Combined Small-Angle and Ultra-Small-Angle X-ray Scattering Studies of Nanoparticle Dispersions for Environmental Health and Safety using an *in situ* Flow Cell

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Introduction

Nanoparticle (NP) dispersions (especially in air or in aqueous suspension) are currently of unprecedented interest due to their possible biomedical applications, but also because of their own potential impact on environmental health and safety (nano EHS). Small-angle X-ray and neutron scattering (SAXS and SANS) methods are ideal for quantitative characterization of the statistically representative NP size distribution and morphology, but the dilute nature of most relevant NP systems calls for SAXS measurements at an X-ray synchrotron source. In this context, ultra-small-angle X-ray scattering (USAXS) can cover the scale range from ≈ 1 nm to several mm in a single scan – sufficient for NP nucleation, growth and coarsening processes to be distinguished from other particle agglomeration effects. However, care must be taken to mitigate any X-ray beam damage effects and to ensure that the material in the X-ray beam remains representative of the overall NP suspension.

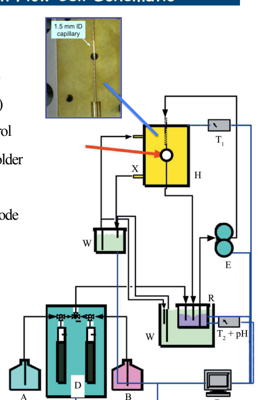
A flow cell for in situ SAXS studies of NP suspensions offers several advantages. The fluid flow prevents settling out of coarse particles. Control and online monitoring of the flow rate, temperature and other conditions (e.g. salinity, pH) enable real-time studies of solution-mediated processes. The transient sampling of sample material in fluid flow removes / mitigates bubble formation or sample damage that may occur in static suspensions exposed to an X-ray synchrotron (undulator) beam.

Flow Cell for *in situ* USAXS/SAXS

Reaction Flow Cell Schematic

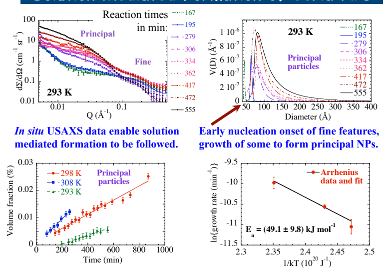
NIST USAXS flow cell

A = feedstock A (e.g., acid)
B = feedstock B (e.g., base)
C = remote computer control
H = isothermal capillary holder
T_1 = thermocouple
T2 + pH = pH/temp. electrode
D = automatic dispenser
X = incident x-ray beam
W = water baths
E = peristaltic pump
R = reaction vessel



In Situ Flow Cell Applications

Solution Mediated Formation of Ceria NPs

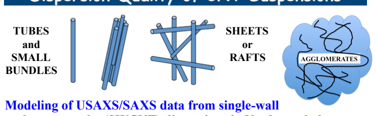


In situ USAXS data enable solution mediated formation to be followed.

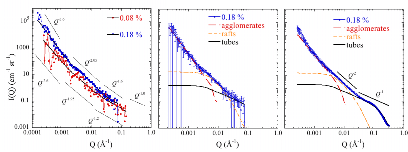
Early nucleation onset of fine features, growth of some to form principal NPs.

Following formation at 3 different temperatures allows determination of activation energy for solution-mediated growth of principal NPs.

Dispersion Quality of CNT Suspensions



Modeling of USAXS/SAXS data from single-wall carbon nanotube (SWCNT) dispersions in Na-deoxycholate:



Unsmoothed USAXS data: 0.08 % and 0.18 % mass

0.18 % mass data: model fit components

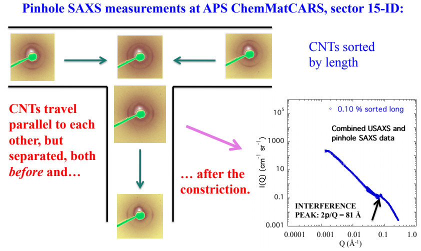
Smoothed USAXS data combined with pinhole SAXS data: model fit

Use of flow cell and absolute intensity calibrated USAXS/SAXS data enables dispersion quality to be quantified:

Tubes / small bundles: 97 % Rafts: 1.6 %, agglomerates: 1.4 % CNT bundle diameter ≈ 2.6 nm

Extensional Flow Using Microfluidic Cell

Pinhole SAXS measurements at APS ChemMatCARS, sector 15-ID:

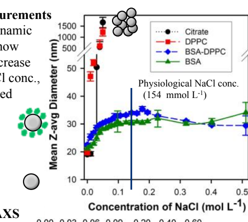


Stability of Ag Nanoparticles in Synthetic Lung Fluid

Silver nanoparticles (Ag NPs) are the most commonly identified nanoscale material in consumer products, mainly due to their broad-spectrum biocidal properties. But Ag NPs, unlike Au, are not inert, and need to be more fully understood in terms of EHS impact and risk if, e.g., they are ingested or digested. *In situ* measurements of the effects of biomedical environments on Ag NP dispersions are therefore of interest, consistent with appropriate NIOSH protocols, as is the development of standard reference materials.

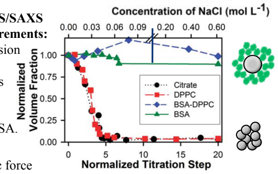
USAXS / pinhole SAXS studies have complemented dynamic light scattering (DLS) studies of AgNP dispersions subjected to increasing salt concentrations up to and above the physiological concentration (marked below) found in human lungs:

DLS measurements of hydrodynamic diameter show massive increase at low NaCl conc., unless coated with BSA:



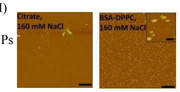
BSA-coated Ag NPs form one of two morphologies:

USAXS/SAXS measurements: suspension loses Ag NPs unless coated with BSA.



Dispersions of Ag NPs in synthetic lung fluid are stabilized as single nanoparticles by adsorbing proteins, e.g., bovine serum albumin (BSA).

Atomic force microscopy (AFM) confirms BSA-coated Ag NPs remain dispersed even at physiological salt concentration.



Scale bars: images: 1 μm; inset, 0.1 mm

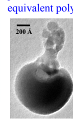
Results indicate: Stabilization under physiological conditions is enabled by protein coating. Secondary components of lung fluid mimic do not significantly impact stability.

Ag Nanoparticle Stability in Acid

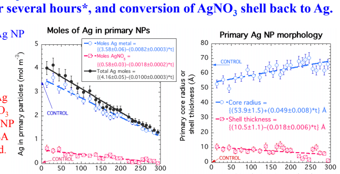
Initial *in situ* measurements of dissolution of BSA-coated Ag NPs in acid made in HNO_3 to avoid AgCl precipitation in HCl (found in stomach).

Addition of dilute 1.0 N HNO_3 results in immediate formation of core-shell structure, then linear dissolution over several hours*, and conversion of $AgNO_3$ shell back to Ag.

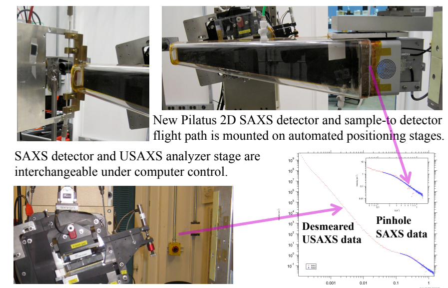
* Assumes NIOSH protocol for Ag NP protective coating with BSA or equivalent polymer coating.



TEM images of larger (800 Å) Ag NPs show $AgNO_3$ erupting off the NP surface once BSA layer is breached.



Combined USAXS / Pinhole SAXS



New Pilatus 2D SAXS detector and sample-to detector flight path is mounted on automated positioning stages.

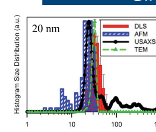
SAXS detector and USAXS analyzer stage are interchangeable under computer control.

Nanoparticle Reference Materials

Gold

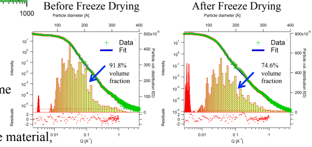
Citrate-stabilized Au nanoparticle NIST Reference Materials (nominally 10 nm, 30 nm and 60 nm) – certificates reported SAXS and USAXS determination of the mean volume-weighted size (*NIST RM 8011, 8012, 8013*).

Silver (in development)



DLS, AFM USAXS and TEM all reveal different Ag NP size distribution sampling. In this nominal 20 nm Ag NP sample, all techniques detect the peak in the size distribution but the weighting clearly varies with technique.

Absolute-calibrated USAXS/SAXS data provide size distribution and volume fraction, two key measurands for a nanoparticle reference material, and facilitates optimization of processing conditions for long-term stable storage.



Combined USAXS / pinhole SAXS instrument gives complete access to nano EHS measurement regime.

References:

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[2] J. Ilavsky, P.R. Jemian, A.J. Allen, F. Zhang, L.E. Levine and G.G. Long; " Ultra-small-angle X-ray scattering at the Advanced Photon Source," with supplementary material, *J. Appl. Cryst.*, **42**, 469-479 (2009).
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