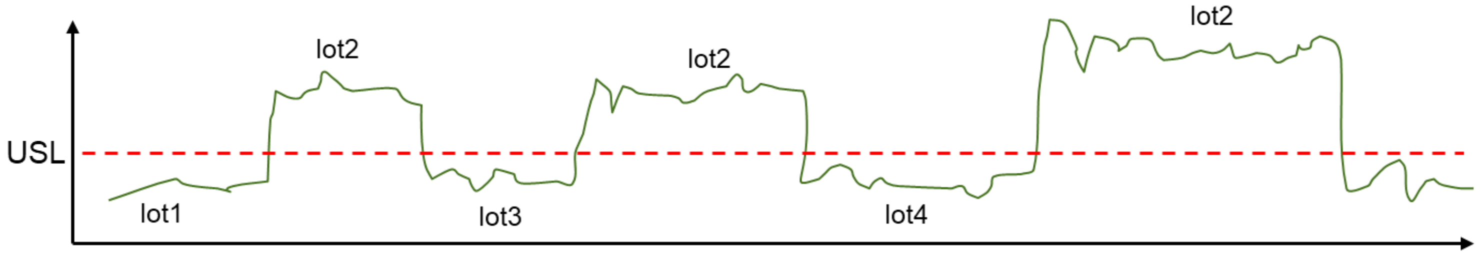
Metrology improvements to reduce variation from particles

particle supplier

distribution system
- dilution
- oxidizer
- filtration

CMP process parameters
- RR / uniformity
- defects
- planarity

slurry supplier
- dilution
- additives
- filtration



Reactive: respond to process parameter excursions for slurry in MFG process
Proactive: New metrology and methods
Particle suppliers: improve PSD metrology → control PSD
Slurry R&D → Optimize abrasive performance → robust CMP performance
Commercial slurry → Avoid ***process excursions*** due to abrasive particle raw material variation

Background – IRDS 2018 & 2020

- 2020 Challenge #5 is a perennial for IRDS Yield Enhancement…

Table YE-2b Yield Enhancement Difficult Challenges--SECC

Near-Term Difficult Challenges: 2020–2027	*Description*
Challenge #1 Control of electrically active and other particles in ultrapure water and liquid chemicals for advanced semiconductor manufacturing (logic key driver)	Insufficient metrology and marginal treatment technology capability
Challenge #2 Control of electrically active and other particles in UPW of EUV mask production	Insufficient metrology and marginal treatment technology capability
Challenge #3 Critical organics in UPW	Insufficient metrology for online speciation of organics
Challenge #4 Metals in H_2O_2	Insufficient metrology capability. Characterization needed for specific critical metals for key process steps and segments.
Challenge #5 Slurry particle characterization and other impurity monitoring	Insufficient metrology capability

https://irds.ieee.org/images/files/pdf/2020/2020IRDS_YE_Tables.xlsx

First Year of IC Production	*2017*	*2018*	*2019*	*2020*	*2021*
Logic 1/2 pitch, nm (contacted)	*18*	*18*	*14*	*14*	*12*
GENERAL					
Fluid purity impact on device yield / performance. Requirements are specific to the chemistry and the Process step that it is used for.					
Contaminant based process control ???					
CHEMICALS - Metrology					
Development of 40 nm particle counter [A]					
Development of 20 nm particle counter [A]					
Development of 10 nm particle counter [A]					
Particle characterization to identify source of contamination [A], (for components and systems)					
Micelle particle size and concentration characterization [B] for surfactant containing chemistries.					
Bubble discrimination of reactive chemistries [A]					
Improved metrology for concentration measurements [B]					
Anion & cation measurement in process chemicals, e.g. cleaning chemicals [A]					
Organic measurement (TOC and speciation) in process chemicals, e.g. H2O2, IPA [A]					
Contaminant characterization in CMP slurries, e.g. zeta potential, large particle size [A]*					
Contaminant characterization in CMP slurries. (Agglomertaes, Foreign Material) [B]					
Characterization of CMP slurries, e.g. Particle size distribution [B]					

Roadmap perspective:

Perpetual need for improvements to particle metrology…

Background – SEMI Standards

Semi standards <u>do not</u> 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

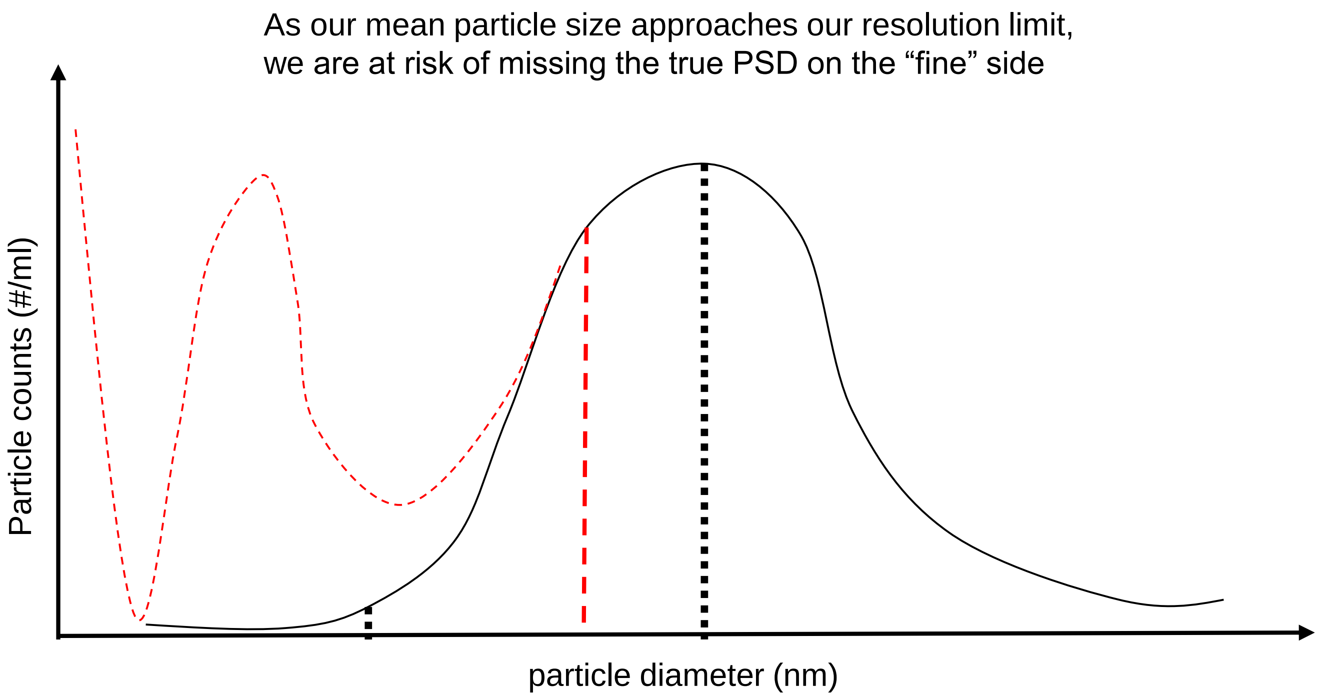
"**Response to Semiconductor Technology Advances**

- **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?



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

Fluorescent Enhancement Techniques

DLS

Laser Diffraction

Disk Centrifuge

E-Microscopy

Fluorescence Correlation Spectroscopy (FCS)

Nanoparticle Tracking Analysis (NTA)
Viewsizer 3000

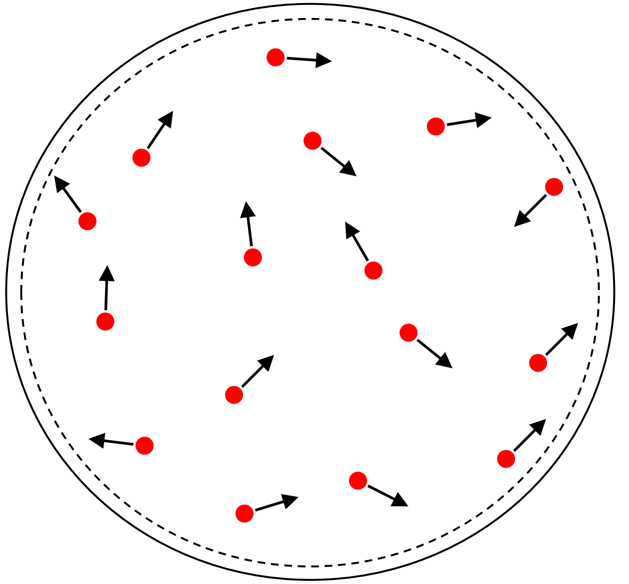
- Multi wavelength
- Dye enhanced

Outline

- Overview of Fluorescence Correlation Spectroscopy (FCS)
- Use of Multiple Dyes in FCS Analysis and Application of Fluorescence Lifetime Analysis (FLA)
- FCS Characterization of Different Dyes Adsorbed Silica Abrasives
- FCS Characterization of the Small Particle Tail in Silica Particle Size Distributions Using Fractionation via Differential Sedimentation Analysis of Supernatant Fractions
- Conclusions and Directions for Future Studies

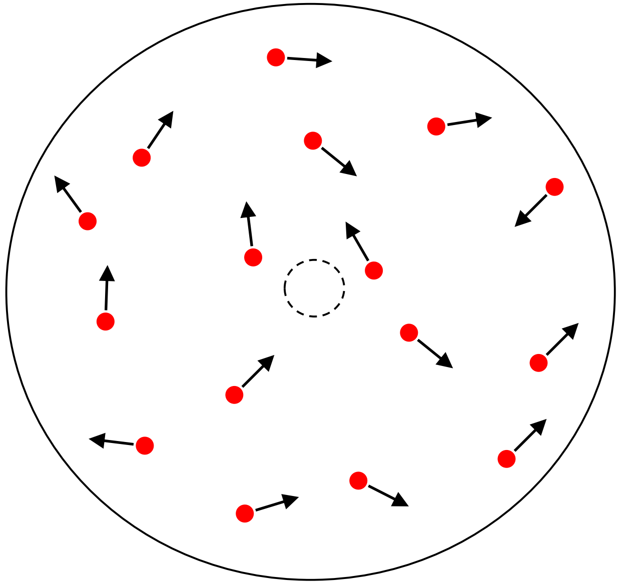
Fluorescence Correlation Spectroscopy

<u>Consider the following Thought Experiment</u>: Image the fluorescence from a dilute solution of dye molecules.



diameter of sample cell

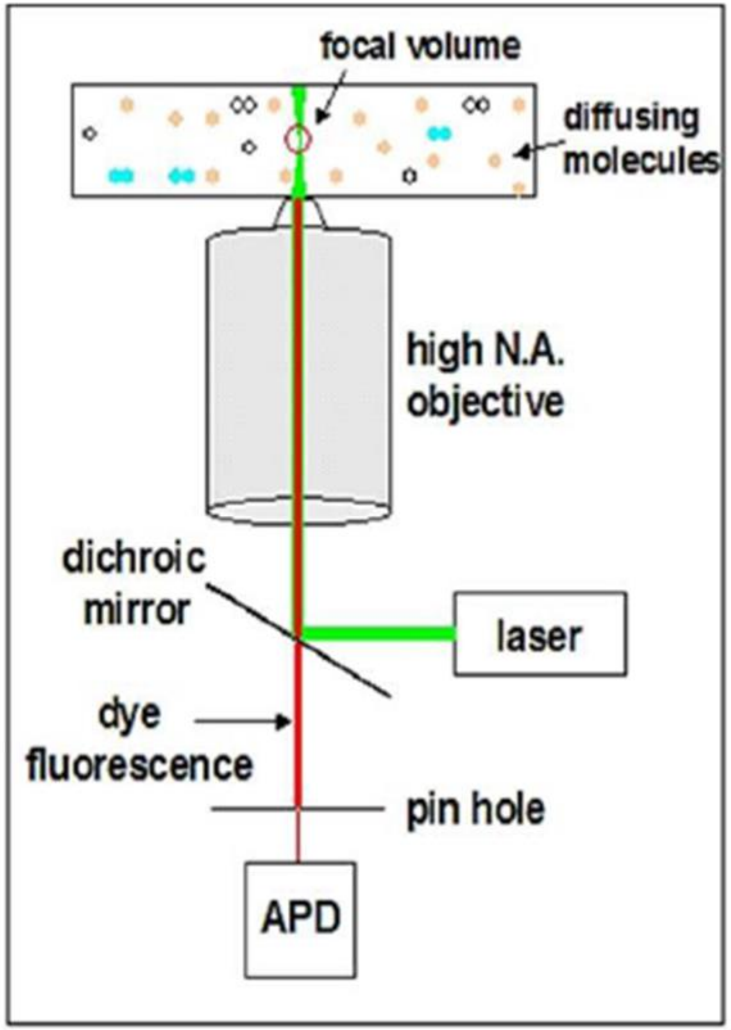
diameter at the focus

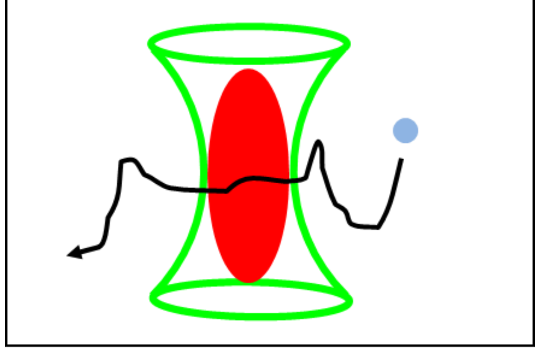


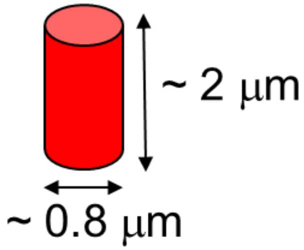
diameter of sample cell

diameter at the focus

Single-Molecule Spectroscopic Analysis
Fluorescence Correlation Spectroscopy (FCS)

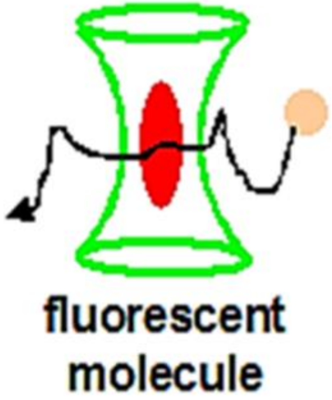


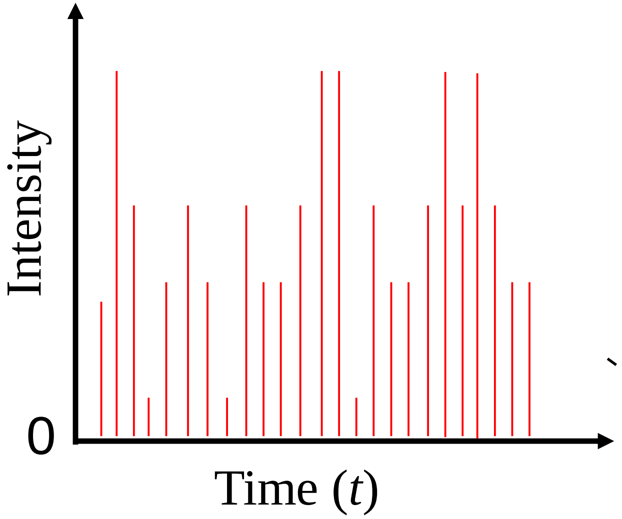


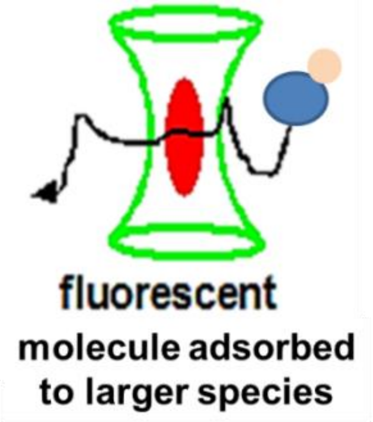


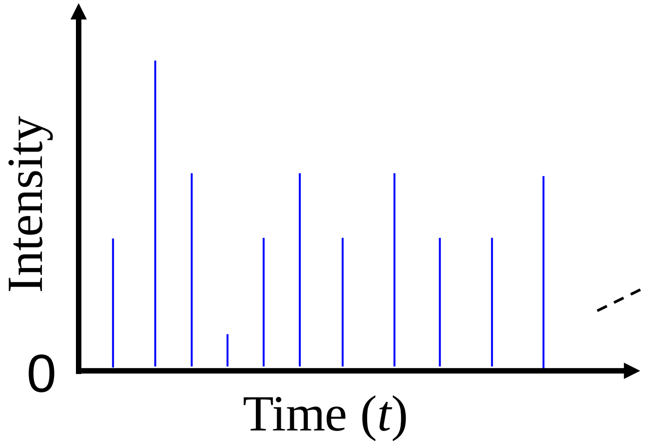
$V = \pi r^2 h$
$= 1.00\ \mu m^3$
$= 1.00$ fL

FCS Measurements: Intensity Fluctuation Autocorrelation Function, $G(\tau)$









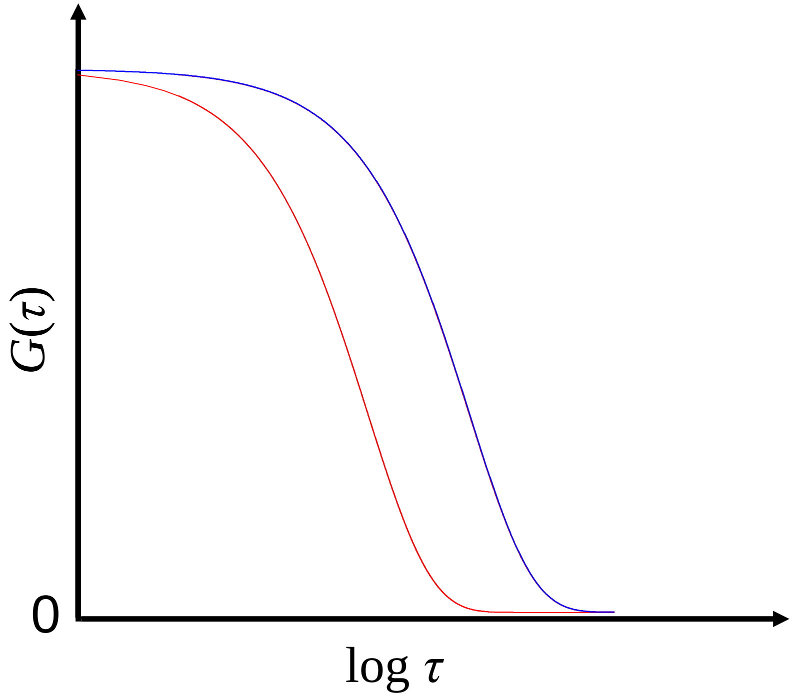
Define the *normalized autocorrelation function*, $G(\tau)$:

$$G(\tau) = \frac{\langle \delta F(t) \bullet \delta F(t+\tau) \rangle}{\langle F(t) \rangle^2}$$

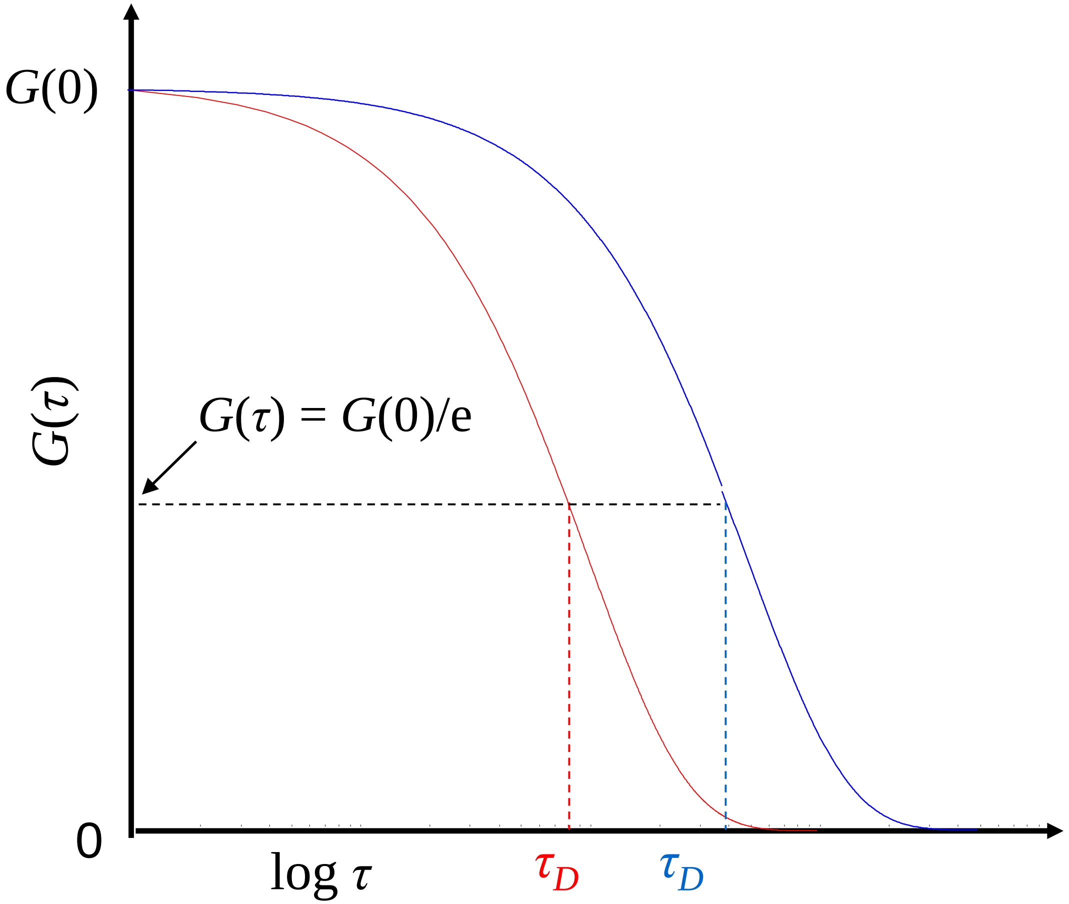
where: $F(t)$ is the intensity at time t

$\delta F(t)$ is the fluctuation in intensity at time t

$\delta F(t+\tau)$ is the fluctuation in intensity at time $t + \tau$



Evaluate the Diffusion Coefficient, D_T, and Number of Fluorophores, N



$$G(\tau) = \frac{1}{N}\,\frac{1}{1 + 4D_T\tau/r_0^2}\left[\frac{1}{1+4D_T\tau/(z_0/2)^2}\right]^{1/2}$$

τ_D is related to the *translational diffusion coefficient*, D_T:

$$\tau_D = r_0^2 / 4D_T$$

where: r_0^2 is the radius of focal volume (~0.5 µm)

D_T is related to the *hydrodynamic diameter*, d_h :

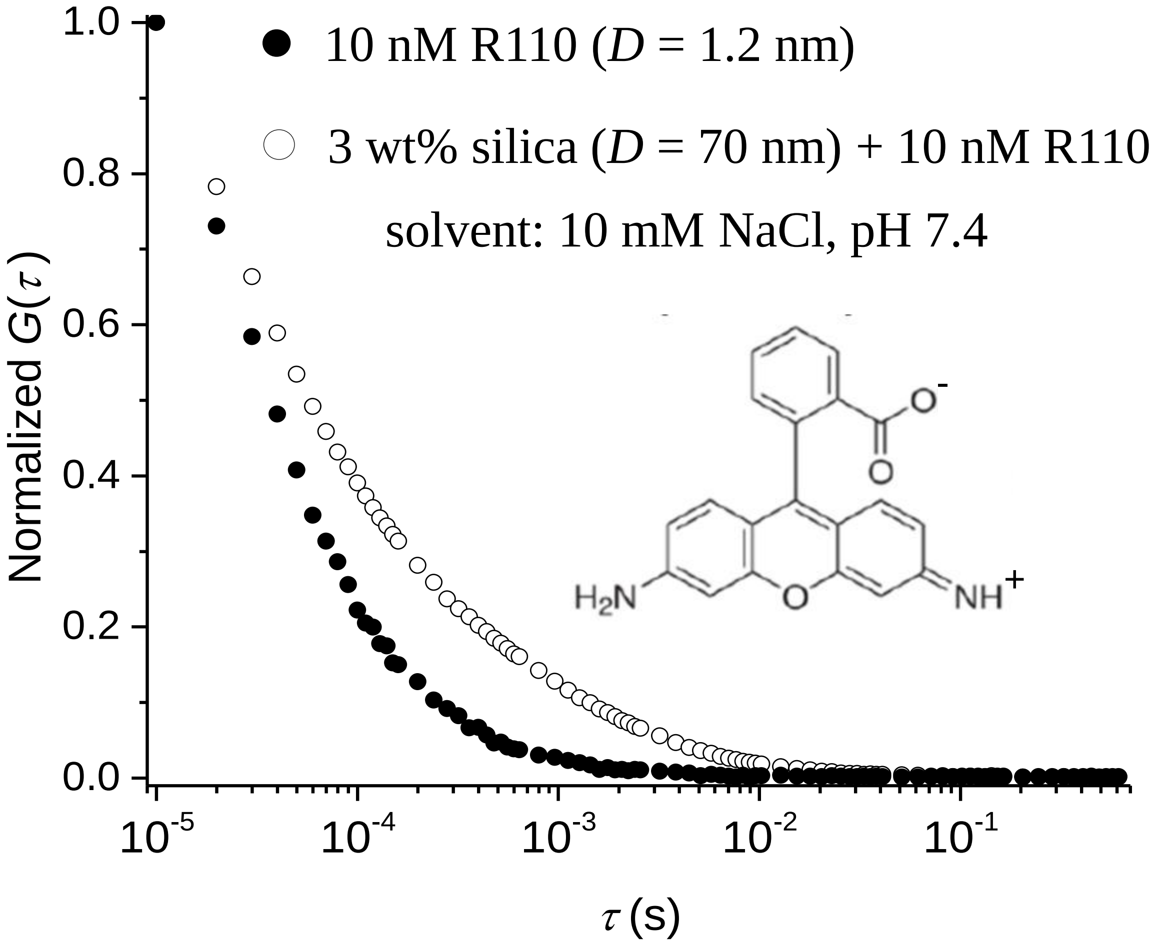
$$D_T = kT / 3\pi\eta d_h \quad \text{(Stokes-Einstein equation)}$$

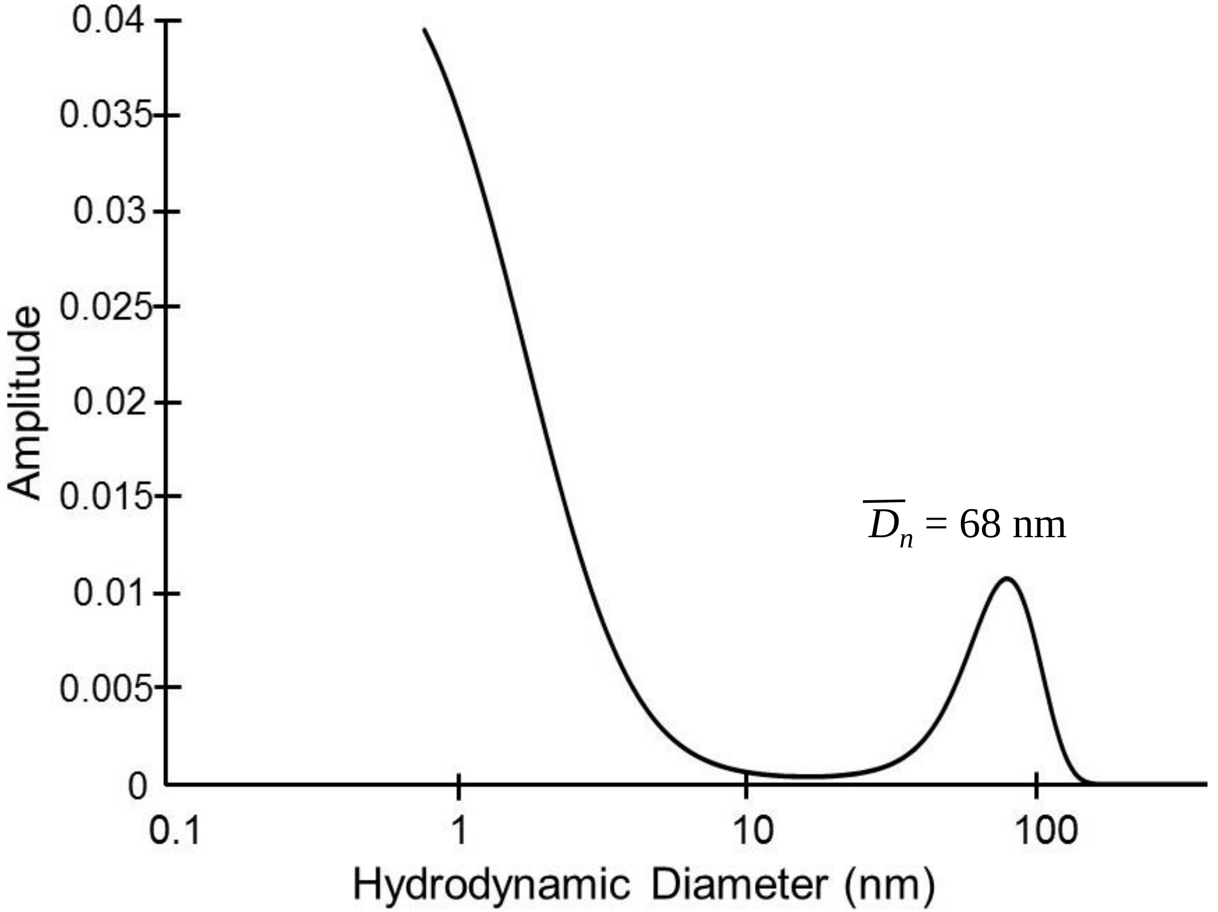
where: k is the Boltzmann constant.
T is the absolute temperature.
η is the solvent viscosity.

$G(0)$ is related to the *average number of fluorophores in the focal volume*, N:

$$G(0) = 1 / N$$

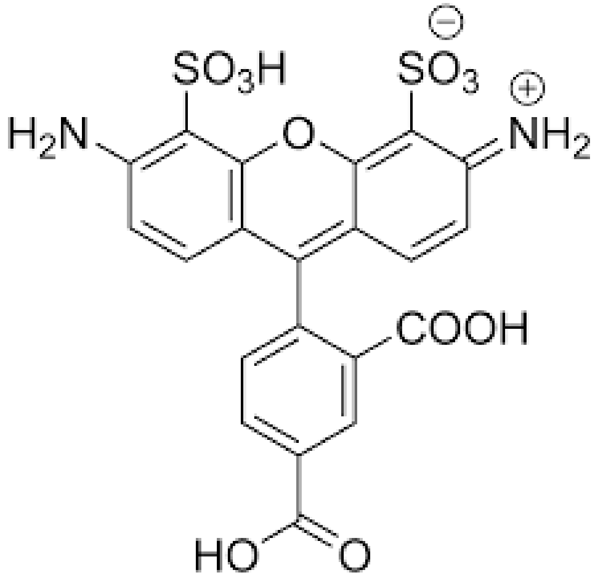
Representative FCS Analysis of Dispersed Silica Abrasive Using Adsorbed Rhodamine 110



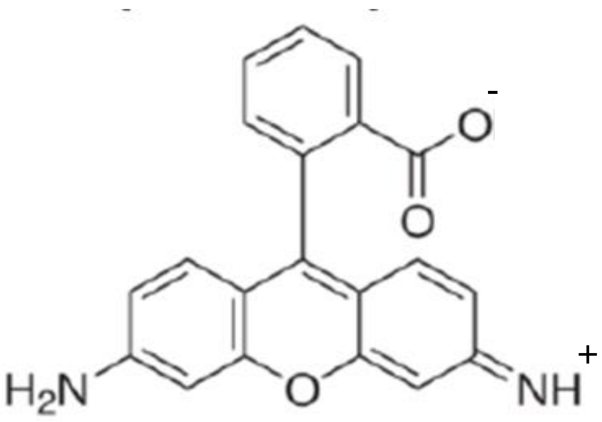


Jacobson, L.M.; Turner, D.K.; Wayman, A.E.; Rawat, A.K.; Carver, C.T.; Moinpour, M.; Remsen, E.E. *ECS J. Solid State Sci. Tech.* **2015,** *4*, P5053-P5057.
Schorr, D.K.; Smith, M.A.; Rawat, A.K.; Carver, C.T.; Mansour, M.; Remsen, E.E. *ECS Trans.* **2016** *72*, 43-51.

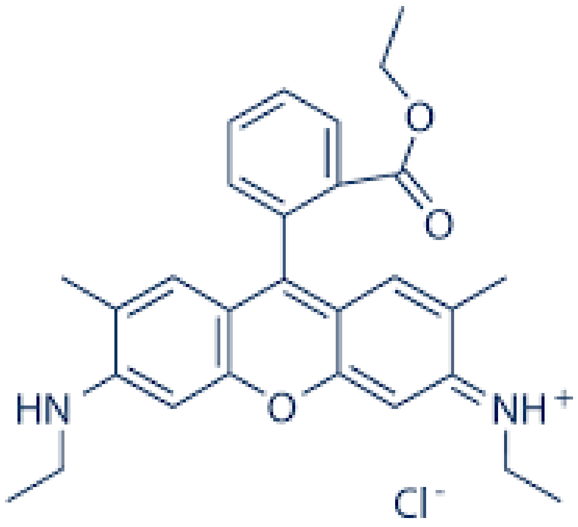
Fluorophores Employed in FCS Studies of Silica Abrasive Dispersions



Alexa fluor 488 (A488)
λ_{ex} = 490 nm, λ_{em} = 525 nm

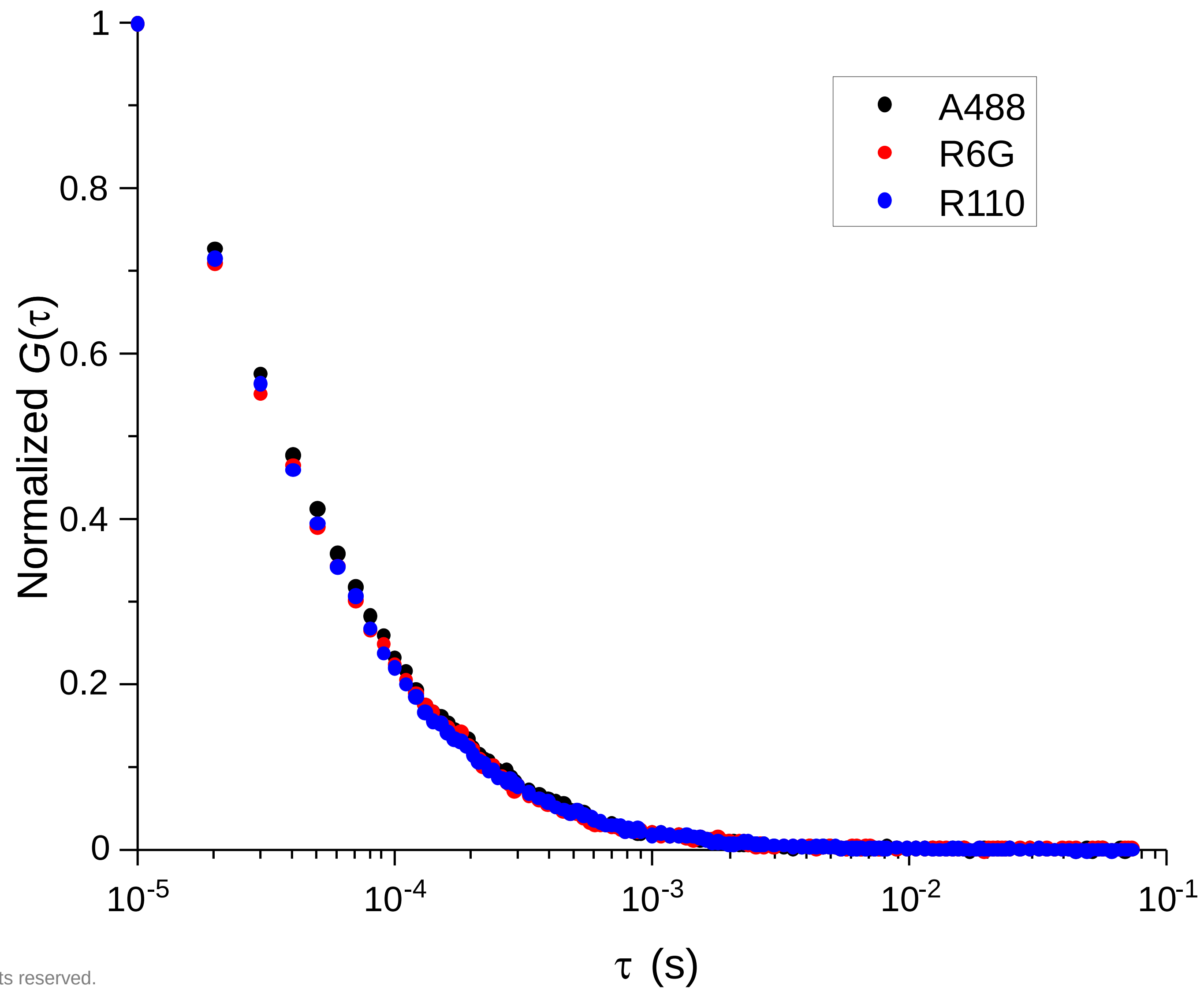


Rhodamine 110 (R110)
λ_{ex} = 496 nm, λ_{em} = 520 nm

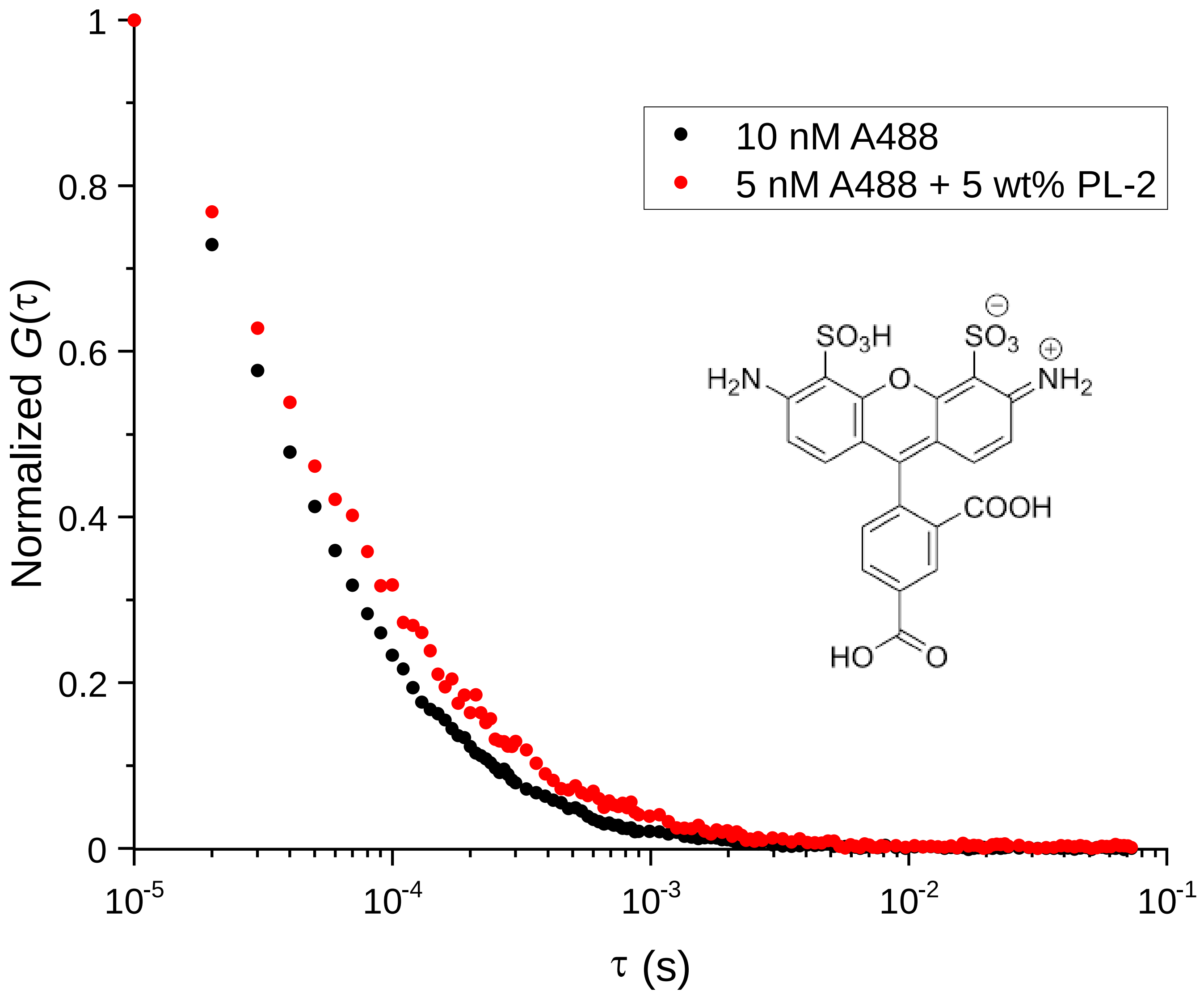


Rhodamine 6G (R6G)
λ_{ex} = 530 nm, λ_{em} = 565 nm

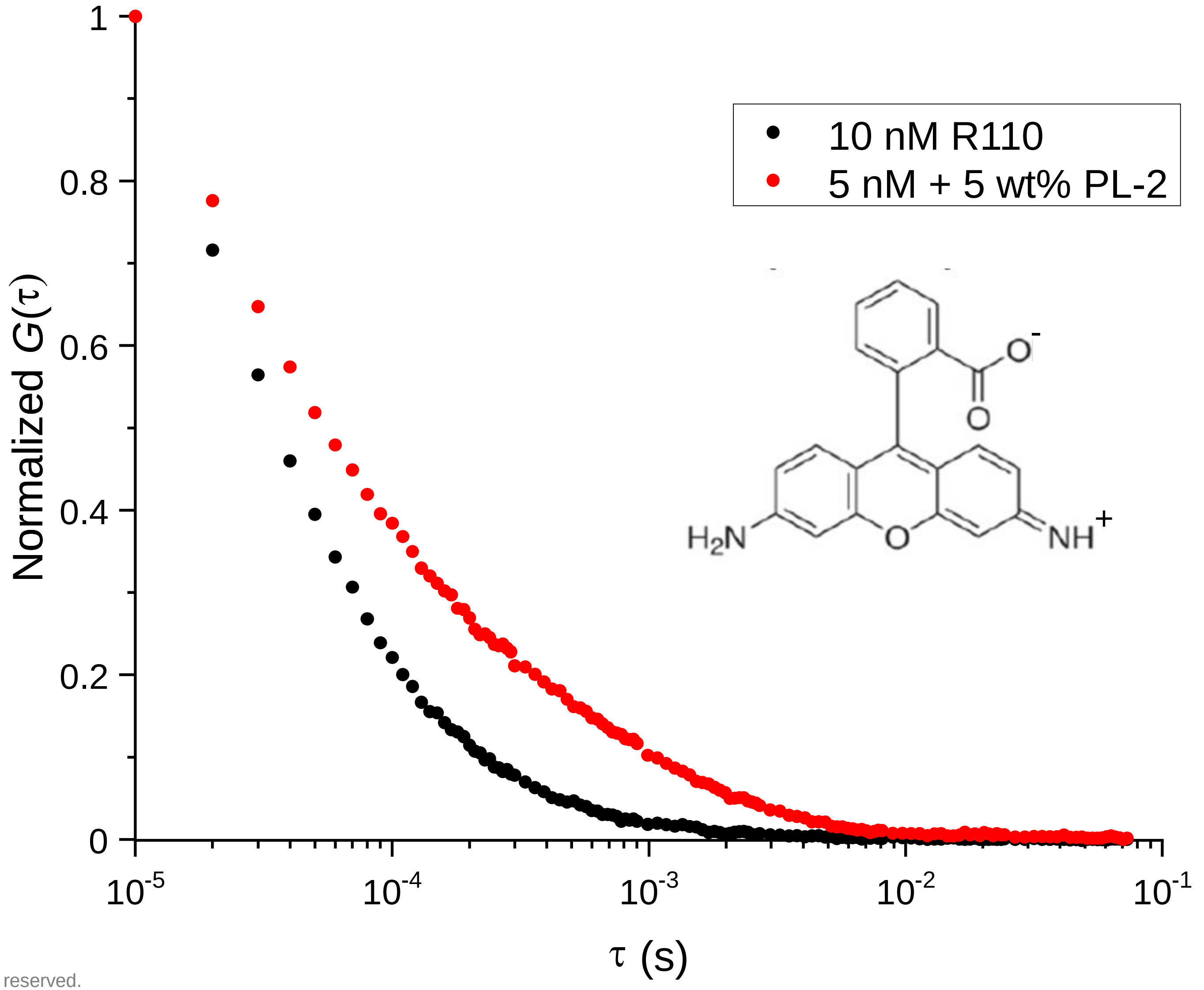
Overlay of Normalized FCS ACFs for 10 nM A488, R110 and R6G



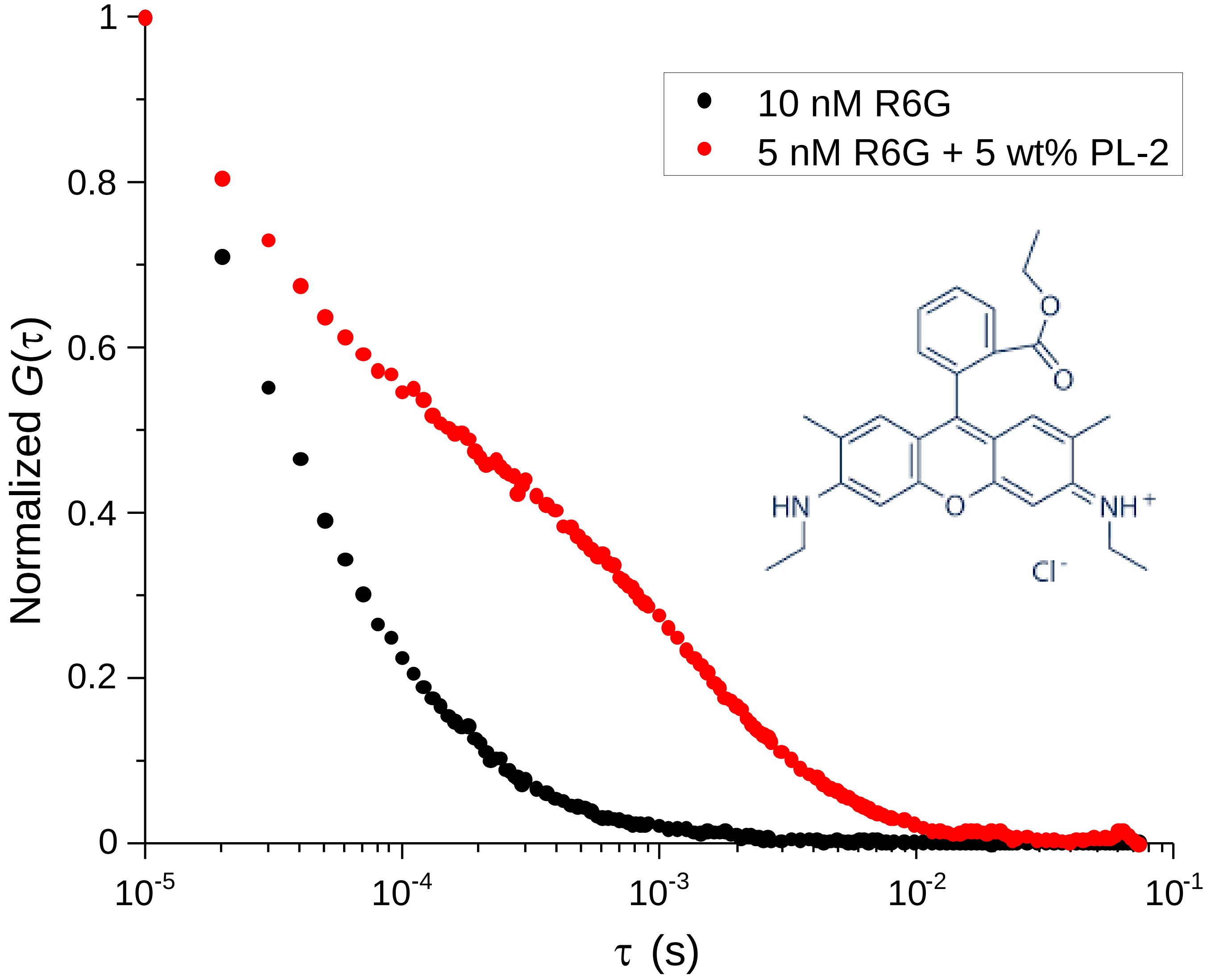
Overlay of Normalized ACFs for A488 and Adsorbed A488 on PL-2



Overlay of Normalized ACFs for R110 and Adsorbed R110 on PL-2



Overlay of Normalized ACFs for R6G and Adsorbed R6G on PL-2



Overlay of Normalized ACFs for Adsorbed A488, R110 and R6G on PL-2

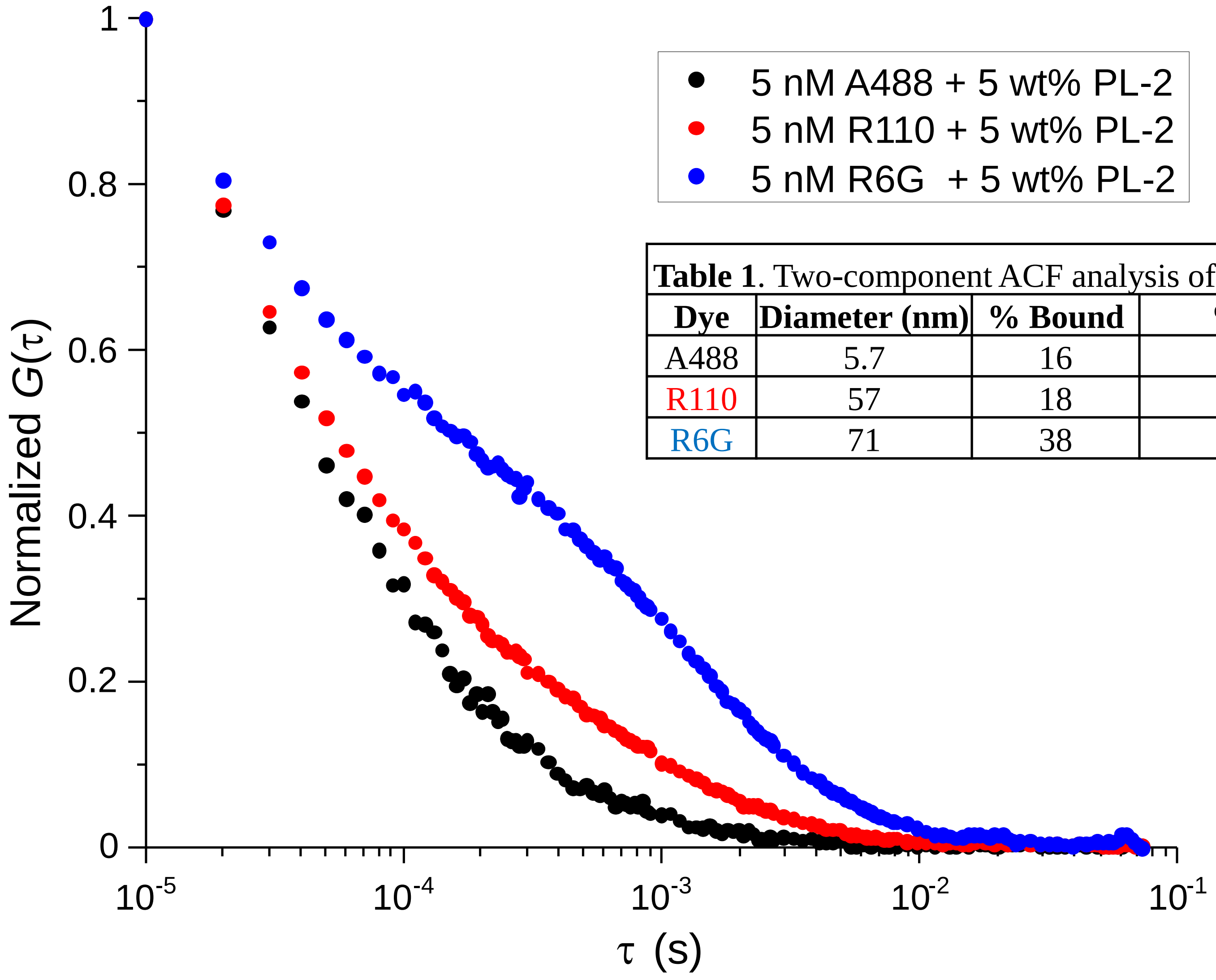


Table 1. Two-component ACF analysis of Dye + PL-2

Dye	Diameter (nm)	% Bound	% Free
A488	5.7	16	84
R110	57	18	82
R6G	71	38	62

Overlay of Normalized ACFs for Supernatants from Centrifuged R110 + S3 Mixtures as Function of Spin Time at 14,500 rpm

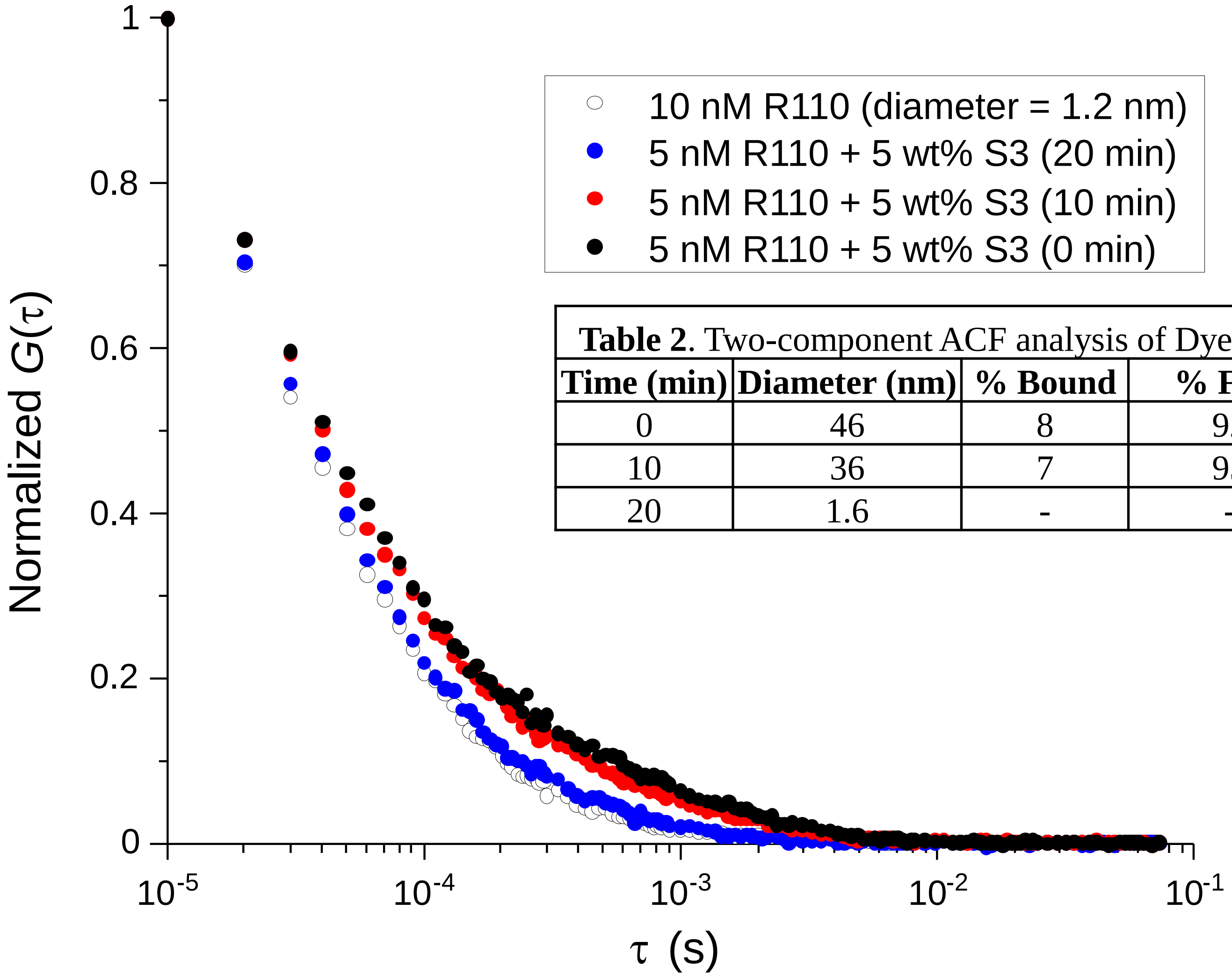


Table 2. Two-component ACF analysis of Dye + S3

Time (min)	Diameter (nm)	% Bound	% Free
0	46	8	92
10	36	7	93
20	1.6	-	-

Overlay of Normalized ACFs for Supernatants from Centrifuged R110 + S3 Mixtures as Function of Rotor Speed for 60 min

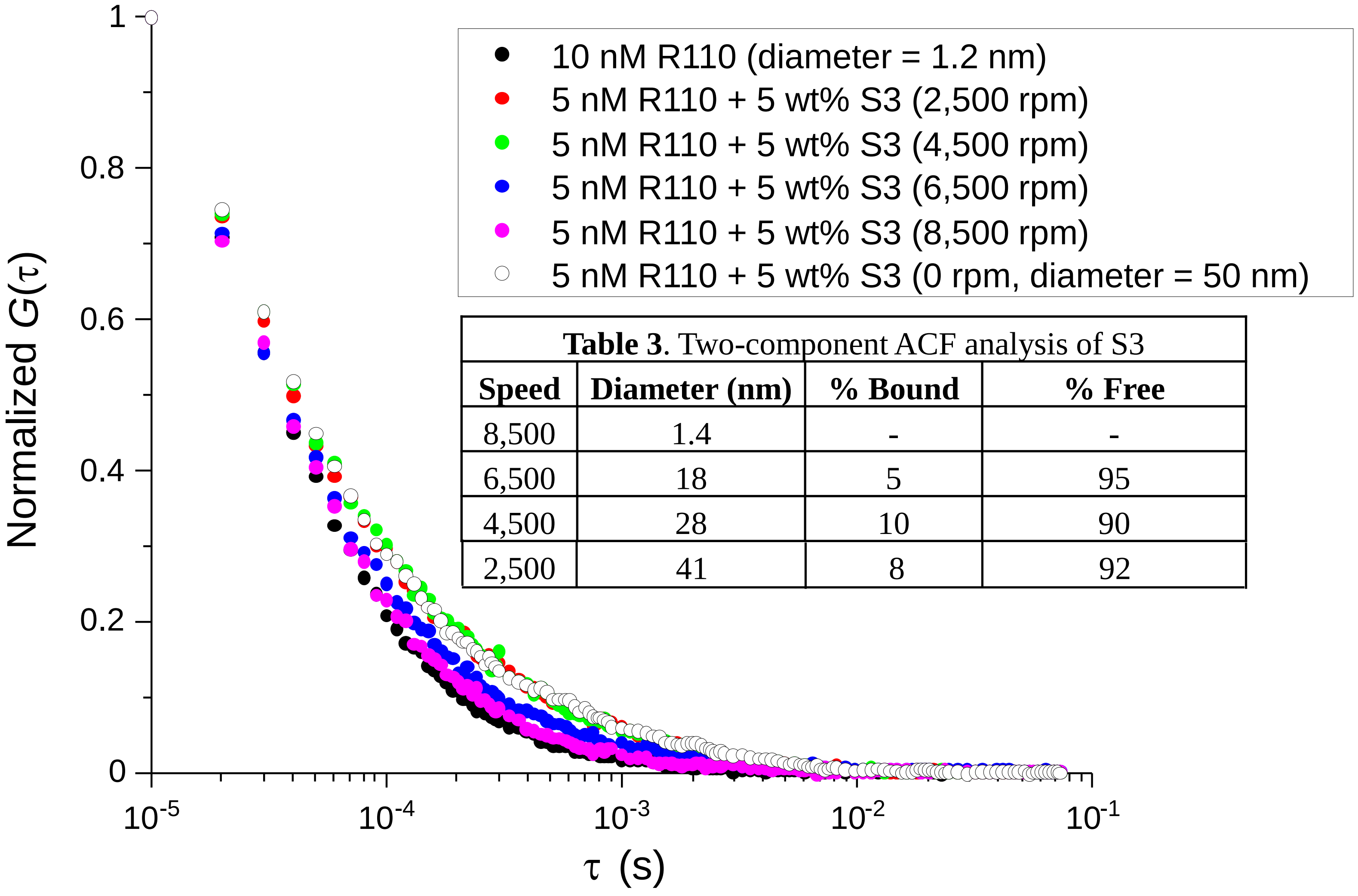


Table 3. Two-component ACF analysis of S3

Speed	Diameter (nm)	% Bound	% Free
8,500	1.4	-	-
6,500	18	5	95
4,500	28	10	90
2,500	41	8	92

Conclusions and Directions for Future Studies

- A488, R110 and R6G adsorbed to silica without significant static or dynamic quenching

- The adsorption of the dyes to silica increases in the following order:

  A488 < R110 < R6G

- Differential sedimentation of silica allows isolation and analysis by FCS of the small particle tail of the particle size distribution (PSD)

- Use R6G adsorption in conjunction with differential sedimentation for highest resolution of the small particle tail of the PSD

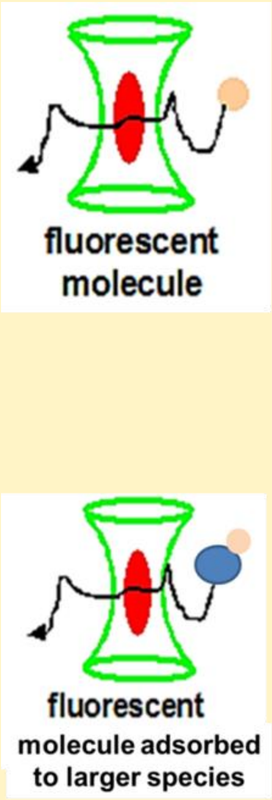
- Use FCS to quantify the adsorption isotherm of the dye interaction with silica

Outline

- Overview Nanoparticle Tracking Analysis (NTA, MANTA)
  - Ultramicroscope → NTA
- NTA with 3 lasers → How the Viewsizer is differentiated from classic NTA
  - Improved PSD
  - Tagging specific particles
- Concept: Enhancing the detection of fluorescent-tagged fine particles
- Choice of suitable particle and dye
- Series of experiments
- Conclusions and Directions for Future Studies

Ultra Microscope Concepts → NTA: Nanoparticle Tracking Analysis

The projected scatter is detected as a 2D image captured by a microscope (or high resolution camera).
Invented in 1912 for colloids in a fluid → Nobel Prize in 1925



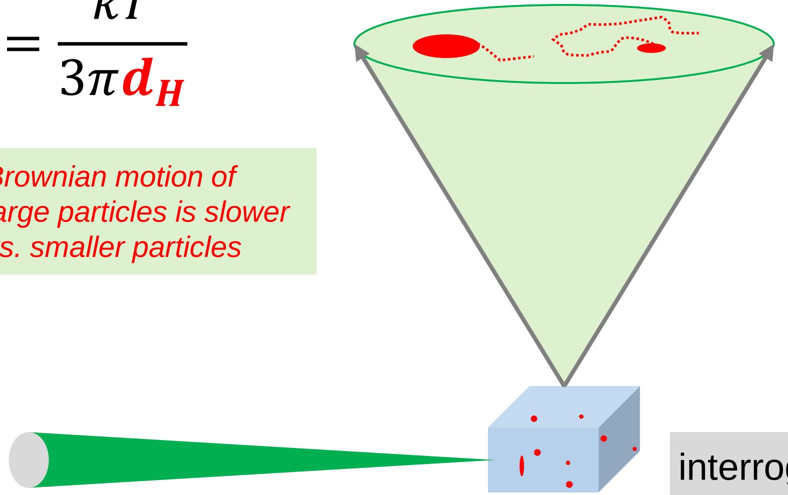
← Single molecule scale for FCS

Single particle scale for NTA →

$$D = \frac{kT}{3\pi d_H}$$

Brownian motion of large particles is slower vs. smaller particles

projected scatter
detected by optical system and camera



Scattered "image" resolution is much lower than the wavelength of illumination

interrogated volume

focused beam

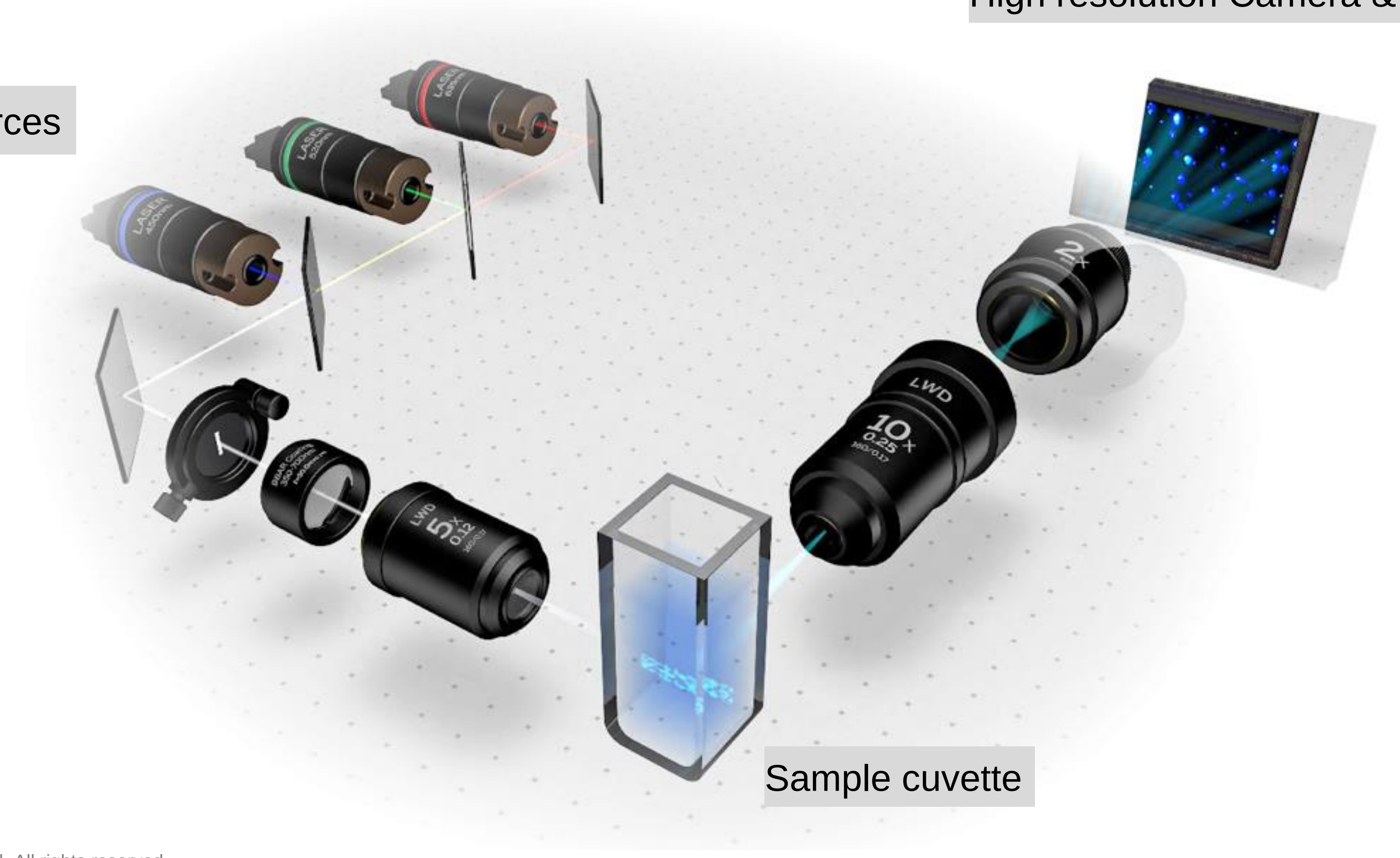
The incident beam is scattered by particles within the interrogated volume of the optical system.
Detection by scattering intensity, *Sizing* by Brownian Diffuision

Viewsizer 3000: Multispectral Nanoparticle Tracking Analysis

NTA – Nanoparticle Tracking Analysis
MANTA - Multi Spectral Nanoparticle Tracking Analysis

High resolution Camera & video capture

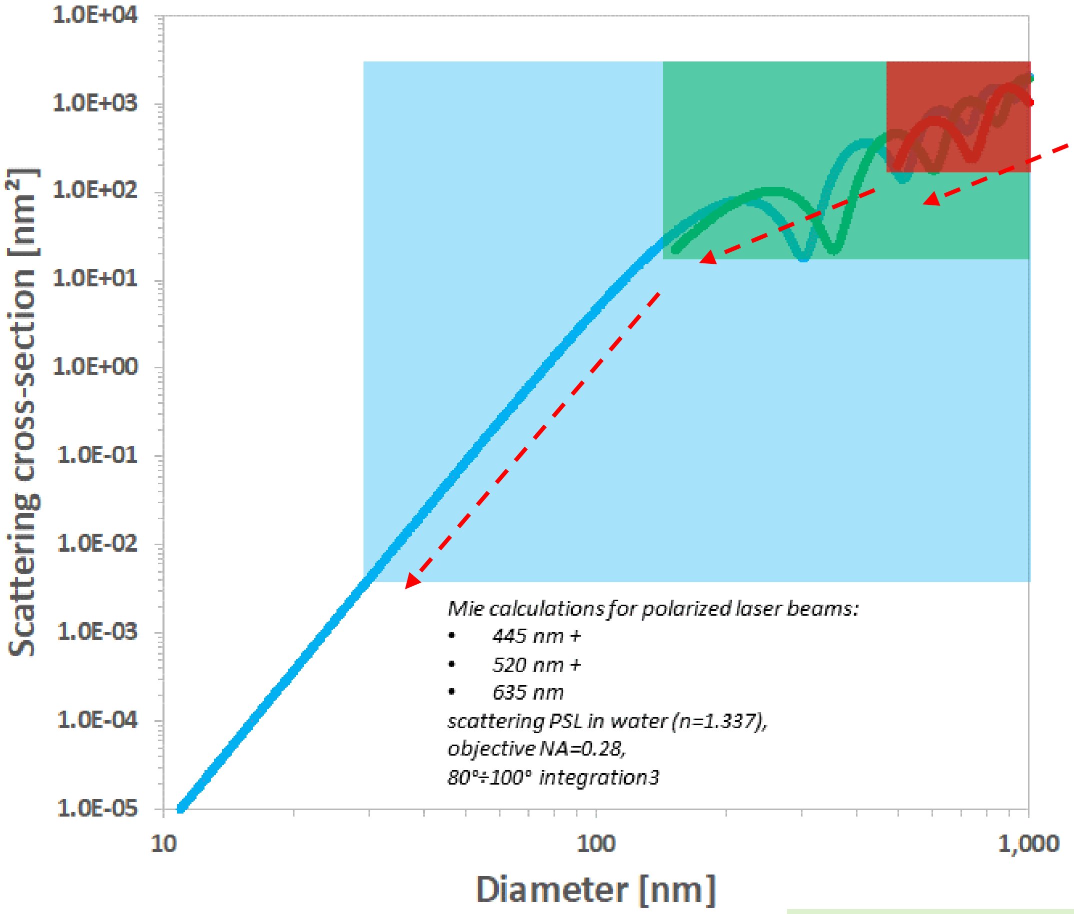
3 laser sources

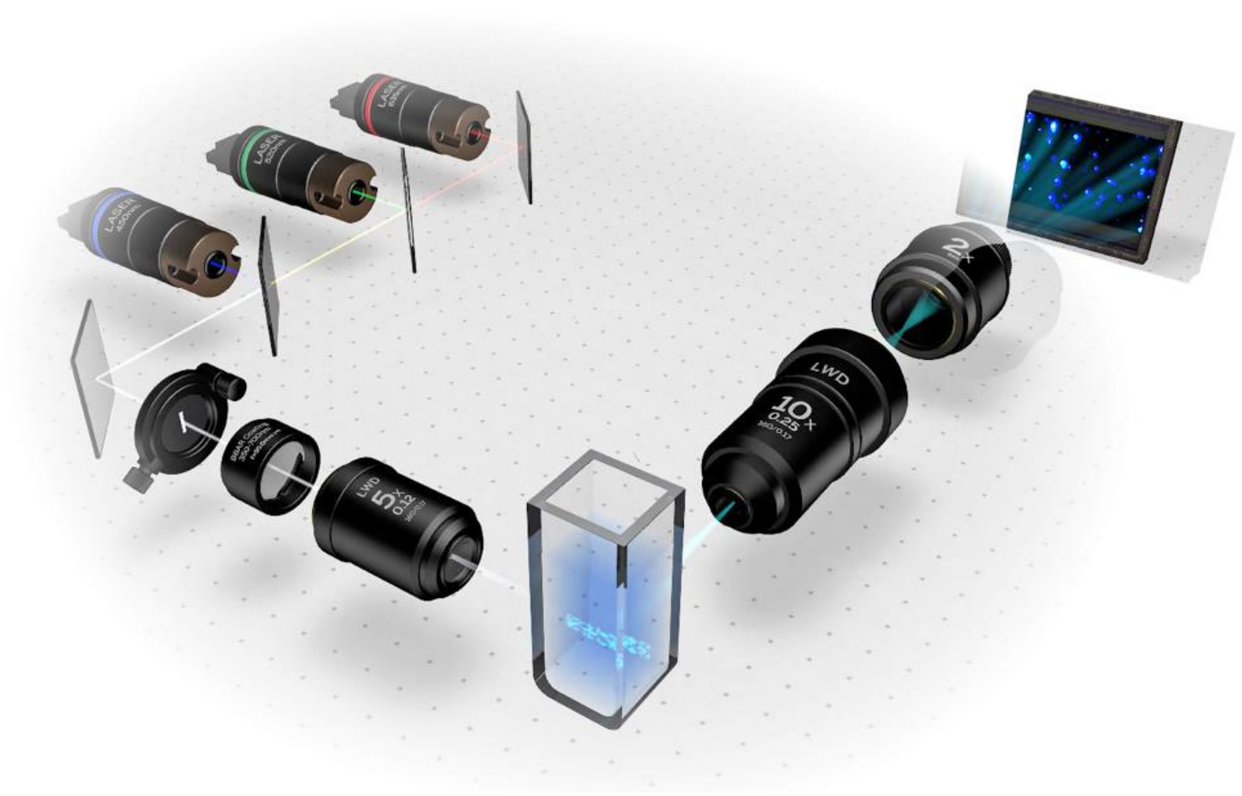


Sample cuvette

Viewsizer 3000: Multispectral Nano Particle Tracking Analysis

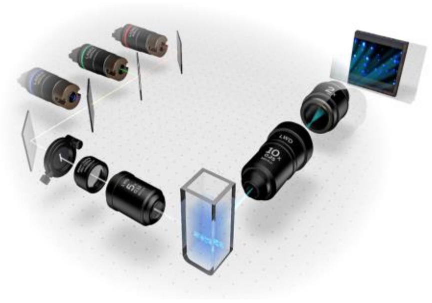
3 lasers produce a wide range of particle detection



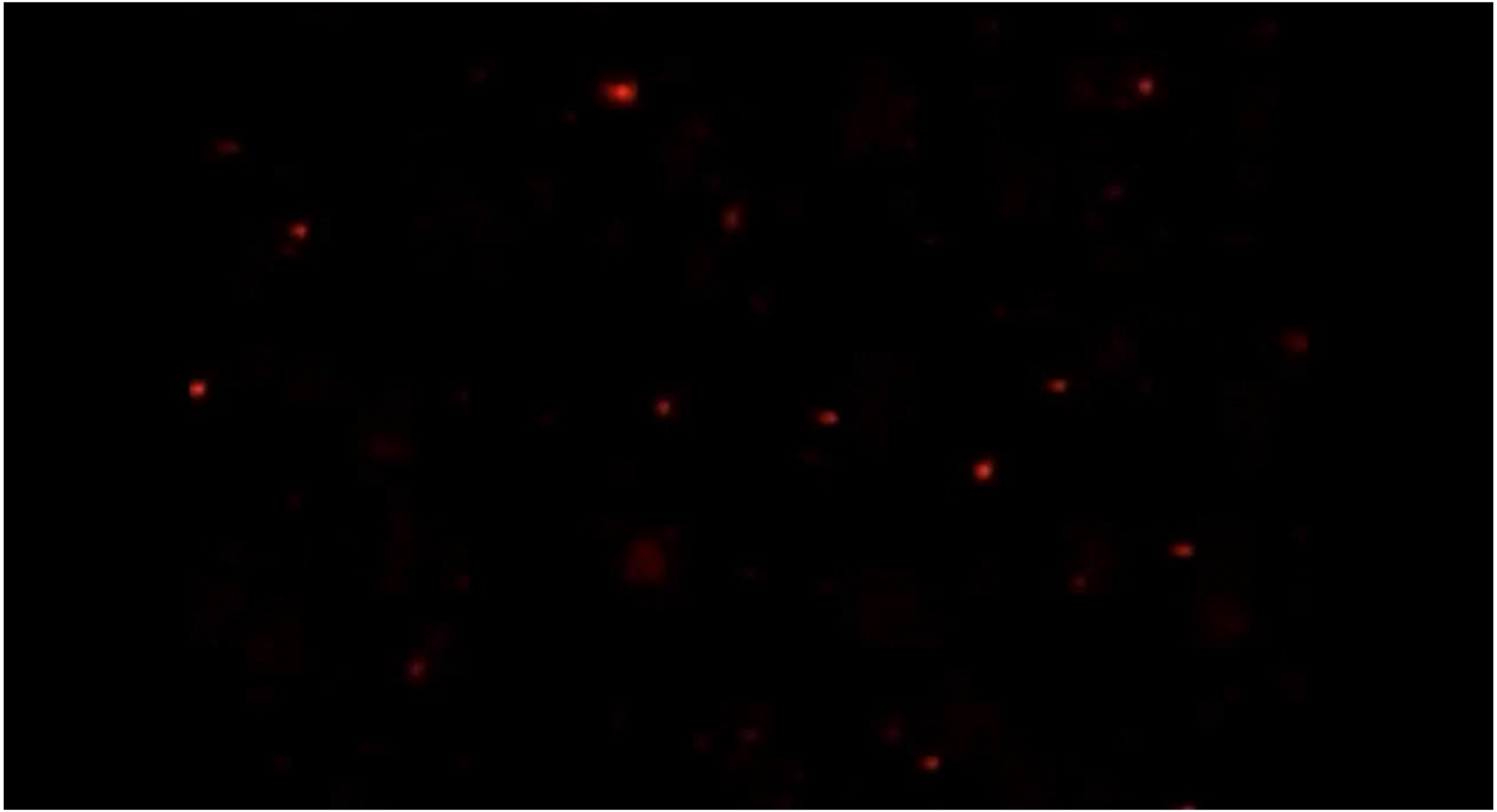


Detection by scattering intensity, *Sizing* by Brownian Motion

Viewsizer 3000 Video Capture

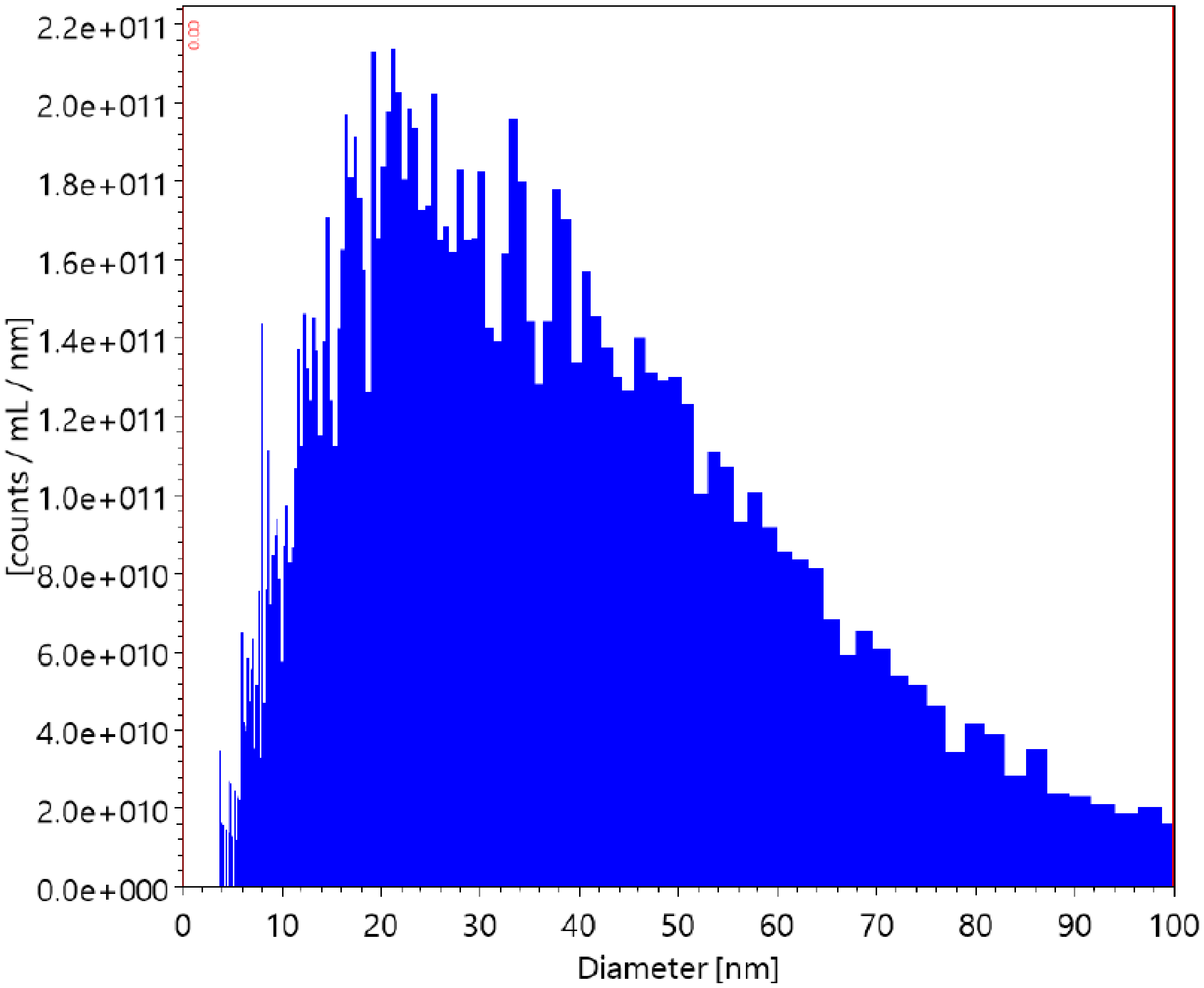


Colors added to help distinguish particle sizes



Viewsizer 3000: Multispectral Nano Particle Tracking Analysis

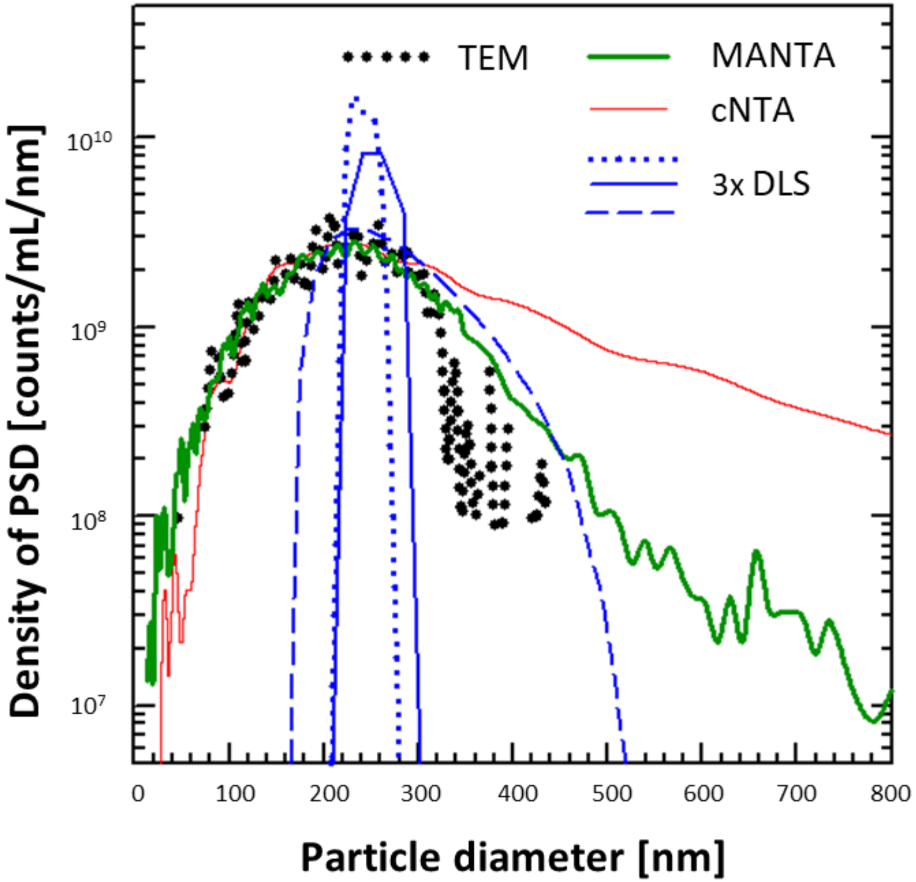
- Particles are tracked, sized, counted
- counts/ml for each definable bin

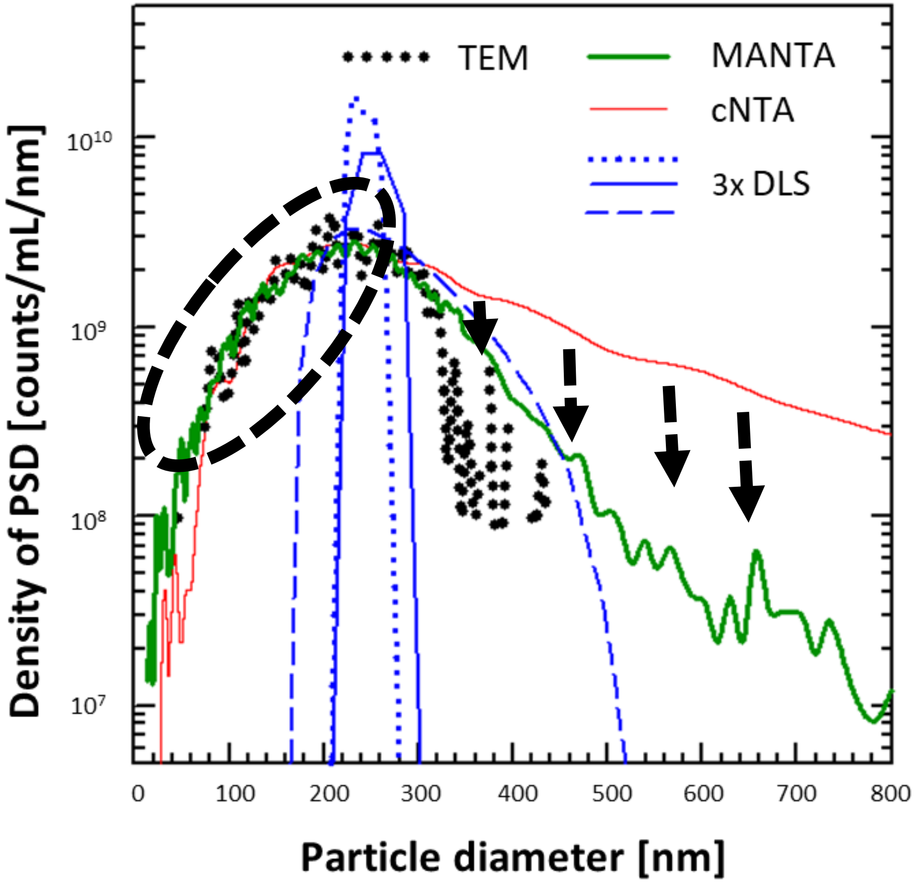


Discreet counts of a discreet volume; not estimations of a fitted curve.
More video capture → more individual counts → true PSD

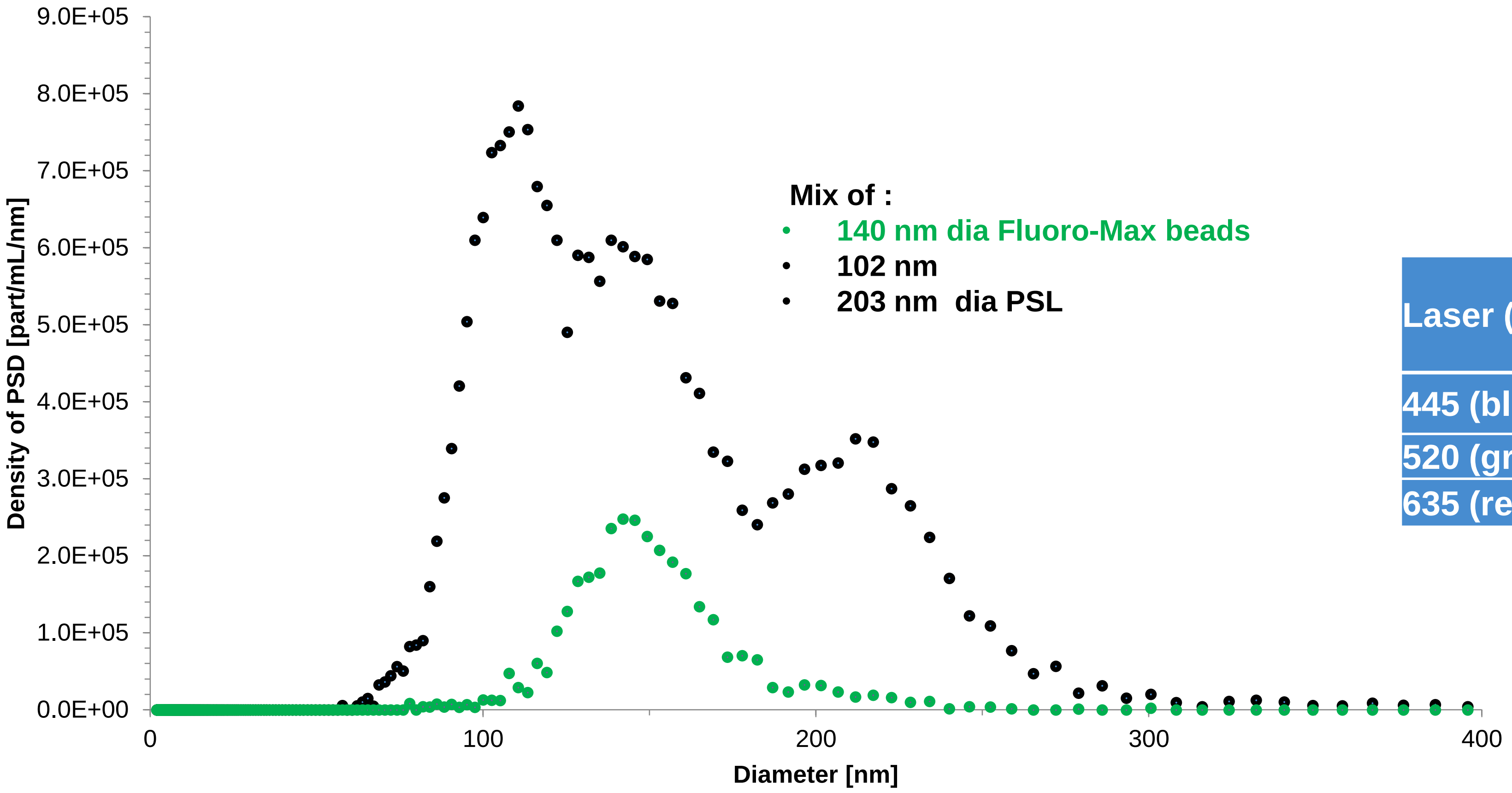
Multispectral NTA

Simultaneous illumination with 3 lasers give an accurate size through the PSD compared to similar methods; fines and coarse are measured accurately.





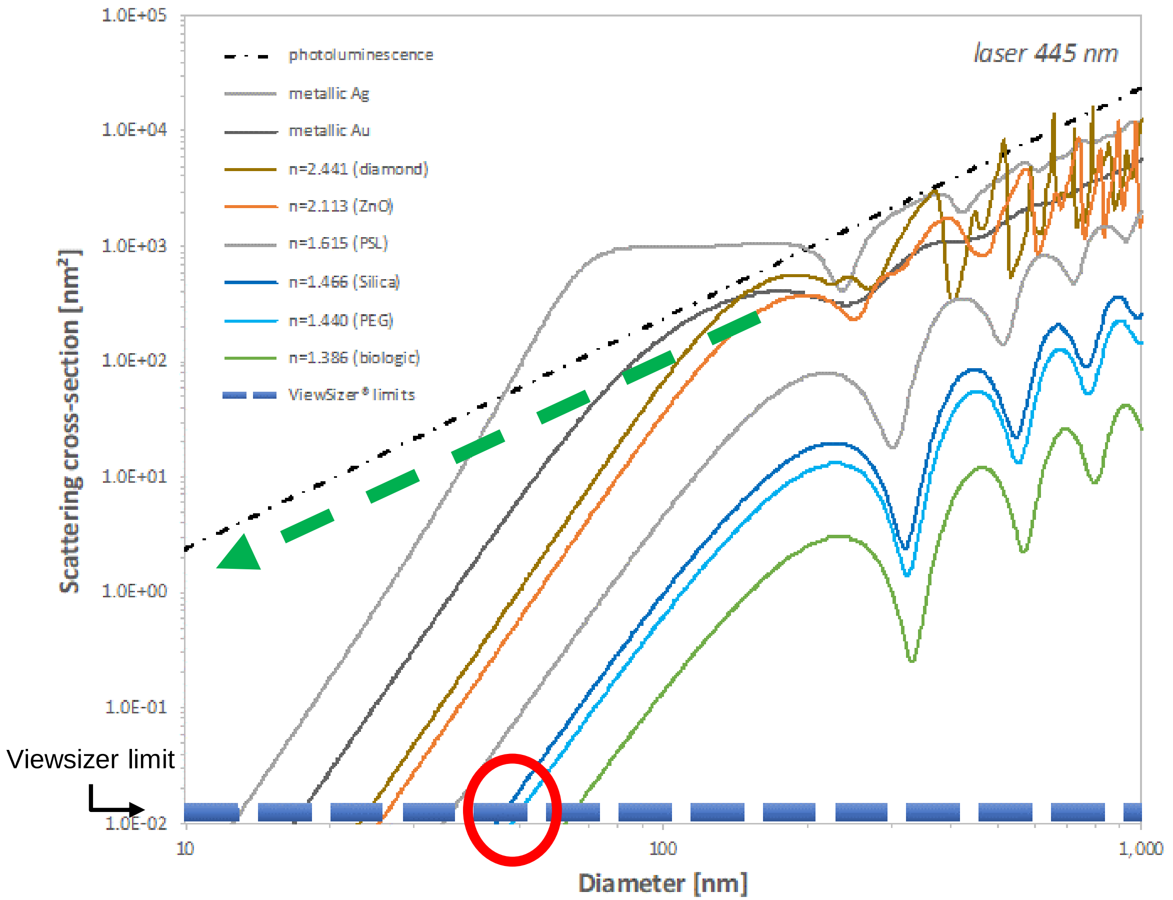
Fluorescence for Selective Tagging



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 – Scattering vs Fluorescent Emission



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

Rayleigh Scattering

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

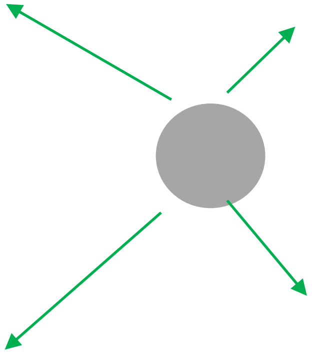
I	=	scattered intensity
Theta	=	viewing angle
R	=	viewing distance
lamda	=	wavelength of light
n	=	particle refractive index
d	=	particle diameter

Rayleigh scattering diminishes quickly ~ d^6

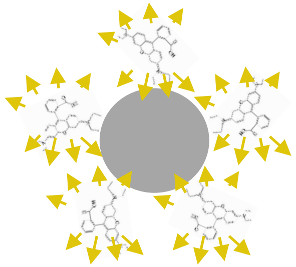
Calculated limit for detecting scatter in silica is ~ 40 nm.

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

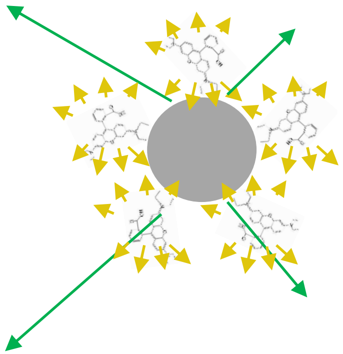
Concept for Improving Detection Limits



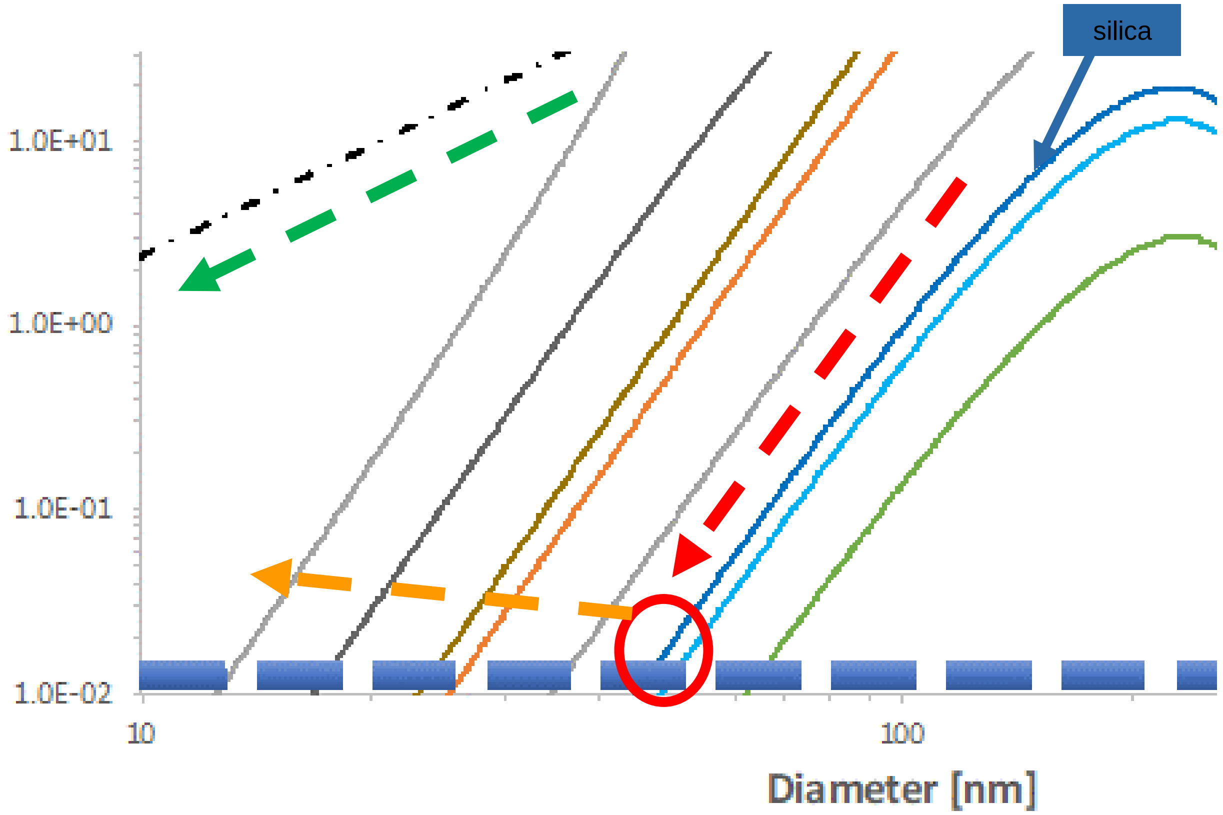
Scattered signal
Rayleigh scattering degrades ~ d^6



Fluorescent emission
Fluorescence signal degrades ~ d^2



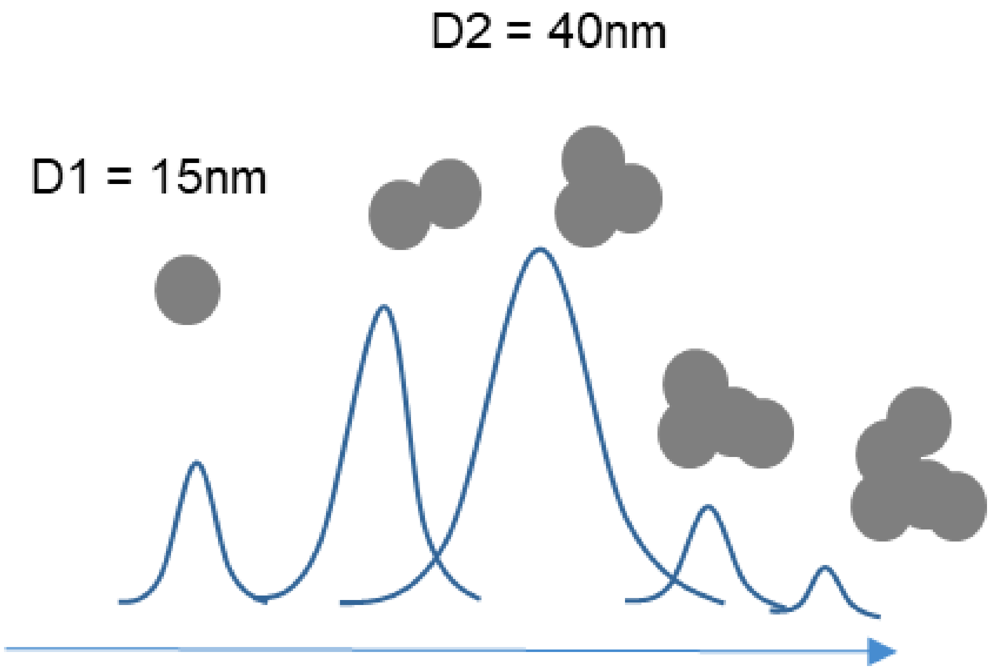
Detection may improve with added fluorescence



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

Aggregate ratio = 40nm / 15nm
=2.7



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.

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

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

- ソ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

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

Test the Concept: An Efficient Dye

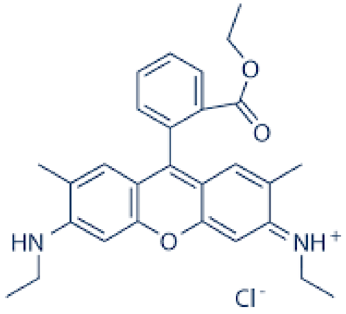
Cationic dye can interact electrostatically with the negative surface charge colloidal silica

- 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

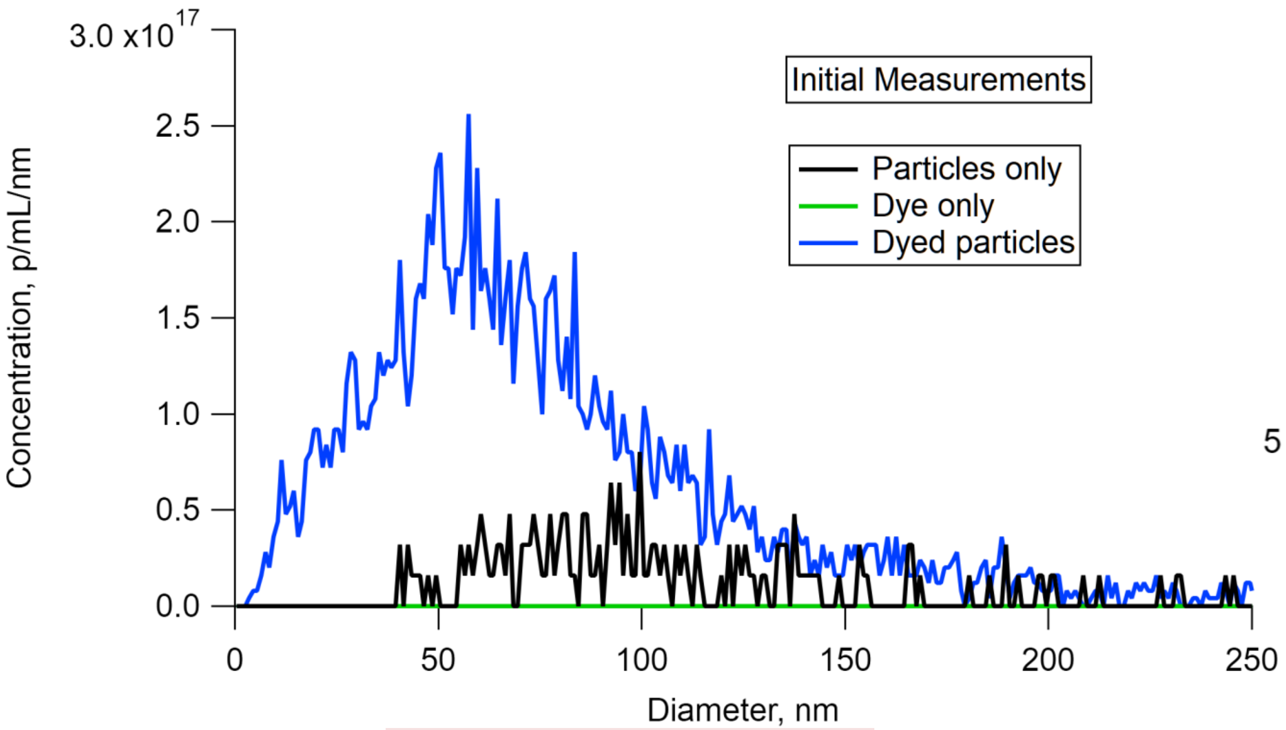
Adsorptive removal of methylene blue from aqueous solution using coal fly ash-derived mesoporous silica material *Ning Yuan*
Adsorption Science & Technology 2019, Vol. 37(3–4) 333–348



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**

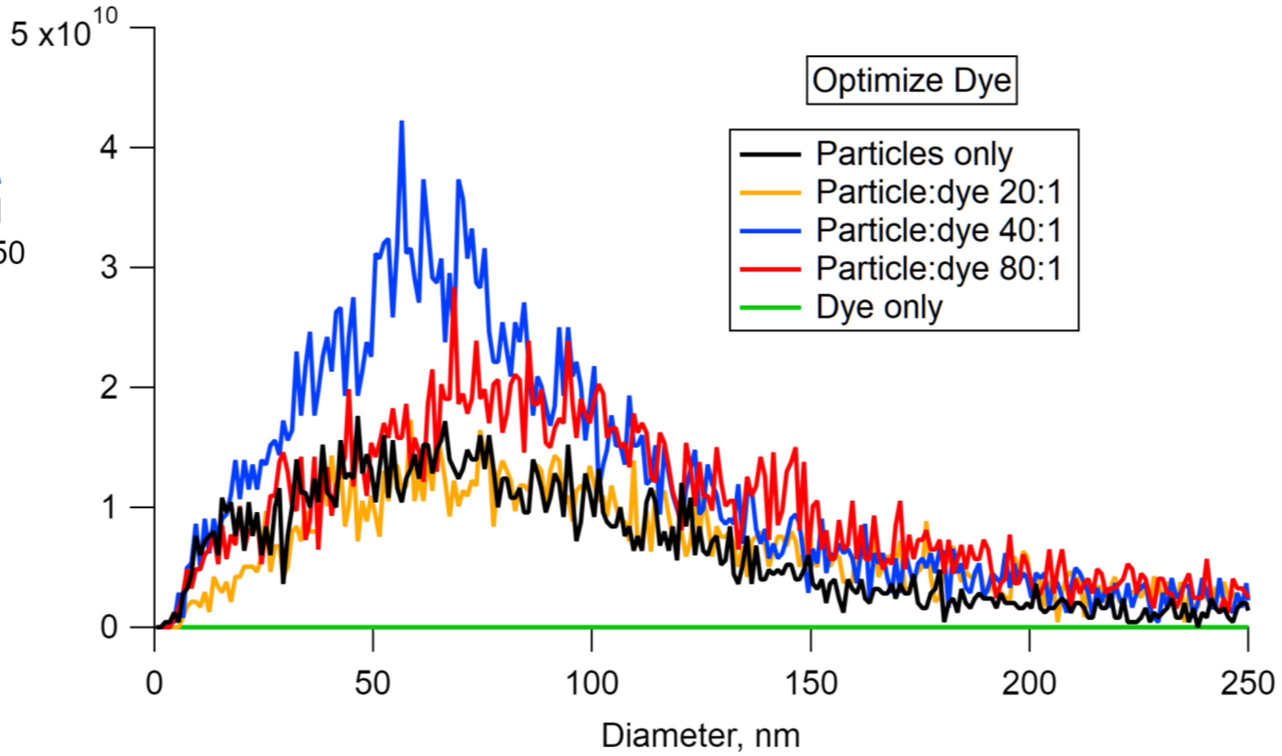
Test the Concept: Series of Experiments



Proof of concept

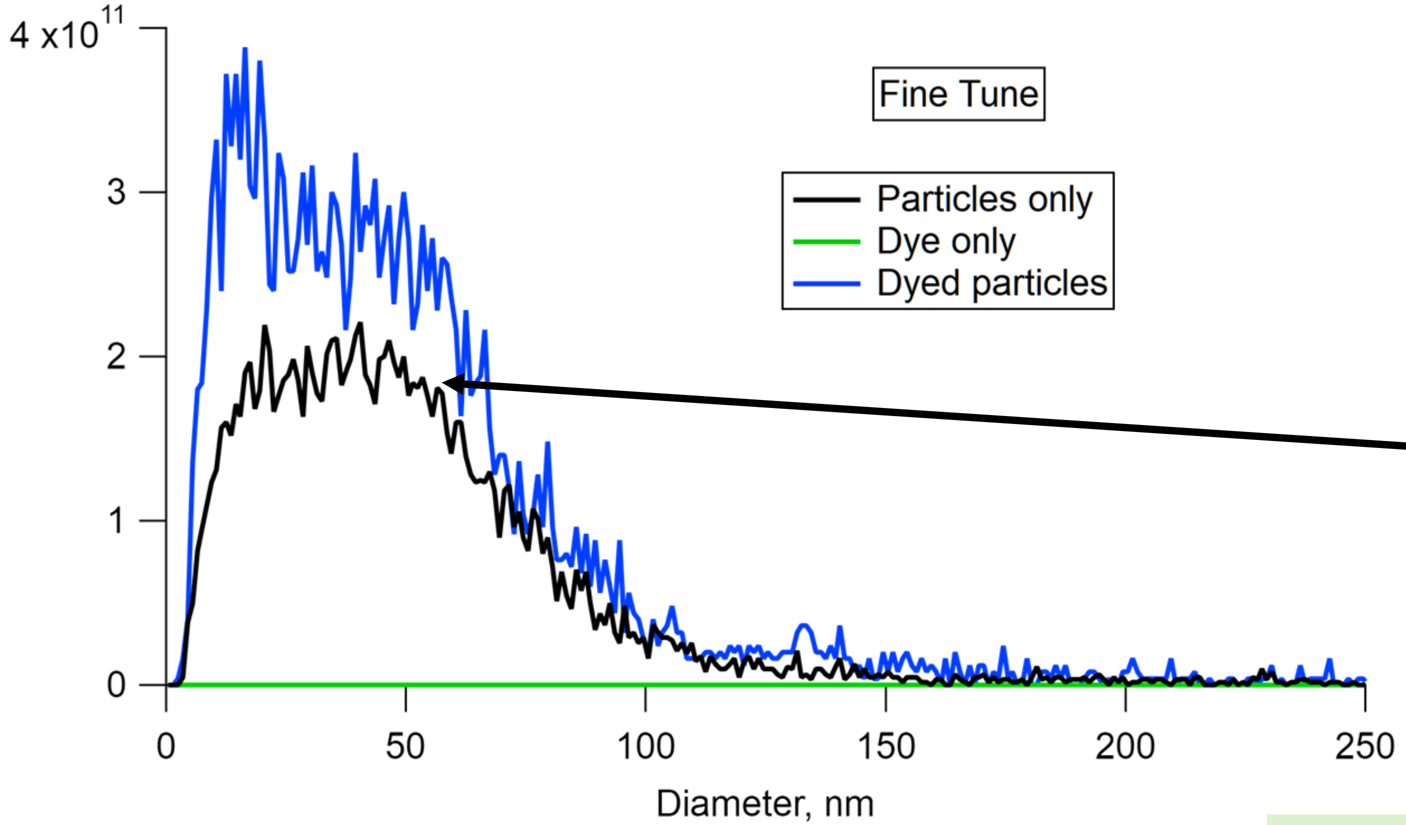
- “standard settings”
- increased counts
- detected finer particles

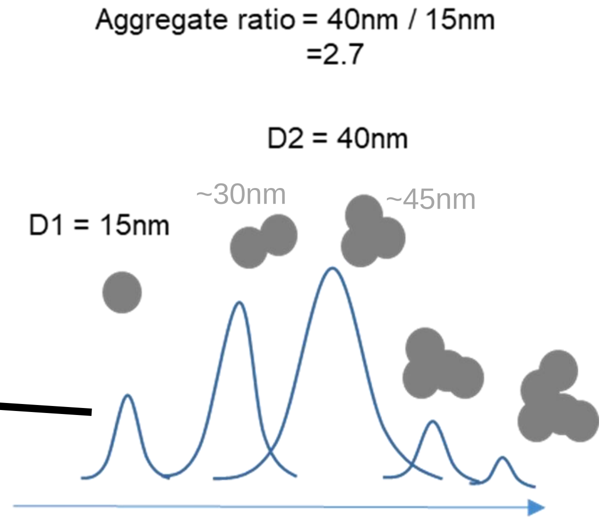
Optimized dye: silica ratio
Proportions to boost detection



HORIBA Semiconductor

Optimized Conditions

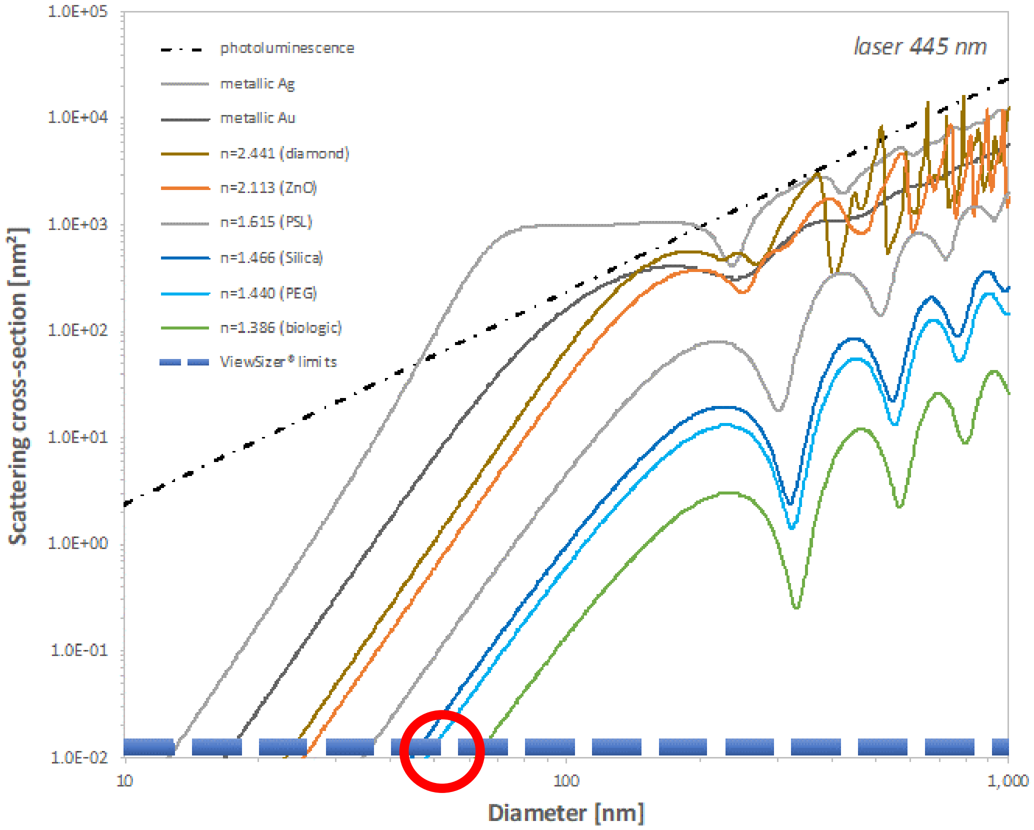




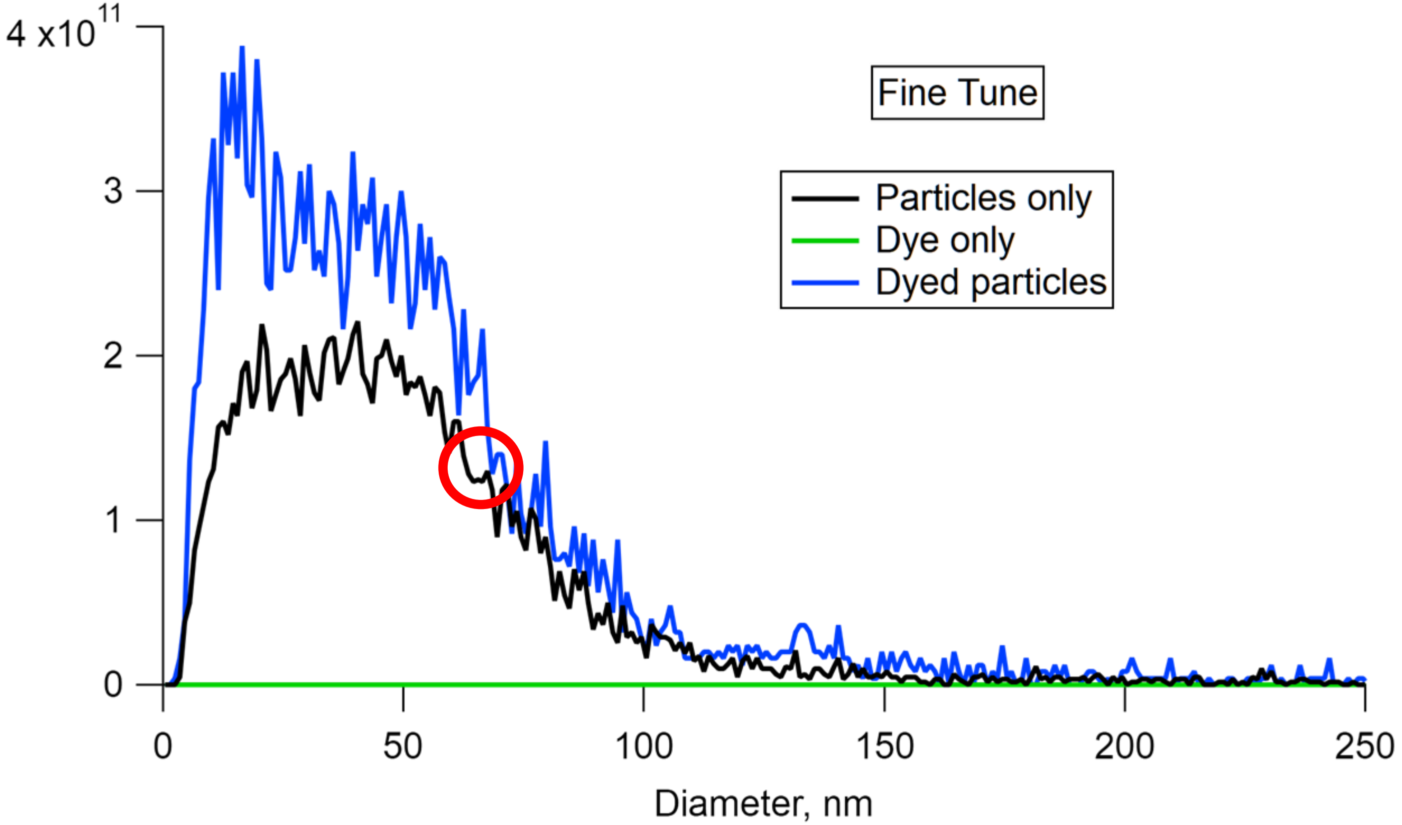
Optimizing the trends seen in the previous experiments;
- dye : silica,
- optimal dilution
- optical settings (higher gain)

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

Series of Experiments

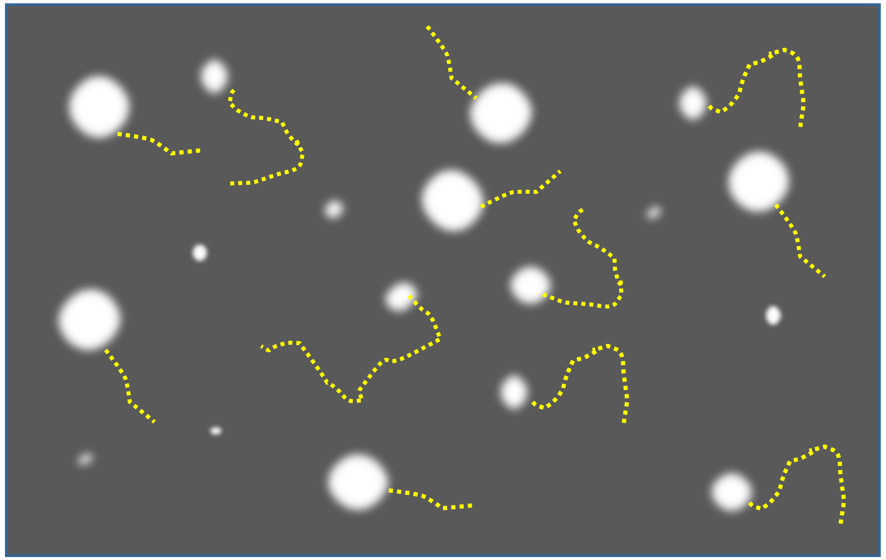


in water (n=1.337), laser 445 nm wavelength, polarized, objective NA=0.28, 80°÷100° integration

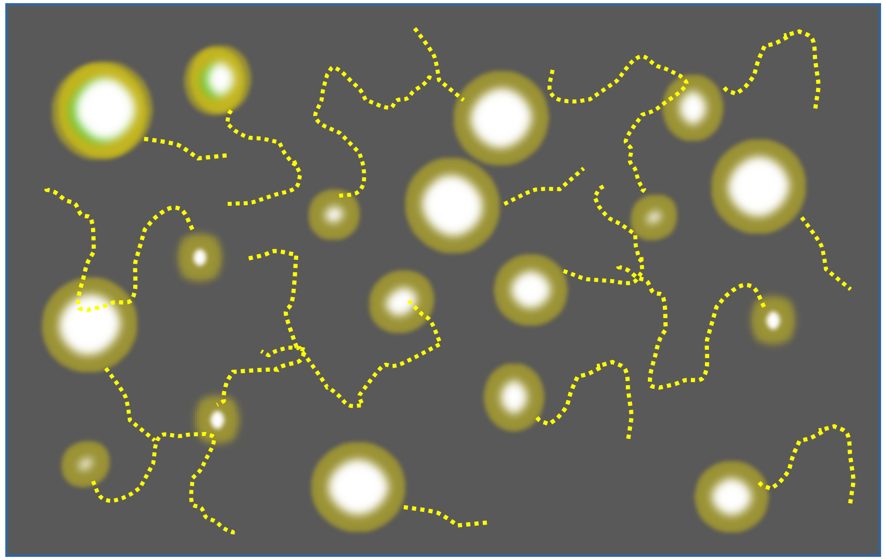


Comparing the calculated limit of scattering detection for the Viewsizer and the enhanced signal of the dyed particles,
The improved detection is pronounced at sizes smaller than ~ 65nm.

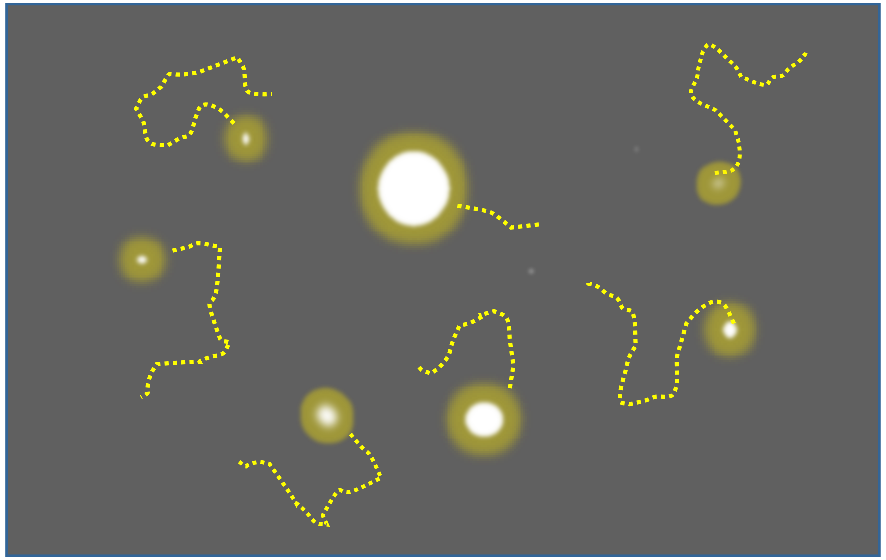
Illustration of the Experiments



Standard process
Fines poorly detected



Dyed particles increase counts
Need dilution to count all particles

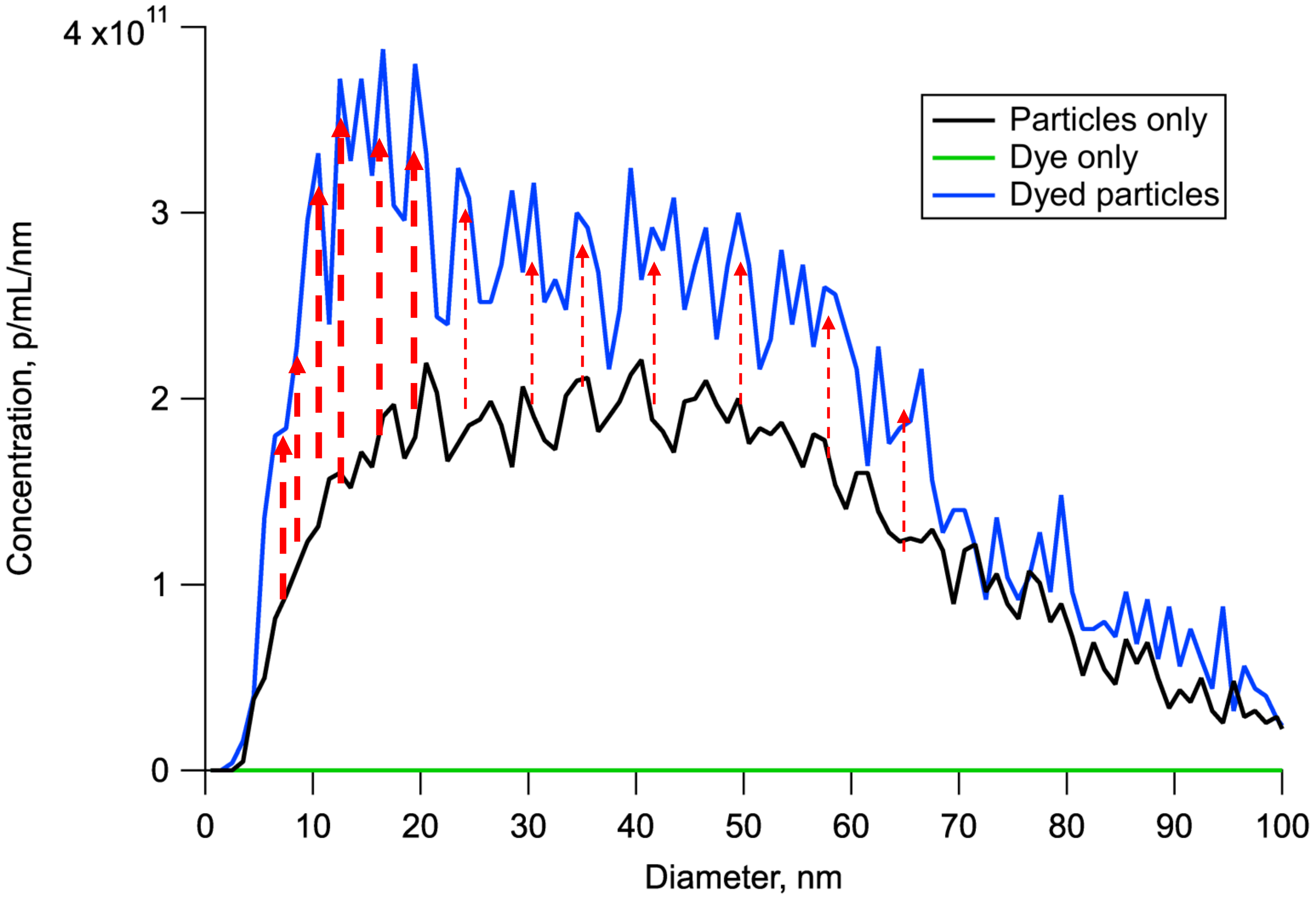


Dyed and diluted, we can optimize the optical settings to improve detection of fines

Summary of Experiments

Addition of Rhodamine 6G to Fuso PL-1:

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



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
Terima kasih
நன்றி
谢谢
Gracias
Tack ska du ha
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