Australian Government
National Measurement Institute

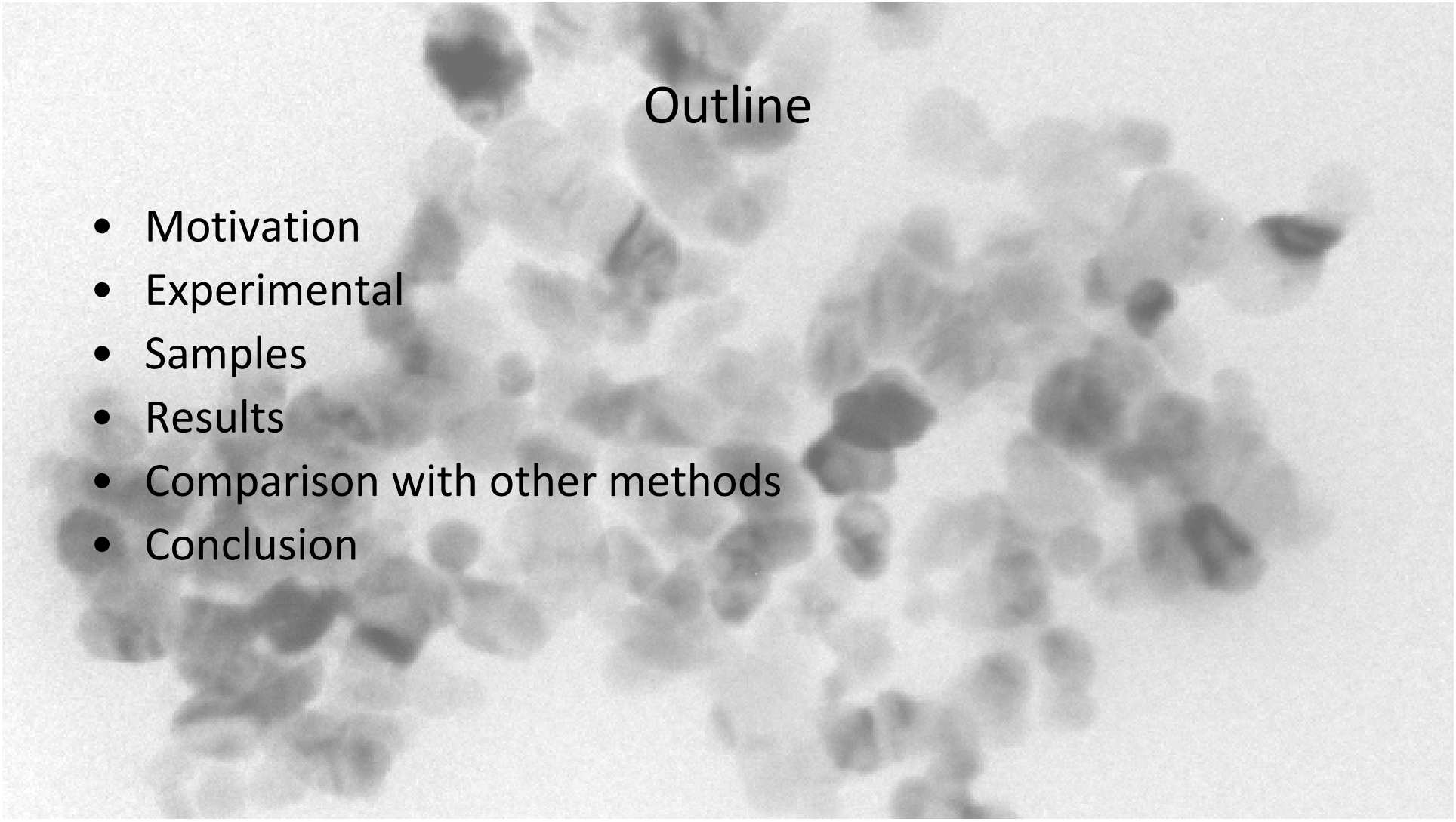
Ultra-Small-Angle X-Ray Scattering Study of the Aggregation State of Nanoparticles in Commercially Available Sunscreens

V. A. Coleman[1], B. Ingham[2], K. M. Collins[1], J. Ilavsky[3] and M. F. Toney[4]

[1] National Measurement Institute, Australia
[2] Industrial Research Limited, New Zealand
[3] Argonne National Laboratory, USA
[4] Stanford Synchrotron Lightsource, USA

ICONN 2012, Perth, WA

measurement.gov.au



Outline

- Motivation
- Experimental
- Samples
- Results
- Comparison with other methods
- Conclusion

TOXICOLOGICAL SCIENCES **118(1)**, 140–149 (2010)
doi:10.1093/toxsci/kfq243
Advance Access publication August 12, 2010

Small Amounts of Zinc from Zinc Oxide Particles in Sunscreens Applied Outdoors Are Absorbed through Human Skin

Brian Gulson,*·†·[1] Maxine McCall,‡ Michael Korsch,‡ Laura Gomez,* Philip Casey,§ Yalchin Oytam,‡ Alan Taylor,¶ Malcolm McCulloch,‖ Julie Trotter,‖ Leslie Kinsley,‖ and Gavin Greenoak‖‖

*Graduate School of the Environment, Macquarie University, North Ryde, New South Wales 2109, Australia; †CSIRO Earth Science and Resource Engineering, North Ryde, New South Wales 2113, Australia; ‡CSIRO Future Manufacturing Flagship, North Ryde, New South Wales 2113, Australia; §CSIRO Future Manufacturing Flagship, Clayton, Victoria 3168, Australia; ¶Department of Psychology, Macquarie University, Sydney, New South Wales 2109, Australia; ‖Research School of Earth Sciences, Australian National University, Canberra ACT 2601, , University, Sydney, New South Wales 2(

[1]To whom correspondence should be addressed at Department of Environment and Geogr Macquarie University, Building E8B Room 322, Sydney, New South Wales 2109, Austr

Received June 7, 2010; accepted Aug

Progress in Organic Coatings 62 (2008) 313–320

The interaction of modern sunscreen formulations with surface coatings

Philip J. Barker, Amos Branch

BLUESCOPE STEEL

Suncreen concern reaches into the school grounds

ABC website, 30th Jan 2012

http://www.abc.net.au/environment/articles/2012/01/30/3417377.htm

BY STEPHEN LUNTZ

ABC Environment | 30 JAN 2012

Comment

AROUND AUSTRALIA THIS WEEK shoes are being shined, pencils sharpened and lunches packed. At the school gate, parents will farewell little ones with oversized hats and backpacks as they tumble into the school year.

And as they prepare for a new batch of students, teachers will be receiving 50,000 leaflets from environmental group Friends of the Earth encouraging them, and their students, to use sunscreens that don't include nanoparticles - an ingredient the Theraputic Goods Administration (TGA) has deemed to be acceptable in sunscreens.

The leaflet distribution is the result of a resolution passed by the Australian Education Union (AEU) last year. AEU

Is sunscreen containing nano-particles safe for little ones?

Credit: iStockphoto

*"While the jury is still out on how safe nanoparticles are, we are advising schools to be cautious and **consider using nano-free sunscreen**, of which there are a number widely available on the market."* - Mary Bluett

Australian Government
National Measurement Institute

…but how do we know if a sunscreen is **nano-free**?

Rely on information from manufacturer about raw materials used in formulation

or

Perform measurements on sunscreen formulation….

Nano-scale:
(ISO 27687:2008) “size range from approximately 1 nm to 100 nm”

What is nano-free?

< x % (by weight? number?) of particles < 100 nm?

What about aggregates/agglomerates?

nano.foe.org.au

Australian Government
National Measurement Institute

Measuring particles in complex matricies

- Most existing studies have been conducted on particles extracted from formulation or on diluted formulation. This will alter the aggregation/agglomeration state in the formulation.
- Specialised instrumentation required to cope with high density, high viscosity, multi-component formulations
  - Cryo-TEM
  - X-rays

Why Synchrotron?

High intensity

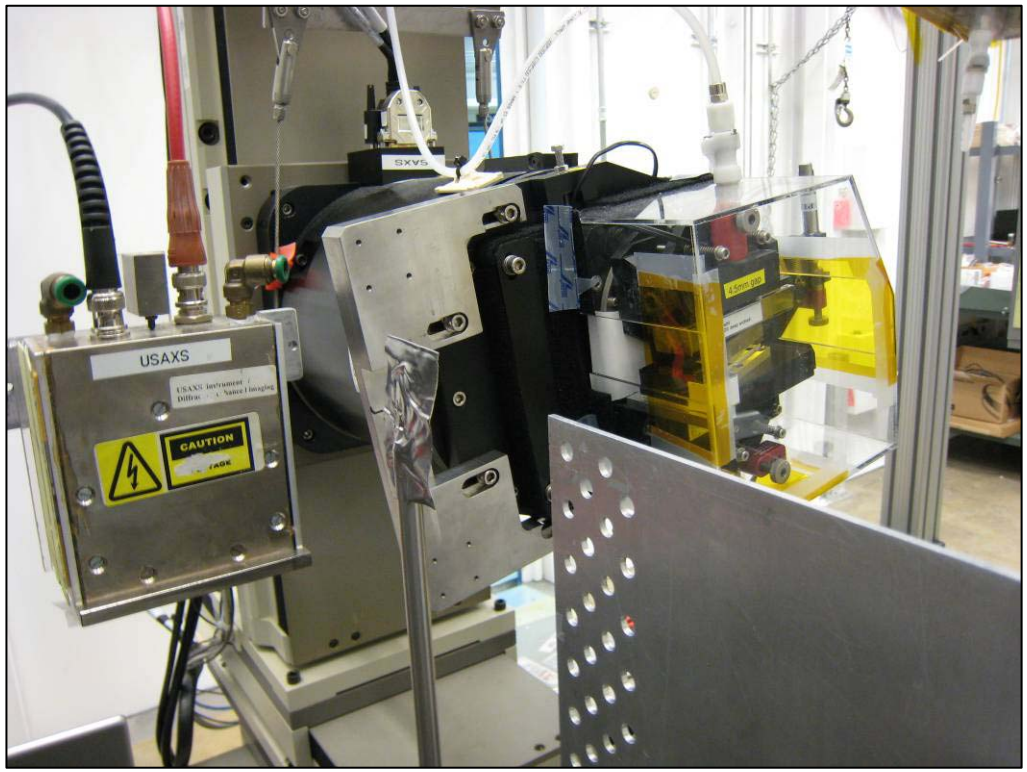
Measurements on the formulation
- no extraction
- no dilution

Results therefore represent the aggregation/agglomeration state of the particles in formulation

Argonne NATIONAL LABORATORY

Australian Government
National Measurement Institute

15ID-D USAXS beamline at the Advanced Photon Lightsource



High intensity and ultra-high dynamic range of CCD enable analysis of high-concentration samples at very low *q* value

Aggregates/agglomerates are large in size and scatter at low *q*

Australian Government
National Measurement Institute

Samples

6 commercial sunscreens, loaded into silicone cells.

Measurements were made on the formulation without dilution, modification or extraction.

	Active	Wt %
A	ZnO	18
B	ZnO	18
C	ZnO	20
D	ZnO + organics	6
E	TiO_2 + organics	5
F	ZnO + organics	6

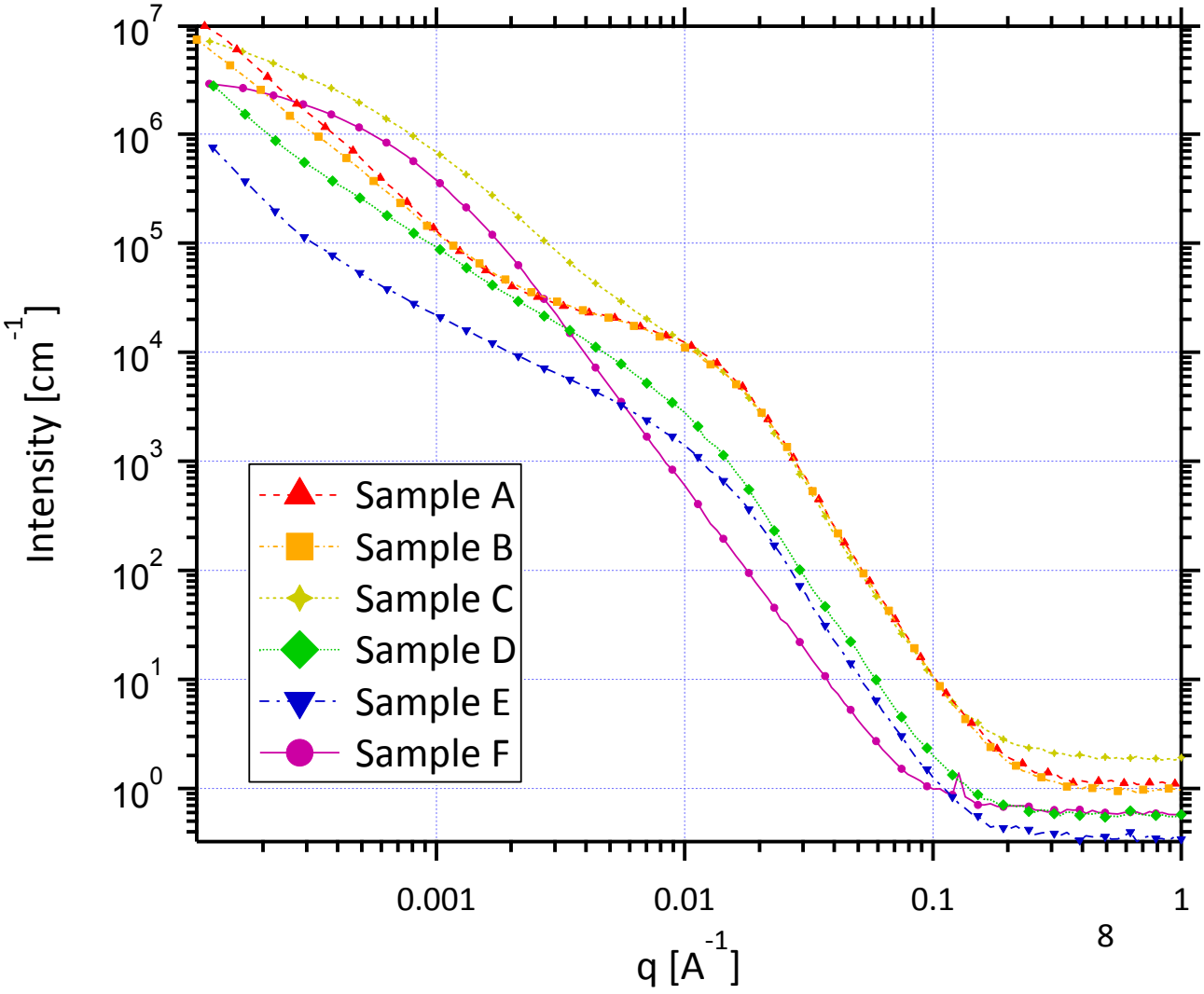
Samples were purchased in April 2011. Sunscreen formulations are frequently modified and the results presented here may not reflect the current formulation in any of these products.

Australian Government
National Measurement Institute

USAXS data

Data measured against air blanks.

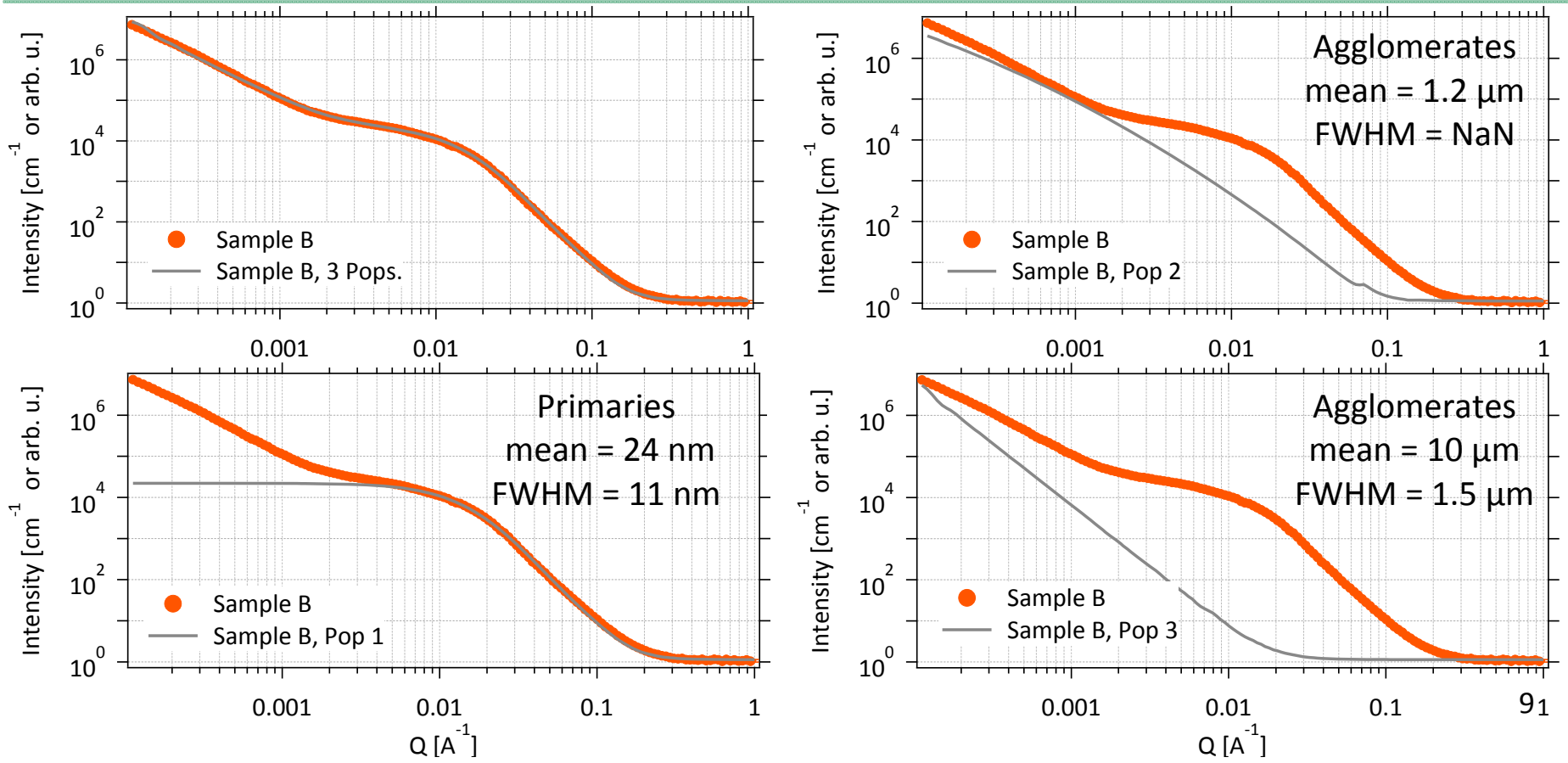
Formulation only measurements were made to check for contribution from other scatterers. Signal was negligible.



Australian Government
National Measurement Institute

Fitting the data

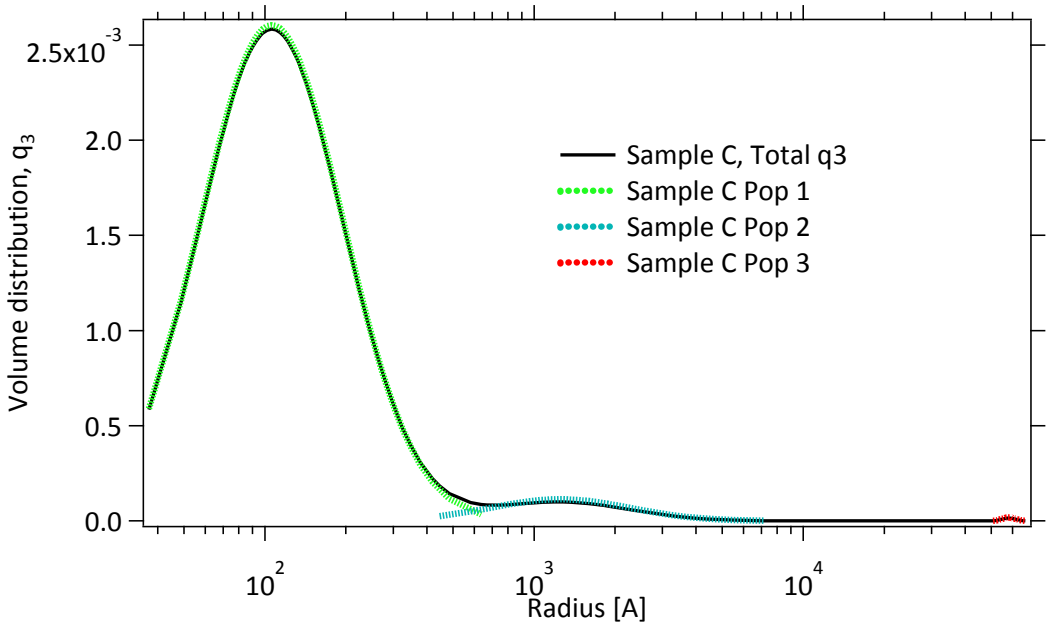
Data fitted with Indra package. (Jan Ilavsky, ANL/APS)
LSQ fit assuming a dilute system and fitting populations with log normal distributions. Assuming (hard) spheroid geometry.



Australian Government
National Measurement Institute

Size distributions

- USAXS measurements show most particles are present in formulation as primary particles (by volume).
- Agglomerates that are very loosely bound (e.g. due to the presence of large surfactant molecules) may contribute to the primary particle distribution.
- There is a small fraction of larger particles which are likely to be aggregates and agglomerates.



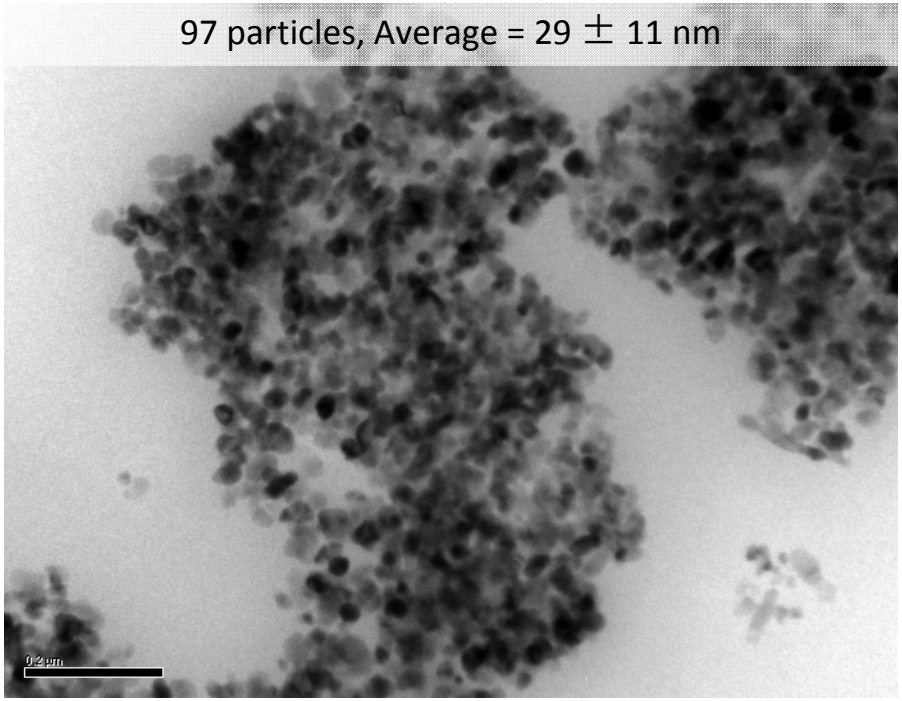
Australian Government
National Measurement Institute

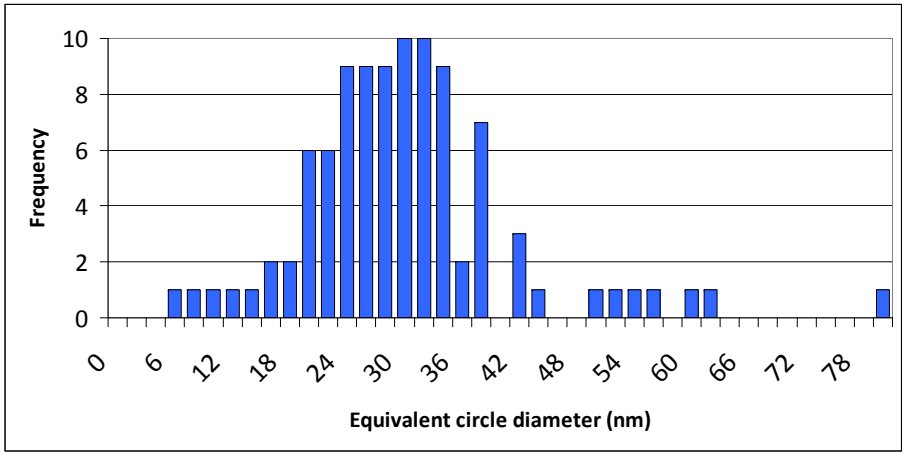
Table of results

	Population 1 (Primaries) Mean, FWHM, Volume	Population 2 (Aggregates) Mean, FWHM, Volume	Population 3 (Aggregates) Mean, FWHM, Volume
Sample A	25 nm, 11 nm, 0.42	814 nm, NaN, 0.13	12 µm, 1.0 µm, 0.19
Sample B	24 nm, 11 nm, 0.47	1.2 µm, NaN, 0.07	10 µm, 1.5 µm, 0.08
Sample C	31 nm, 17 nm, 0.50	354 nm, 189 nm, 0.25	6 µm, 0.9 µm, 0.09
Sample D	32 nm, 19 nm, 0.09	325 nm, 118 nm, 0.04	11 µm, 4.8 µm, 0.05
Sample E	35 nm, 15 nm, 0.06	274 nm, 106 nm, 0.01	11 µm, 4.9 µm, 0.01
Sample F	259 nm, 118 nm, 0.08	560 nm, 253 nm, 0.09	11 µm, 4.9 µm, 0.01

Australian Government
National Measurement Institute

Comparison of results from TEM measurements of particles extracted from **Sunscreen C**





Size of primary particles compares well with the USAXS measurements (mean diameter of 29 vs 31 nm)

Australian Government
National Measurement Institute

Conclusions

- USAXS measurements on unmodified sunscreen were successfully made.
- USAXS indicates main population in sunscreen formulation is of primary particles (or loosely bound agglomerates).
  - Supported by measurements on primary particle size of particles extracted from formulation.
- These results are useful for understanding if the particles in sunscreens are present as primary particles, or aggregates/agglomerates.
- Results do not correlate with reports in the public sphere.
- Accurate measurements **are critical** for supporting informed decisions and education.

Australian Government
National Measurement Institute



Victoria Coleman
Nanometrology
National Measurement Institute
Bradfield Road
West Lindfield NSW 2070
Australia

Phone: + 61 2 8467 3820

Email: victoria.coleman@measurement.gov.au

Learn more about nanoscale measurements:

Åsa Jämting: Monday 2:30, 2.7 (Room 7)

- Nanoparticle characterisation techniques

Jan Herrmann: Tuesday 2:45, 6.8 (Room 8)

- Nanometrology for nanoscale measurements

Bakir Babic: Thursday 2:45, 14.2 (Room 2)

- Development of a mSPM at NMIA

measurement.gov.au