Australian Government
Department of Industry, Innovation and Science
National Measurement Institute

Relative nanoparticle concentration with benchtop methods

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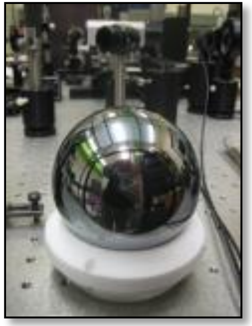
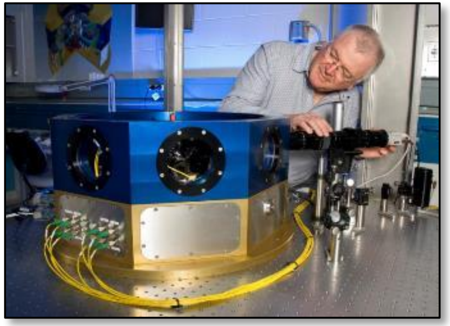
NMIA: Physical, Chemical, Biological and Legal Measurements



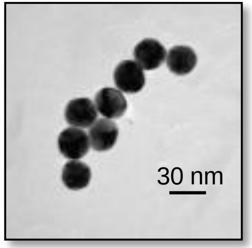










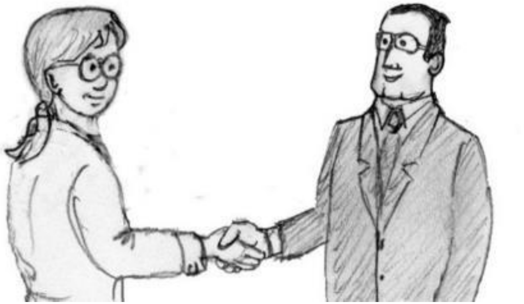



Overview

- A few words of motivation
- Not all y-axis are equal
- Estimating concentration
  - EXDLS
- A more quantitative approach to concentration
  - DCS, PTA and RMM vs ICP-MS
- Questions

Where measurements are important

Product Development



Trade

Quality Control

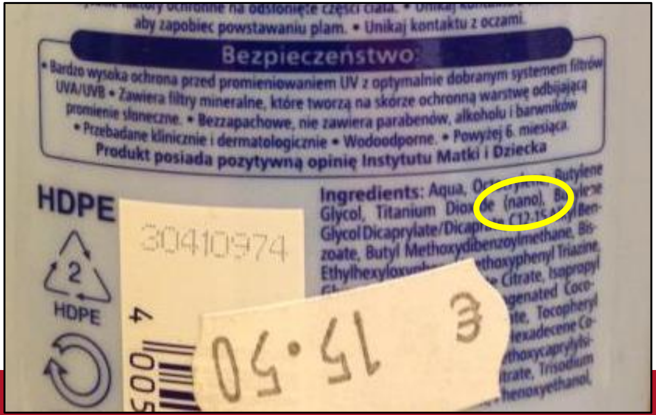
Safety and Informed choice

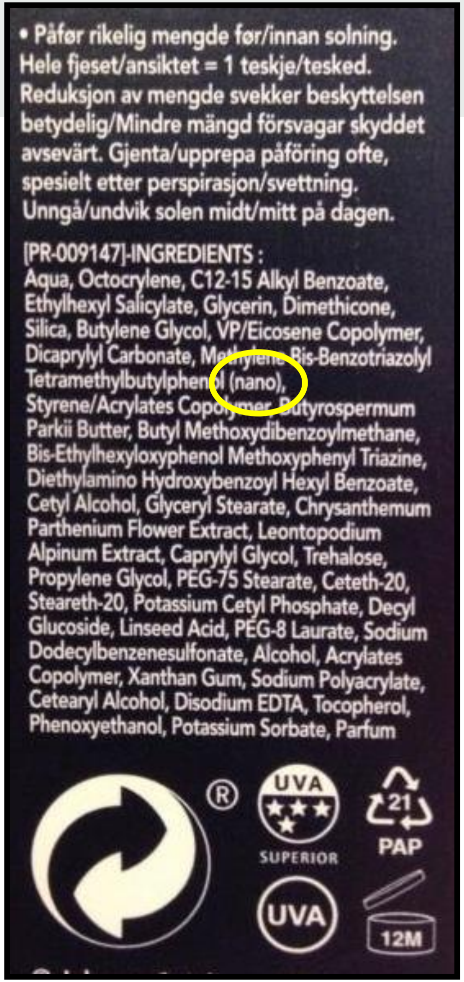
Where measurements are important

Absolute size distributions - quantification of the y-axis

Important for:

- applying the definition of a nanomaterial
- understanding experiments/systems (e.g. dose, activity/response)
- understanding the results delivered by particle characterisation instrumentation





Nanoscale – a regulatory definition

Australian Government
Department of Health
National Industrial Chemicals
Notification and Assessment Scheme

NICNAS working definition for 'industrial nanomaterial'

At present, there is no interna
for regulatory purposes. This

The NICNAS working definitio

*"...industrial materials intentio
composition at the nanoscale,
that is confined in one, two, o
surface structure at the nanos*

*nally produced, manufactured or engineered to have unique p
that is a size range typically between 1 nm and 100 nm, and
r three dimensions at the nanoscale) or is nanostructured (i.e.
cale)"*

Notes to the working definitio

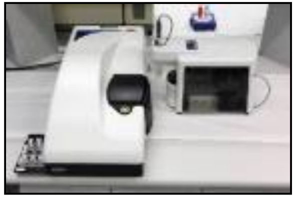
- intentionally produced, manufactured or engineered materials are distinct from accidentally produced materials
- 'unique properties' refe
nanoscale features whe
phenomena (e.g. increa
- aggregates and agglom
- where a material incluc
properties, intentionally produced) NICNAS will consider this to be a nanomaterial.

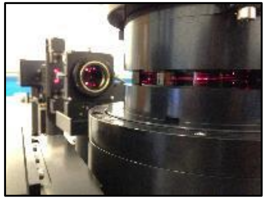
material includes 10% or more number of particles that meet
es, intentionally produced) NICNAS will consider this to be a n

NMIA Nanometrology capabilities

Dimensional properties (‘size’)

Light scattering

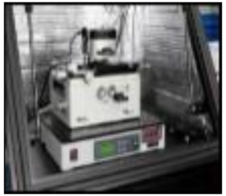


Separation techniques



Microscopy

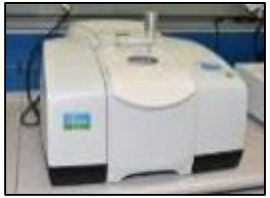



Other

Other physical and chemical properties

Surface area & porosity


Chemical identity

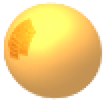


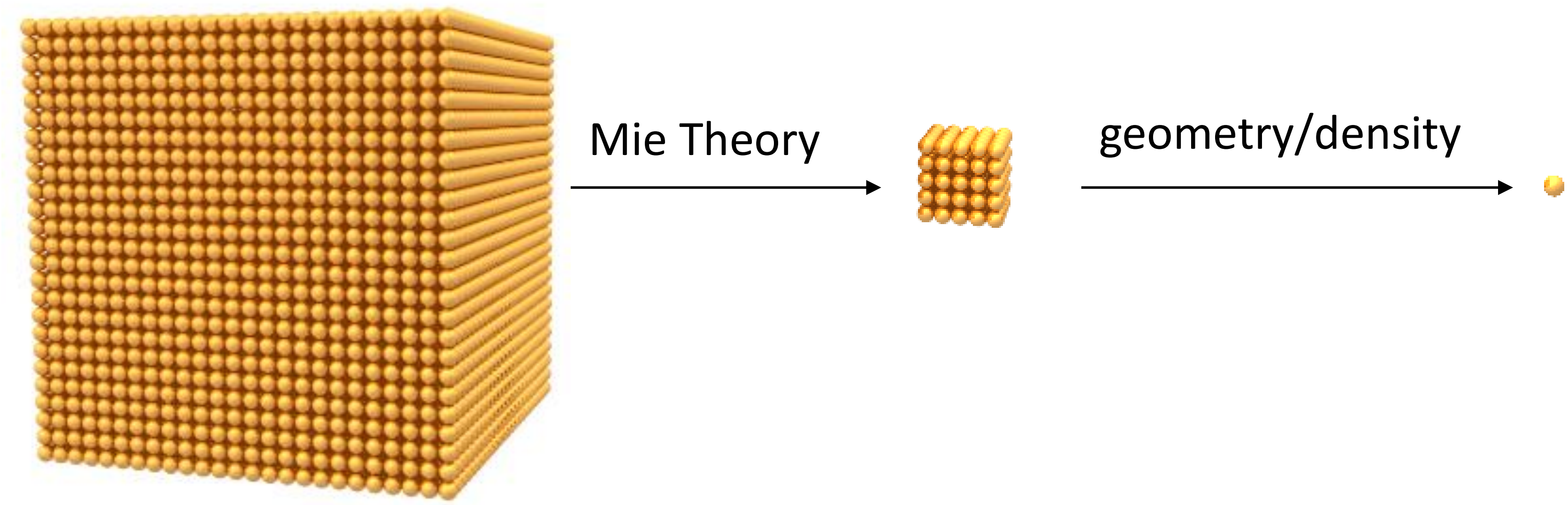

Mass/density

Surface charge


Not all sizing instruments are created equal

Consider 100 nm and 20 nm particles:





Equal light scattering intensity ($I \sim x^6$)
15625 : 1

Equal volume/mass (x^3)
125: 1

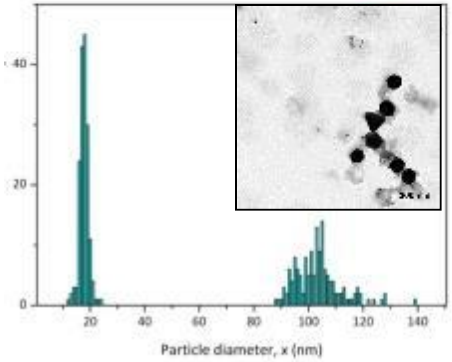
Equal number
1: 1

$x = 100 \div 20 = 5$

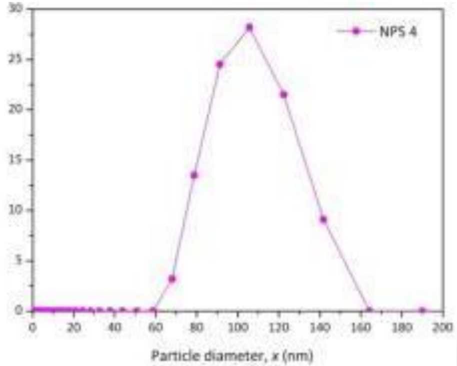
Equal number vs equal intensity: two extremes

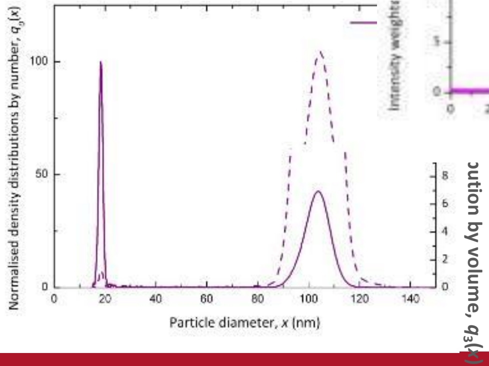
Equal number
1 : 1

TEM



DLS

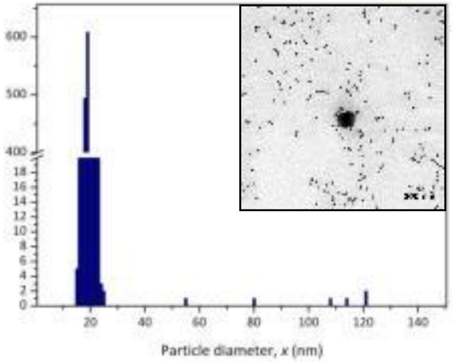




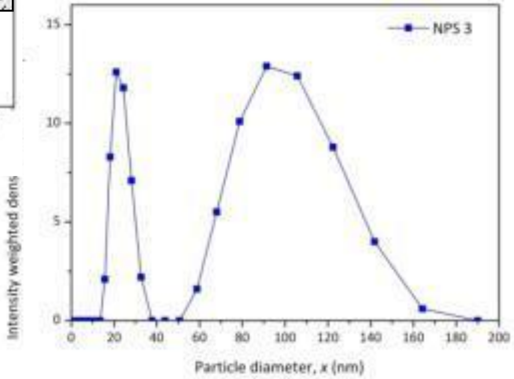
DCS

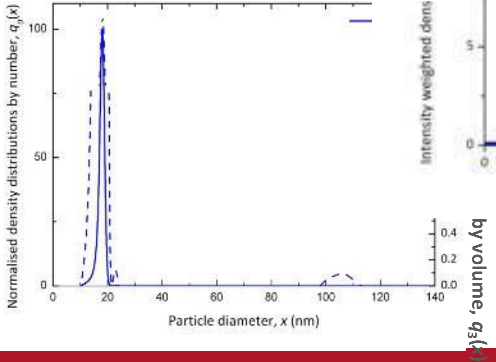
Equal light scattering intensity (I~x^6)
15625 : 1

TEM



DLS

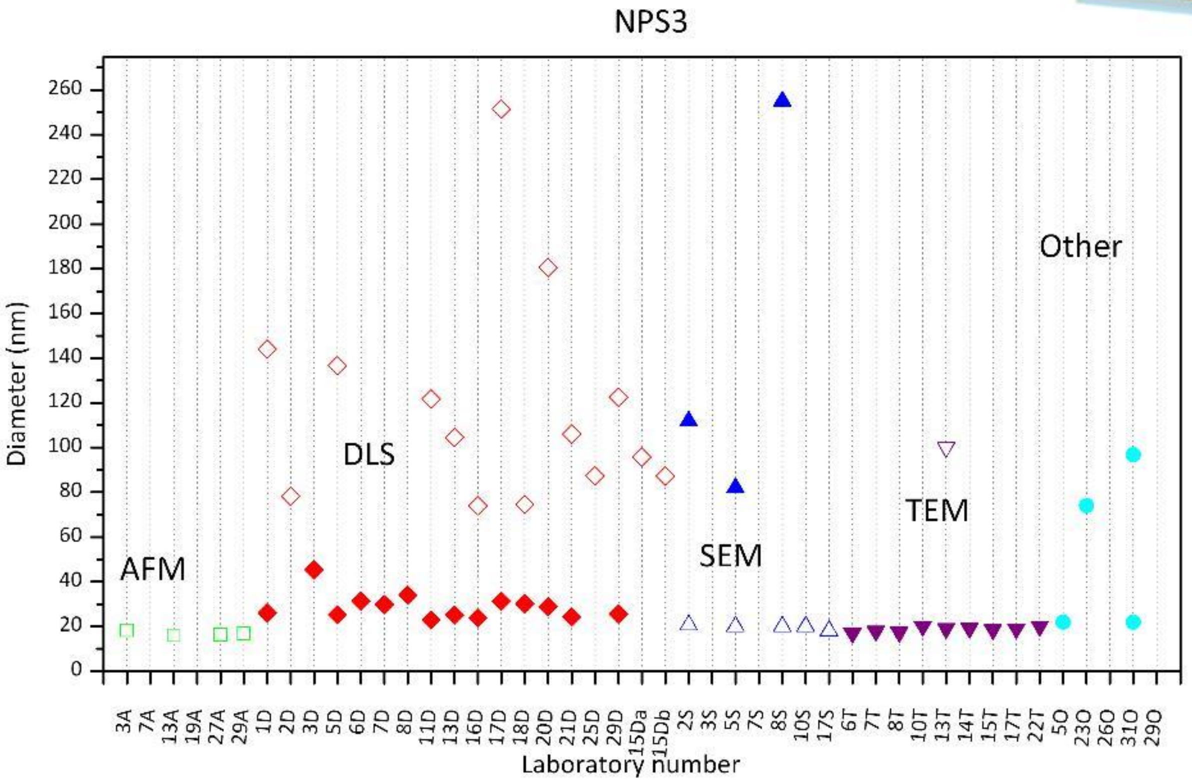




DCS

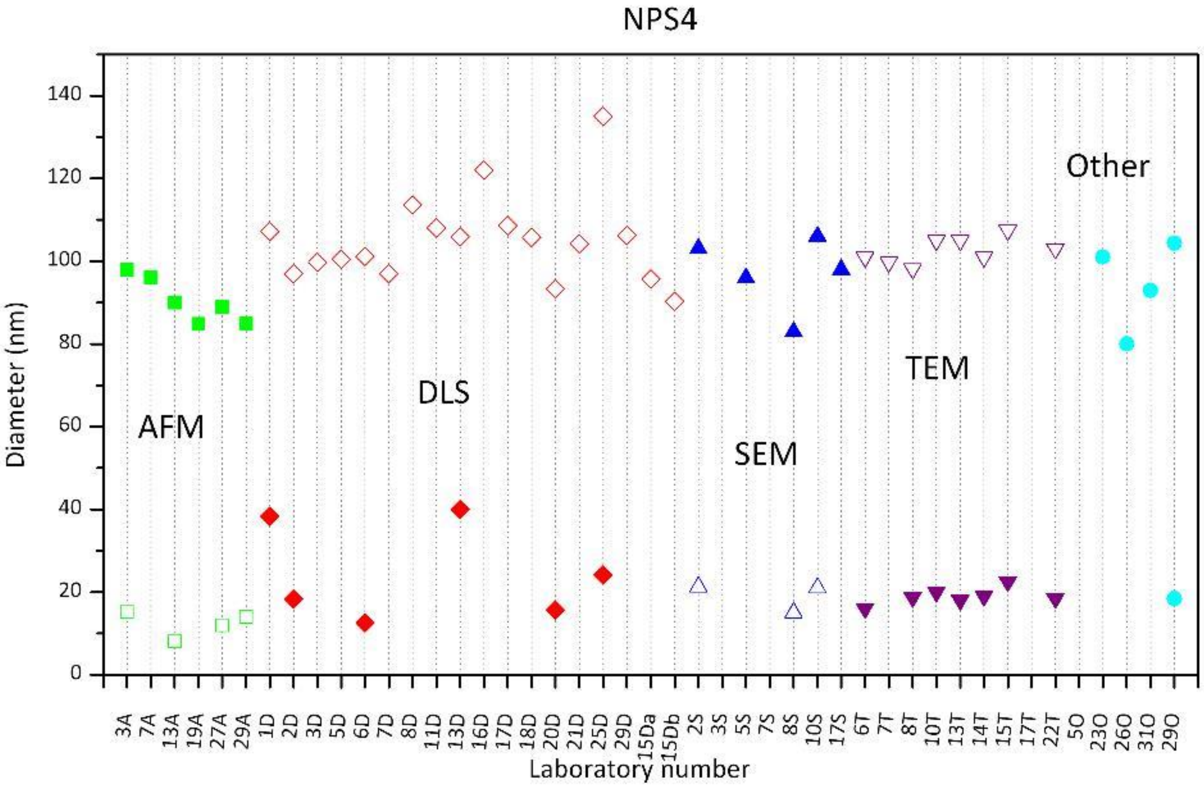
Equal light scattering intensity

Australian nanoparticle intercomparison 2012

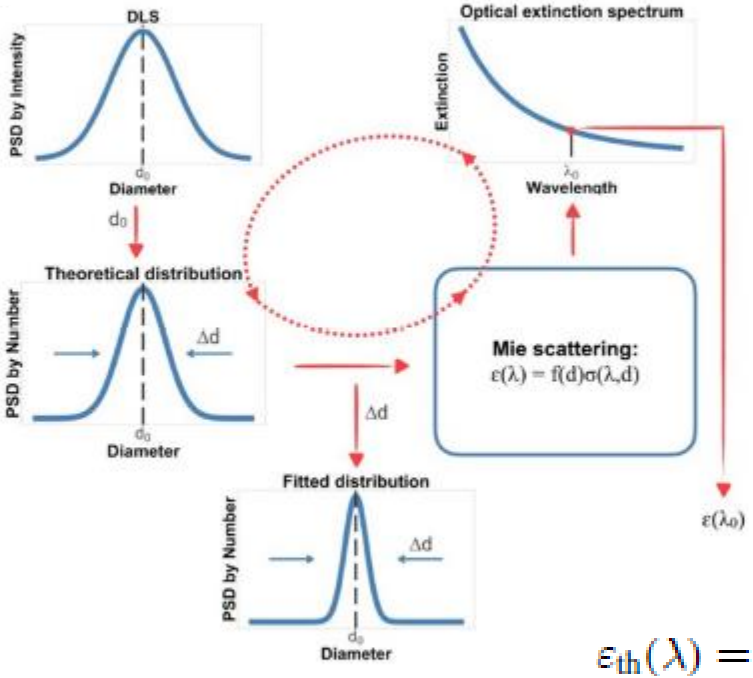


Equal number

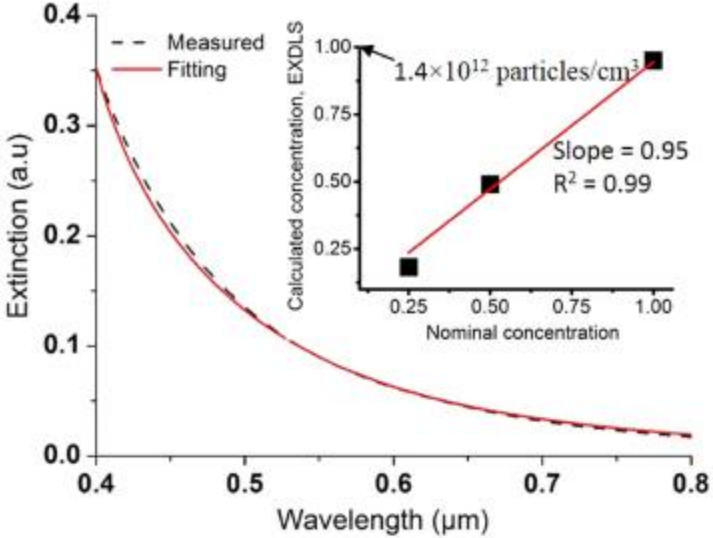
Australian nanoparticle intercomparison 2012



Estimating concentration from extinction and PSD

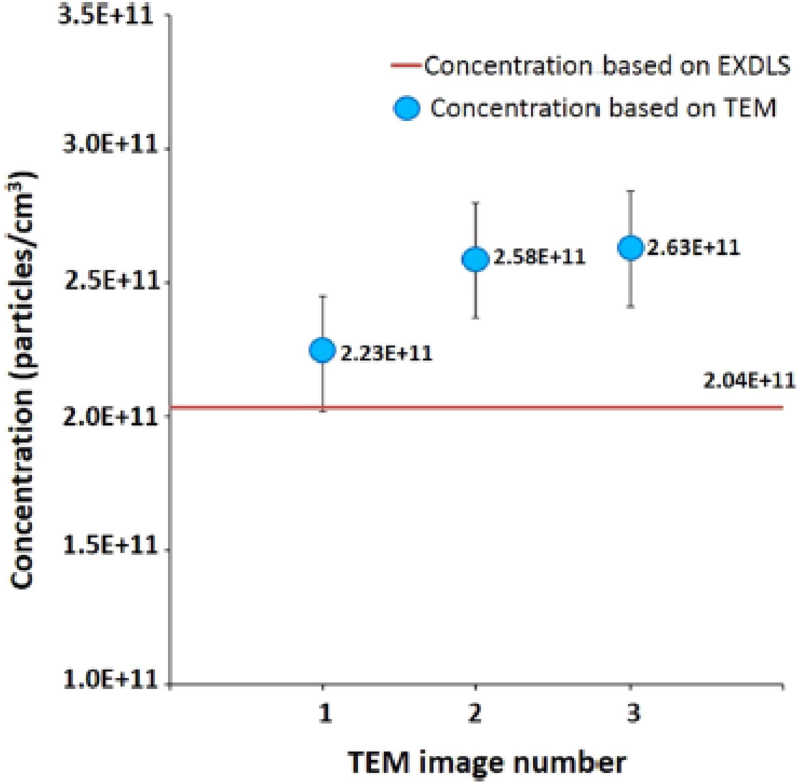


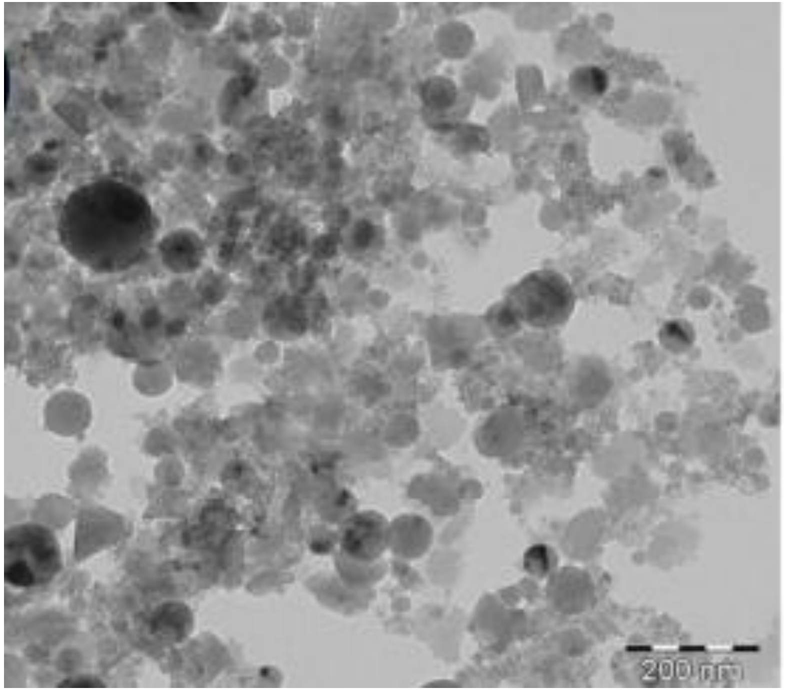
90 nm PSL



$$\varepsilon_{\mathrm{th}}(\lambda) = C_s \sum_d \sigma(\lambda,\ d) f_\mu(d)$$

Estimating concentration – complex samples





Nano rubies

Can we quantify the y-axis directly?

BBI Solutions citrate capped gold nanoparticles – 60 and 100 nm, dilution series of the above with MilliQ water (dilution factors obtained gravimetrically)

Mass concentrations measured by ICP-MS.

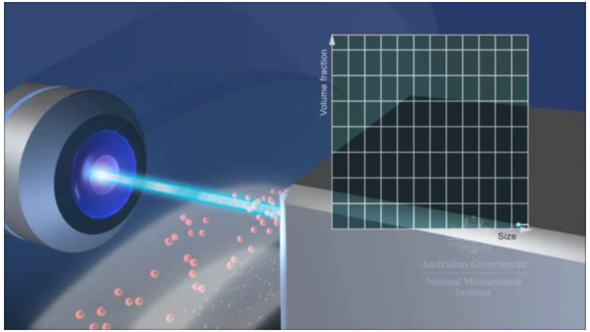
Centrifuged supernatant samples also checked to ensure that the Au mass in the sample was in particles.

Sample	Mass concentration* (µg/L)
BBI-Au 100nm	52100
BBI-Au 60nm	55100
BBI-Au 100nm centrifuged	<5
BBI-Au 60nm centrifuged	290

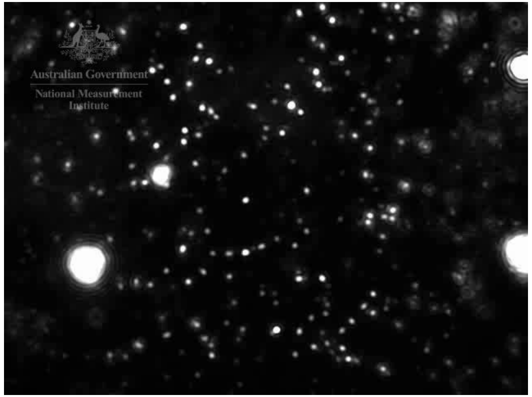
*Values accurate to within 10%

Measure the reference with other techniques

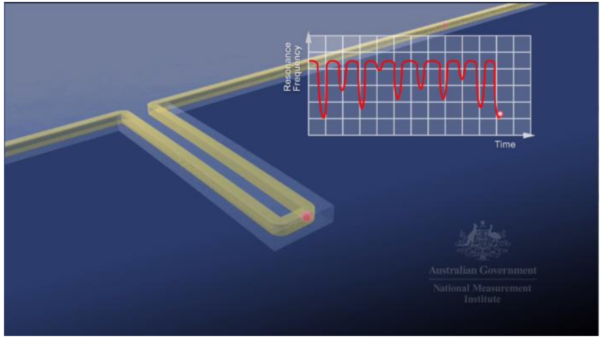
DCS



PTA



RMM



Light absorption (Intensity) – convert to mass and number

Volume
Optical properties

Ensemble Measurement

Number of particles in scattering volume

Scattering volume
(Optical properties)

Single particle

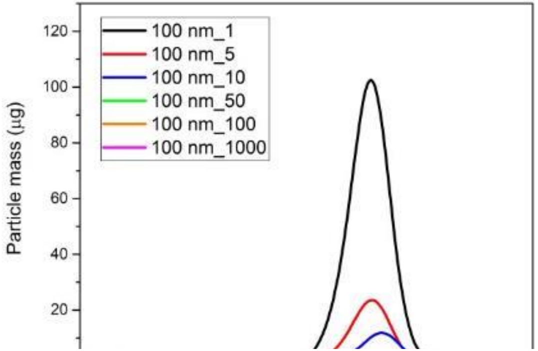
Mass and number of particles flowing through a sensor

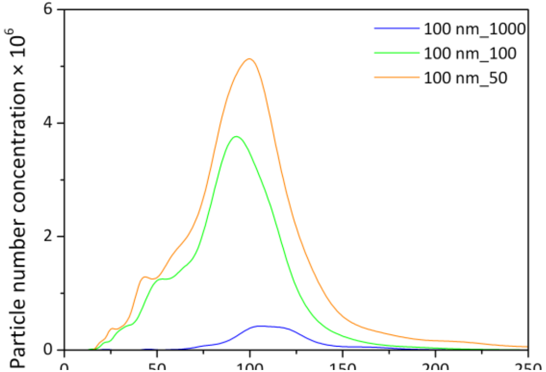
Flow rate
(Density)

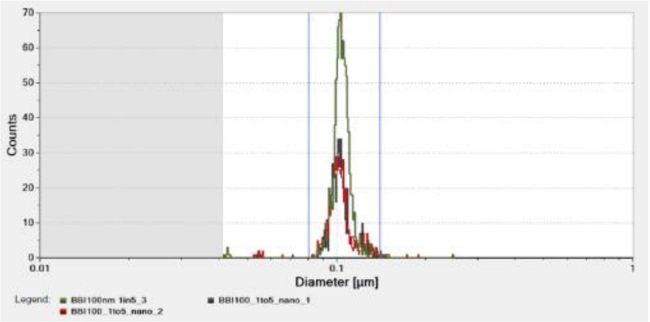
Single particle

Measure the reference with other techniques

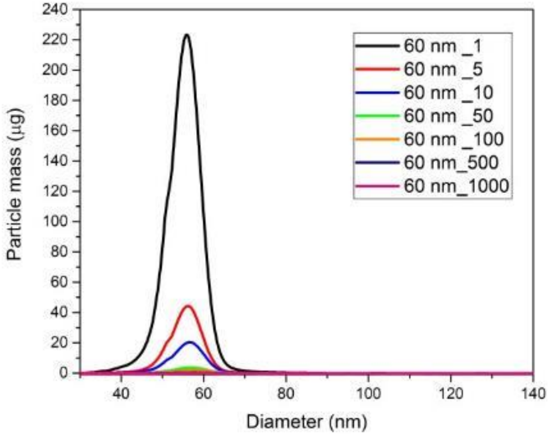
100 nm **DCS** **PTA** **RMM**

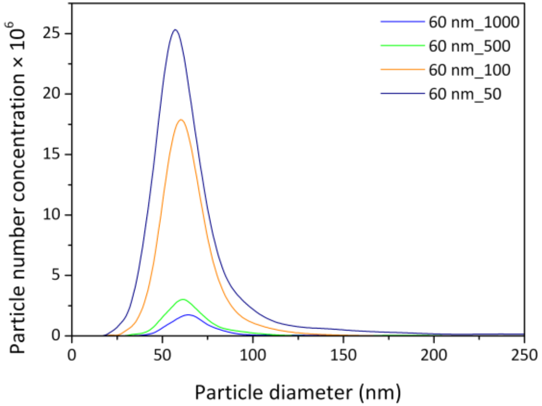


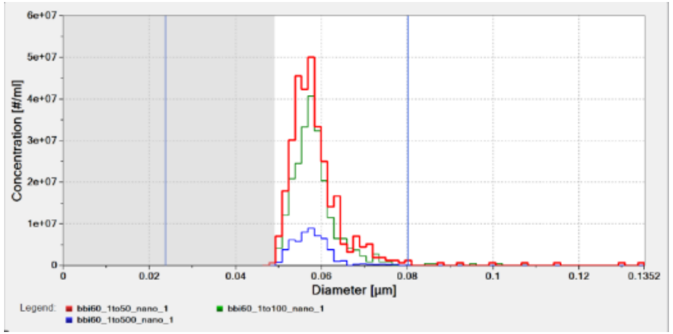




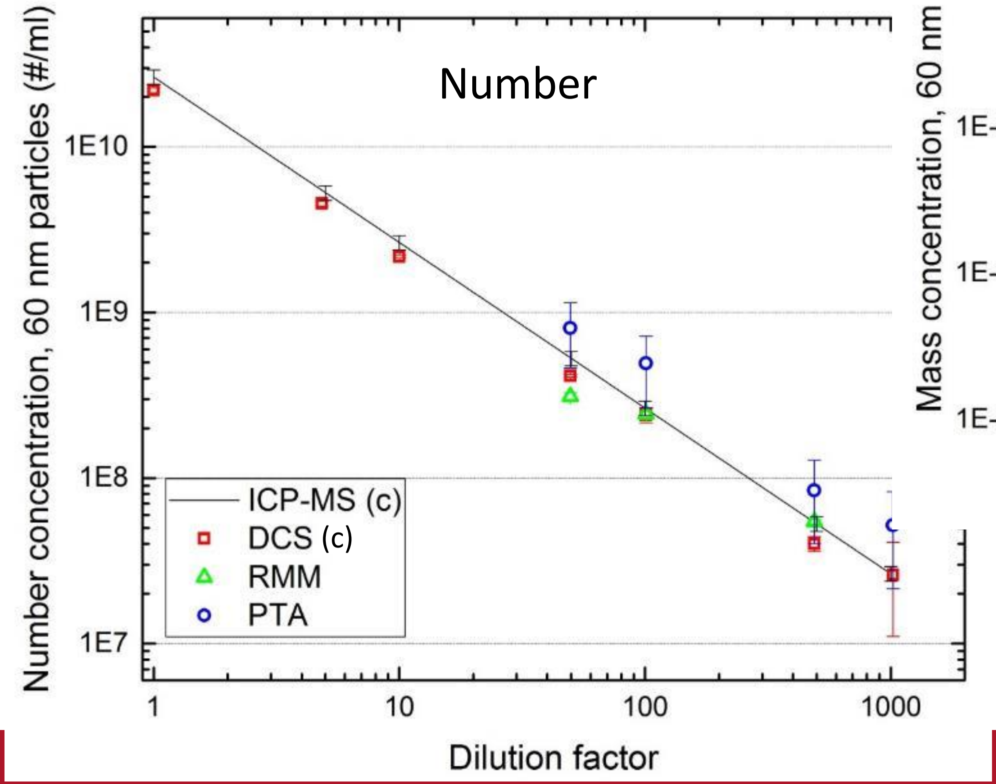
60 nm

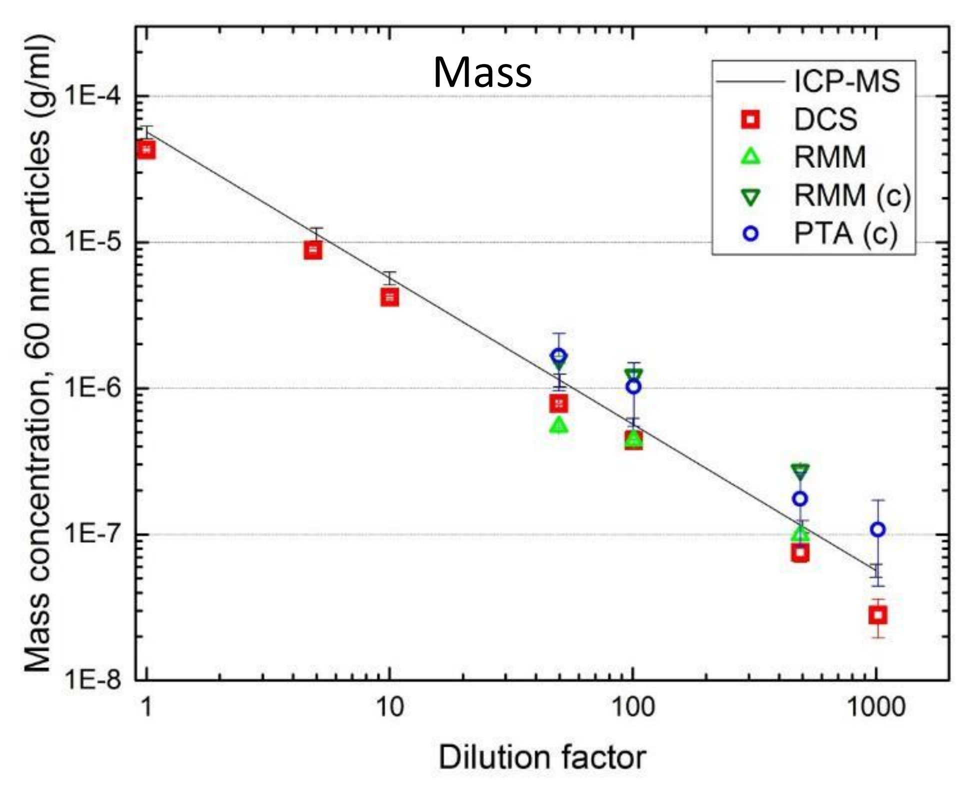




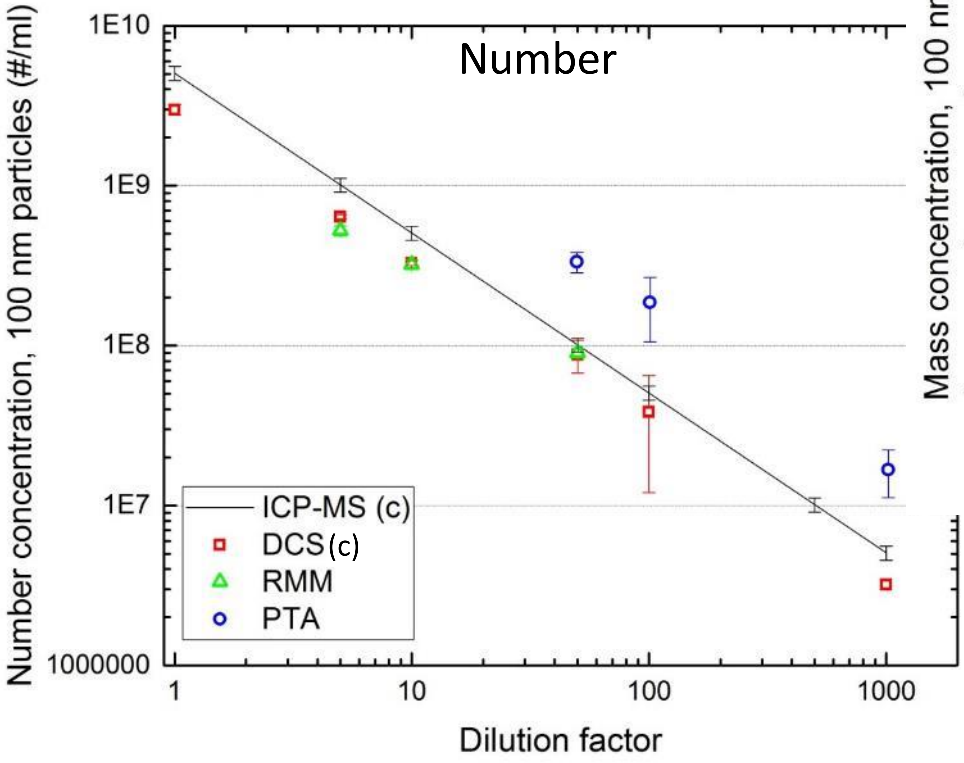


60 nm

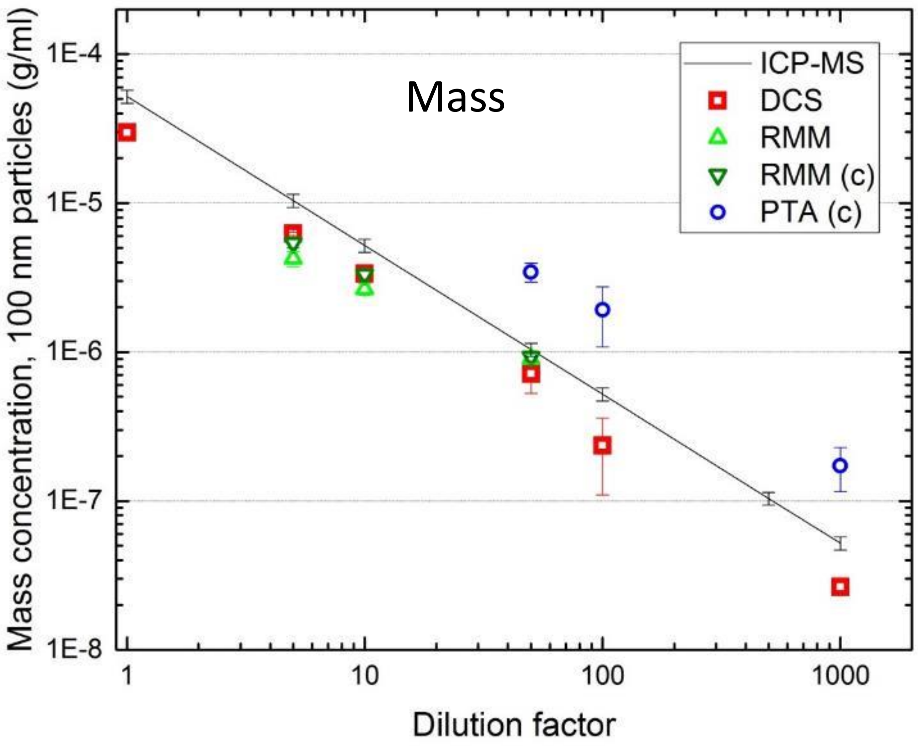

Number
Number concentration, 60 nm particles (#/ml)
1E10
1E9
1E8
1E7
ICP-MS (c)
DCS (c)
RMM
PTA
1
10
100
1000
Dilution factor


Mass
Mass concentration, 60 nm particles (g/ml)
1E-4
1E-5
1E-6
1E-7
1E-8
ICP-MS
DCS
RMM
RMM (c)
PTA (c)
1
10
100
1000
Dilution factor

100 nm



Number
Number concentration, 100 nm particles (#/ml)
1E10
1E9
1E8
1E7
1000000
1
10
100
1000
Dilution factor
ICP-MS (c)
DCS (c)
RMM
PTA



Mass
Mass concentration, 100 nm particles (g/ml)
1E-4
1E-5
1E-6
1E-7
1E-8
1
10
100
1000
Dilution factor
ICP-MS
DCS
RMM
RMM (c)
PTA (c)

DCS errors

- Volume injected (systematic bias + variation due to repeatability)
    - ~4 % variation for 2 μL volume variation.

- Optical properties – errors in either gradient refractive index at the detector position or inputted values for the particle refractive index (real and complex/absorption) will lead to inaccuracies in conversion of intensity weighted data to mass weighted data.
    - ~4 % variation for a change up to ~10 % in RI properties

- Particle density needs to be known for conversion to number-weighted distribution

- Repeatability dependant on signal to noise ratio. For good signal to noise <4 % (mass), <6% (number). For poor signal to noise… >20%!

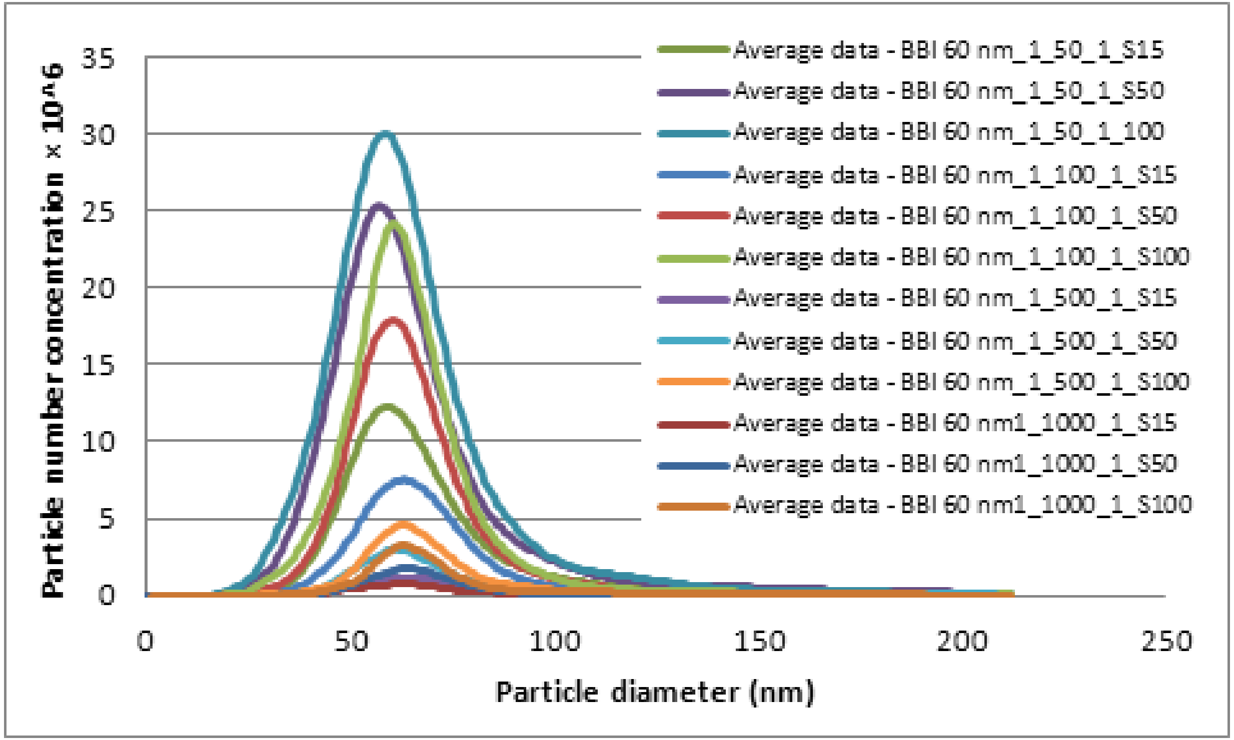
RMM errors

Missing counts or ‘double counts’ (underestimation) – tune concentration! Can be e.g. >30%

Volume flowing through the sensor is not measured directly. Depends on pressure and (inputted) viscosity - difficult to quantify. May be impacted by blockages. Difficult to quantify without reference.

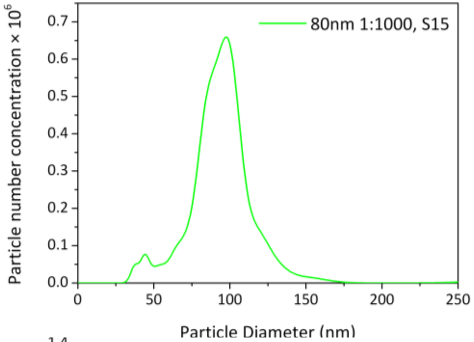
PTA errors

Camera Settings! (LM10)

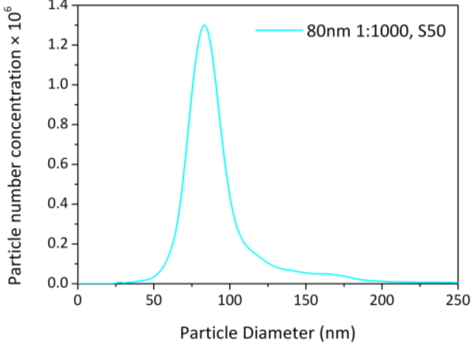


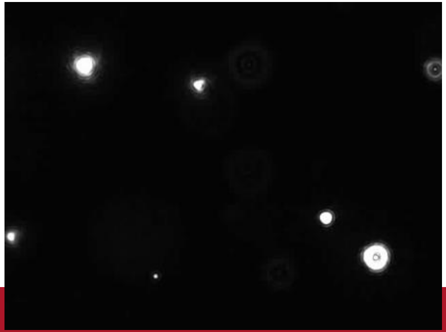
Blur Size	3x3
Detection Threshold Type	Single
Detection Threshold	20
Min track length	10
Min Expected Size (nm)	50

Shutter:15 Gain: 250	
Average # of particles/frame	Equivalent particle concentration
2.5	3.0×10^7

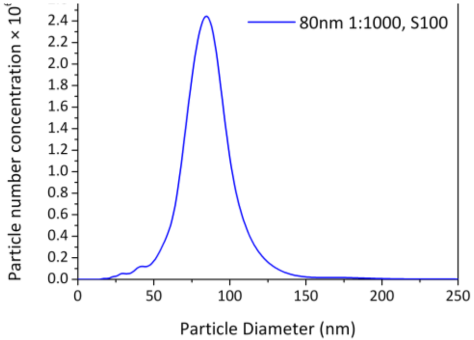


Shutter: 50 Gain: 250	
Average # of particles/frame	Equivalent particle concentration
3.9	4.6×10^7





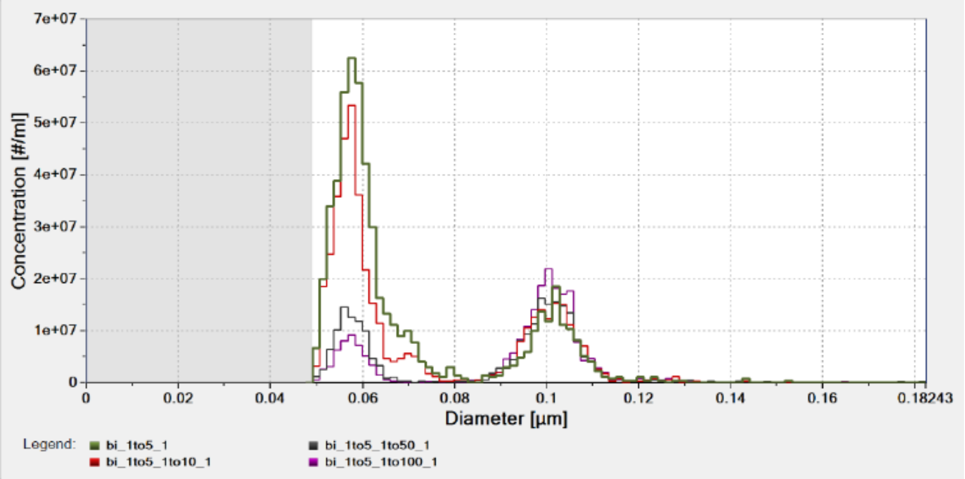
Shutter: 100 Gain: 250	
Average # of particles/frame	Equivalent particle concentration
7.2	8.6×10^7



Bimodal sample - 60:100 (linearity check)

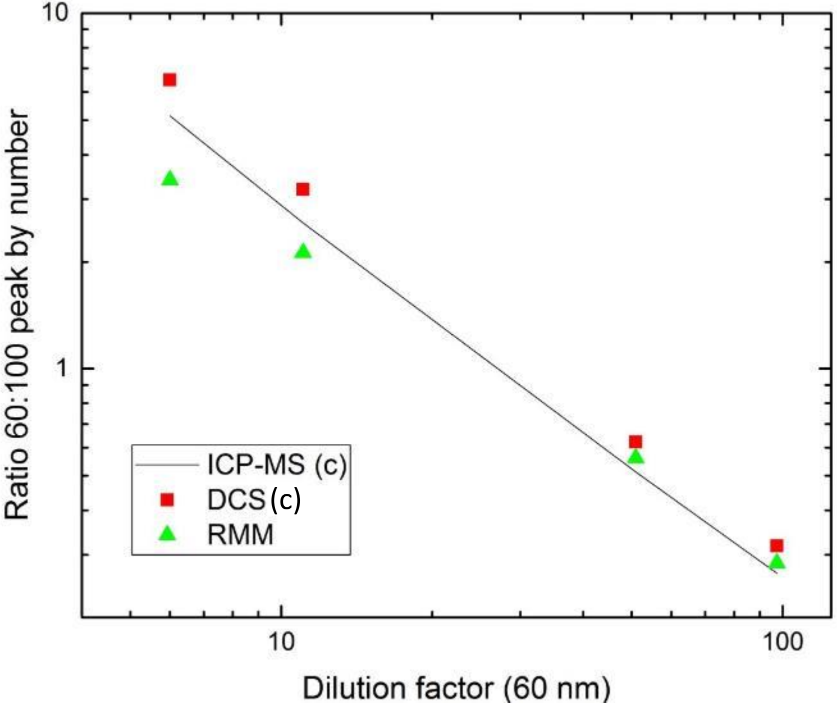
“Bimodal” sample series

1) Nominally 1:5 100 nm Au and 1:5 60 nm Au
2) 1:5 100 nm Au + 1:10 60 nm Au
3) 1:5 100 nm Au + 1:50 60 nm Au
4) 1:5 100 nm Au + 1:100 60 nm Au

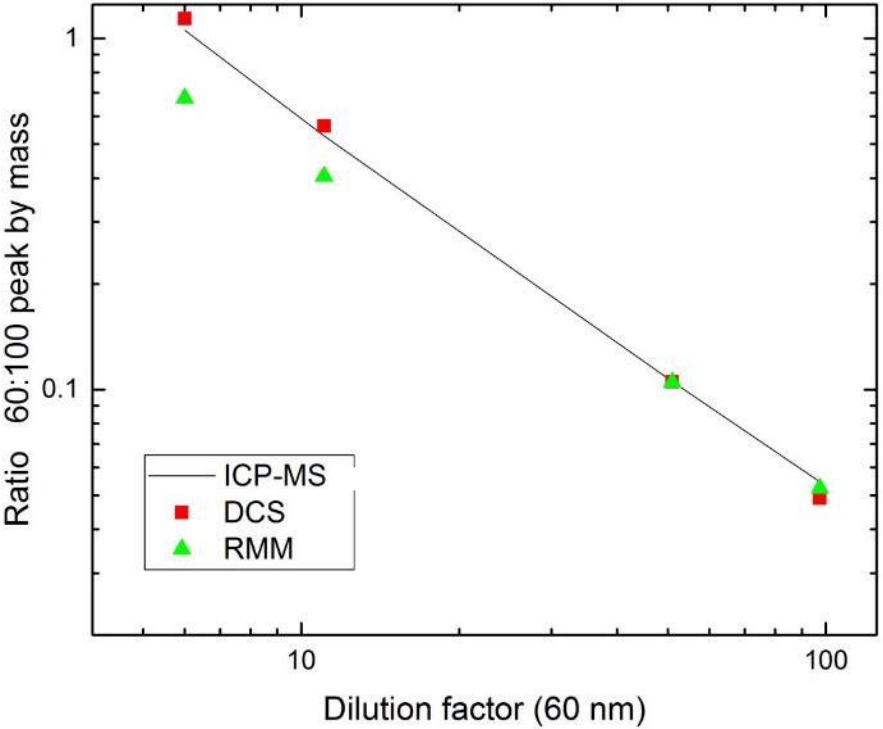


Bimodal sample - 60:100 (linearity check)

Number

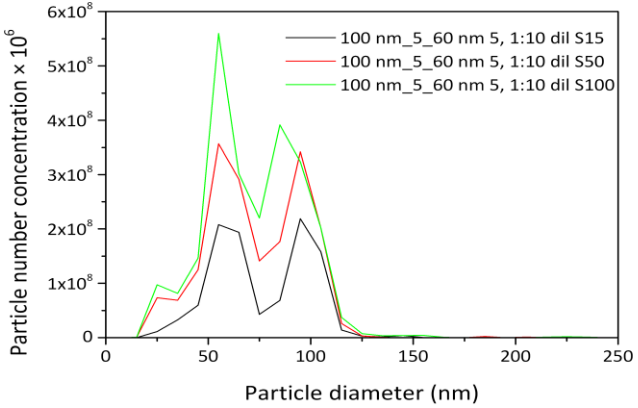


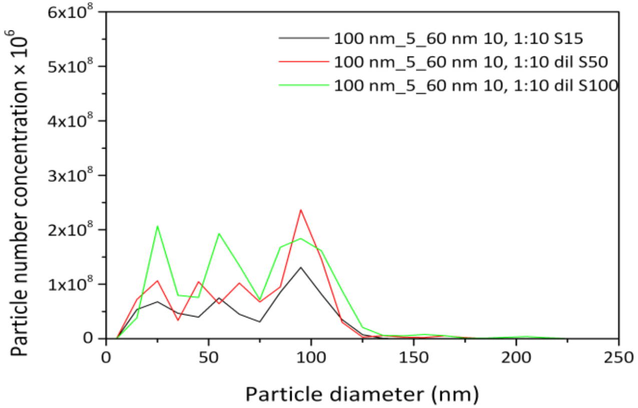
Mass



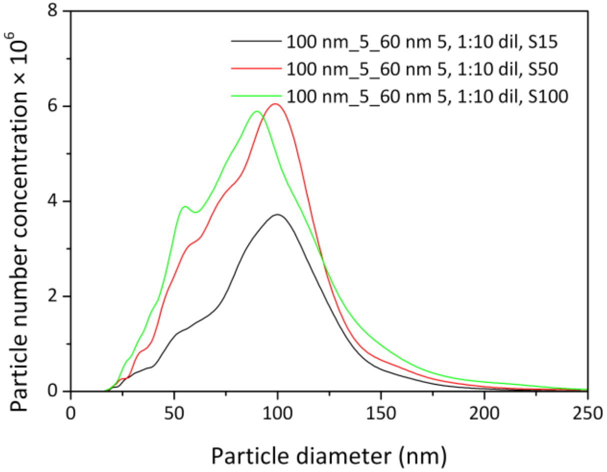
PTA Bimodal 100 + 60 nm

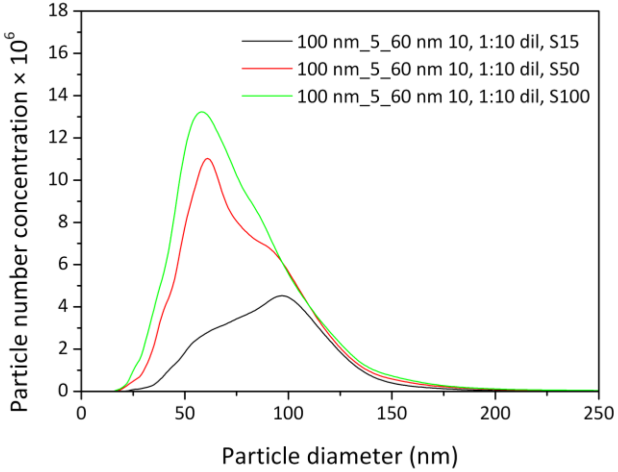
NTA 3.0:





NTA 2.3:





Conclusions

Even with basic instrumentation we can estimate number concentration effectively

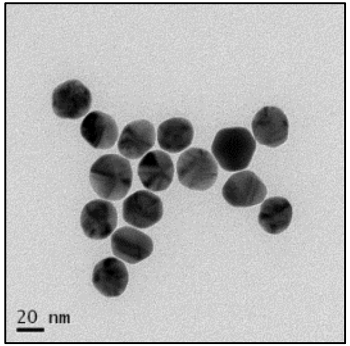
DCS and RMM can measure to within better than 50% of the mass and number concentration values predicted by ICP-MS, and for ‘ideal’ concentrations, RMM can reach values within 10%

Consistent overestimation of concentration by PTA compared to ICP-MS reference values, in excess of 100% - mitigated by better calibration of optical system.

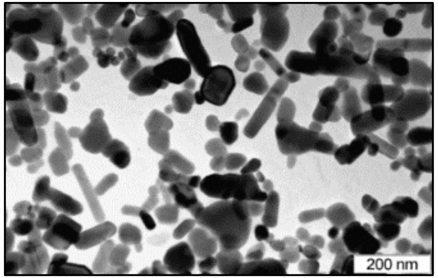
Exciting times for concentration measurement – VAMAS TWA 34 P10

Work to be done on other materials and complex particle size distributions

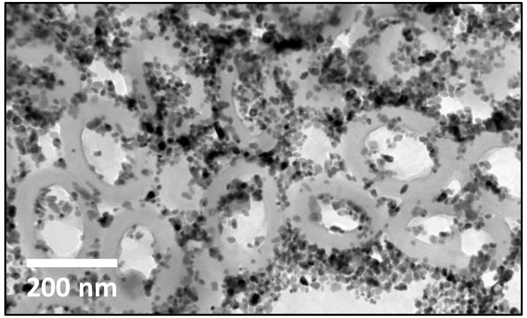
Complexities in new technology areas



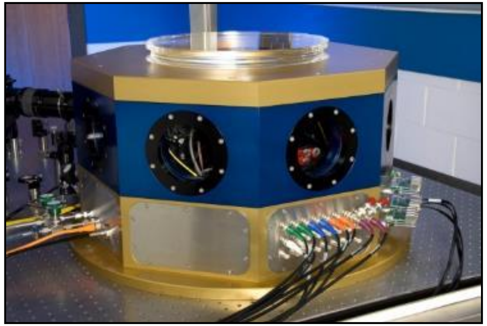
30 nm Au Reference Material



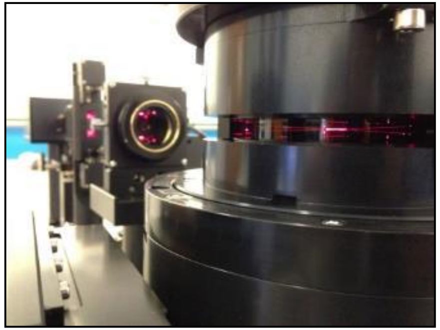
Commercial ZnO powder



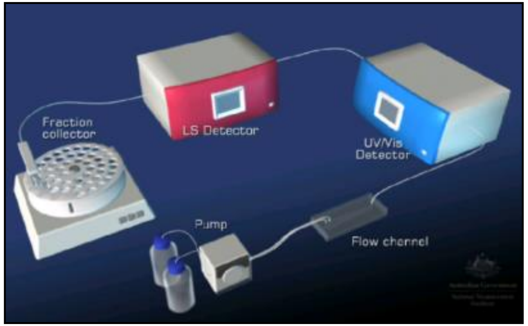
ZnO in sunscreen



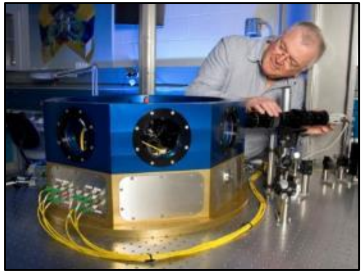
Primary nanoscale standard



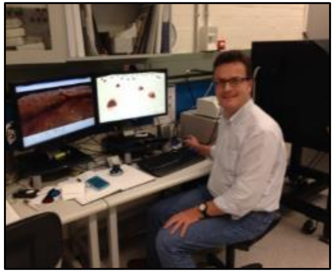
Commercial instrumentation



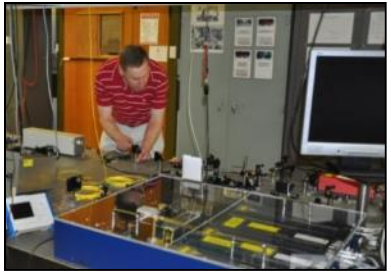
Multi (component and disciplinary) solution



CF

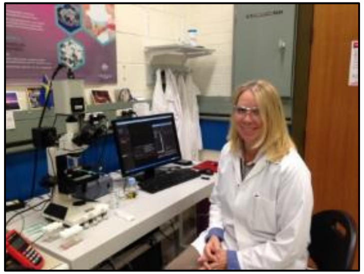


ML



MG

BB, JH



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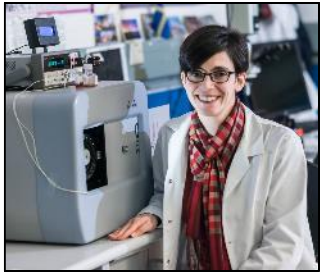

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