



Australian Government
National Measurement Institute

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

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ICONN 2012, Perth, WA

measurement.gov.au



Outline

- Motivation
- Experimental
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- 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

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Received June 7, 2010; accepted Aug

"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

Progress in Organic Coatings 62
(2008) 313–320

*The interaction of modern
sunscreen formulations with
surface coatings*

Philip J. Barker, Amos Branch



Sunscreen concern reaches into the school grounds

ABC website, 30th Jan 2012

BY STEPHEN LUNTZ

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

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 Therapeutic 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

...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?



Measuring particles in complex matrices

- 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

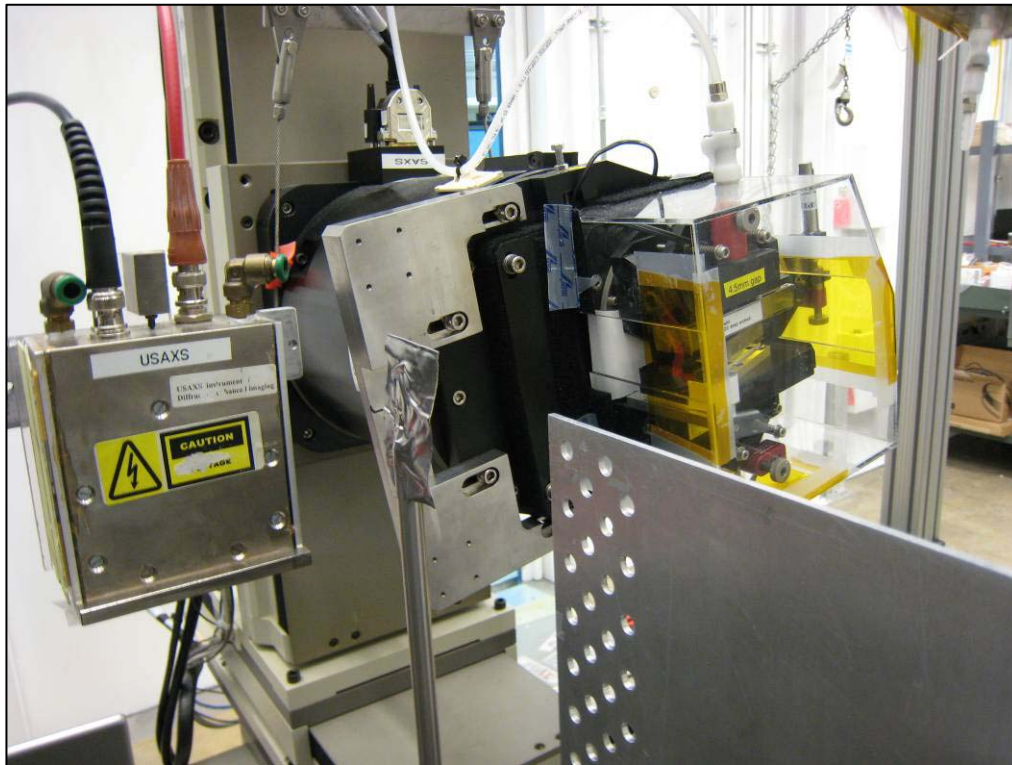
Measurements on the formulation

- no extraction
- no dilution

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



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

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

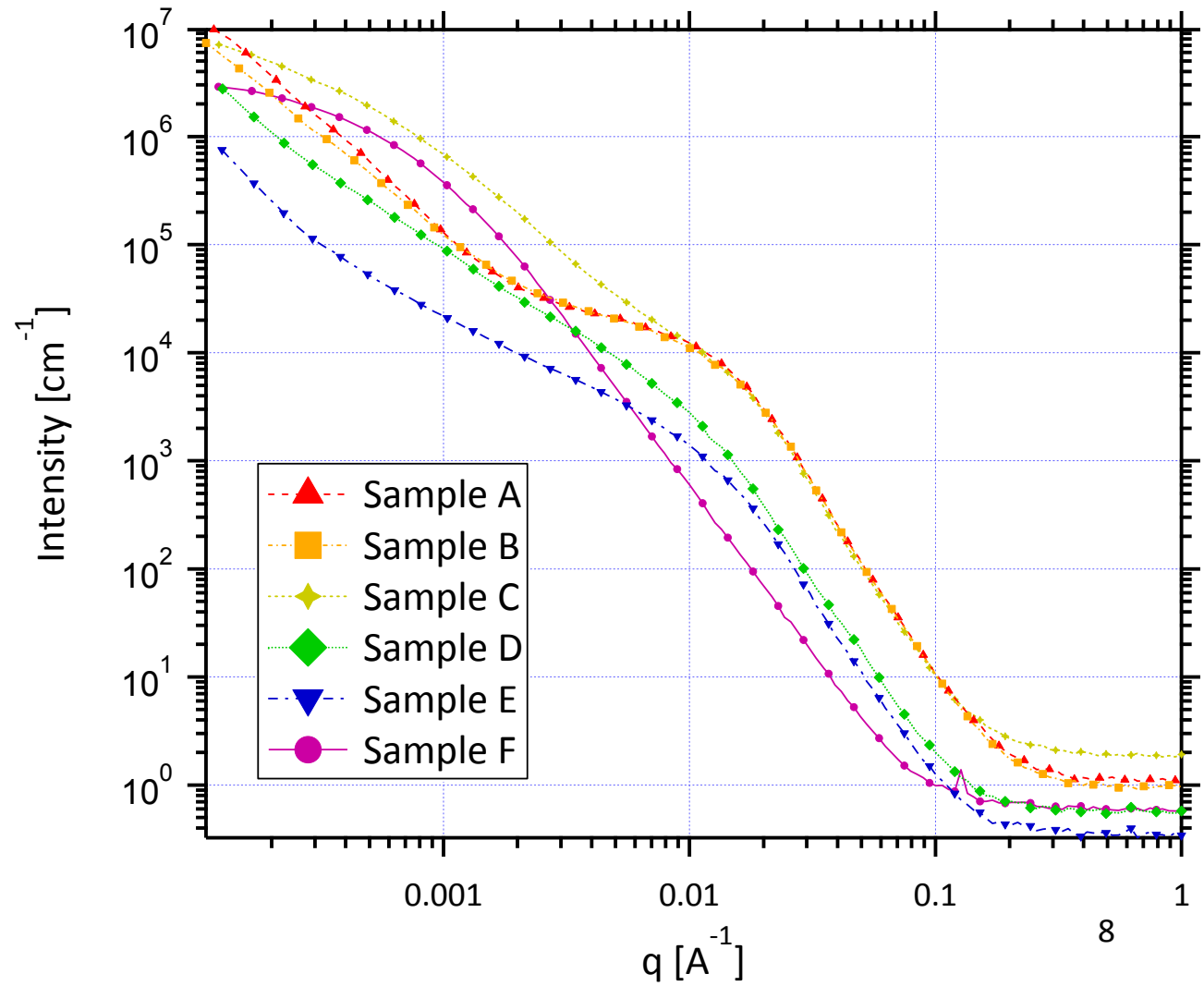


Samples were purchased in April 2011. Sunscreen formulations are frequently modified and the results presented here may not reflect the current formulation in any of these products.

USAXS data

Data measured against
air blanks.

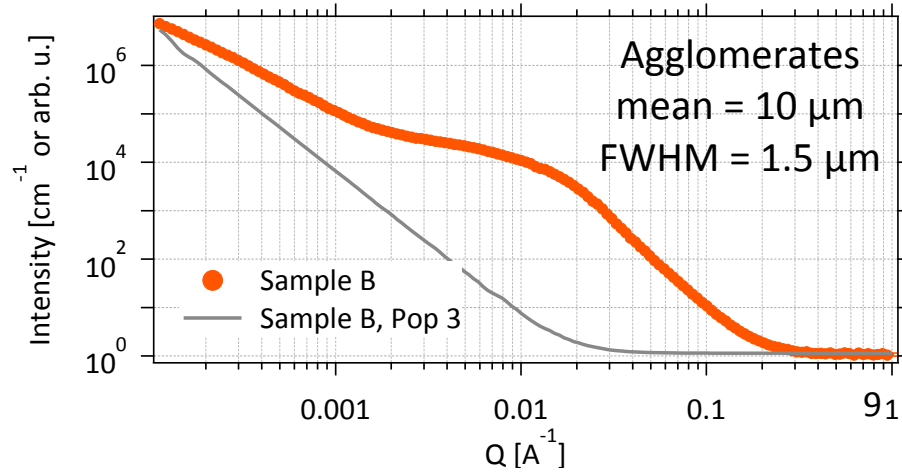
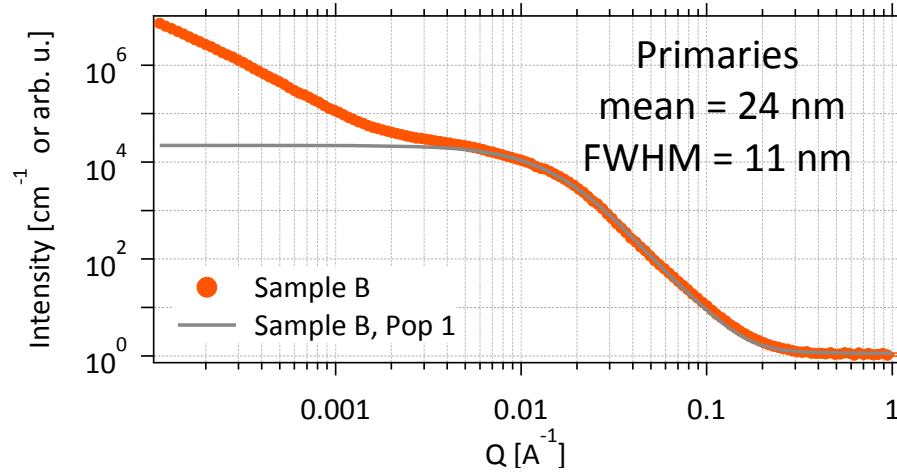
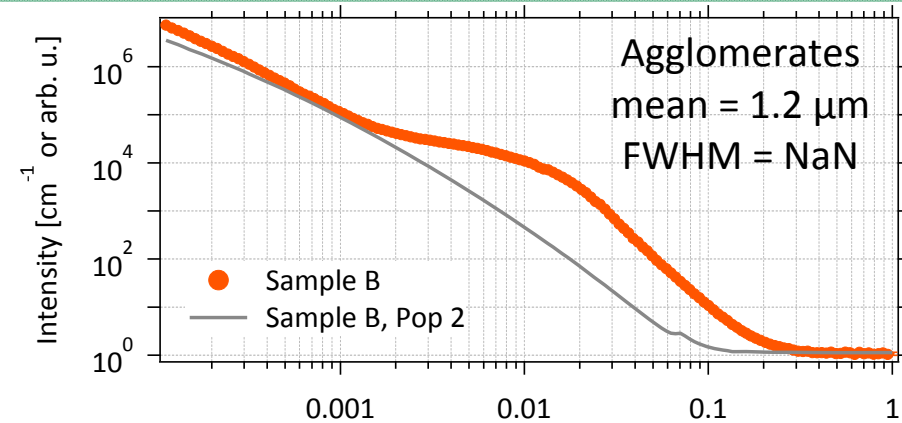
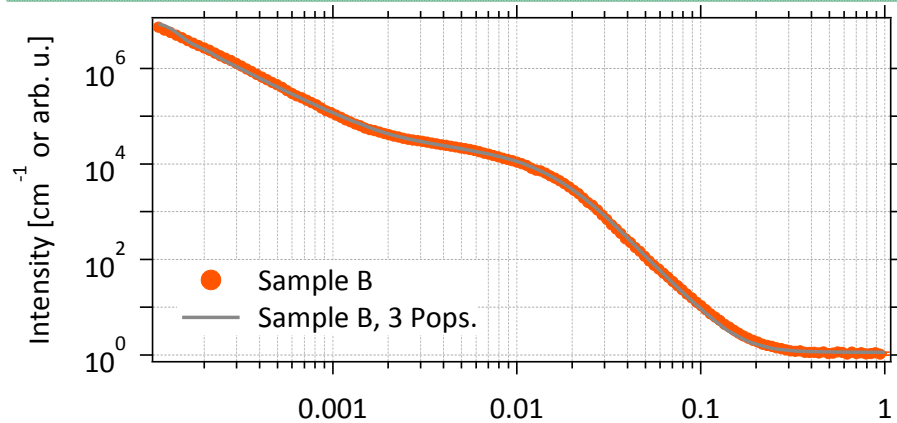
Formulation only
measurements were
made to check for
contribution from other
scatterers. Signal was
negligible.



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.



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.

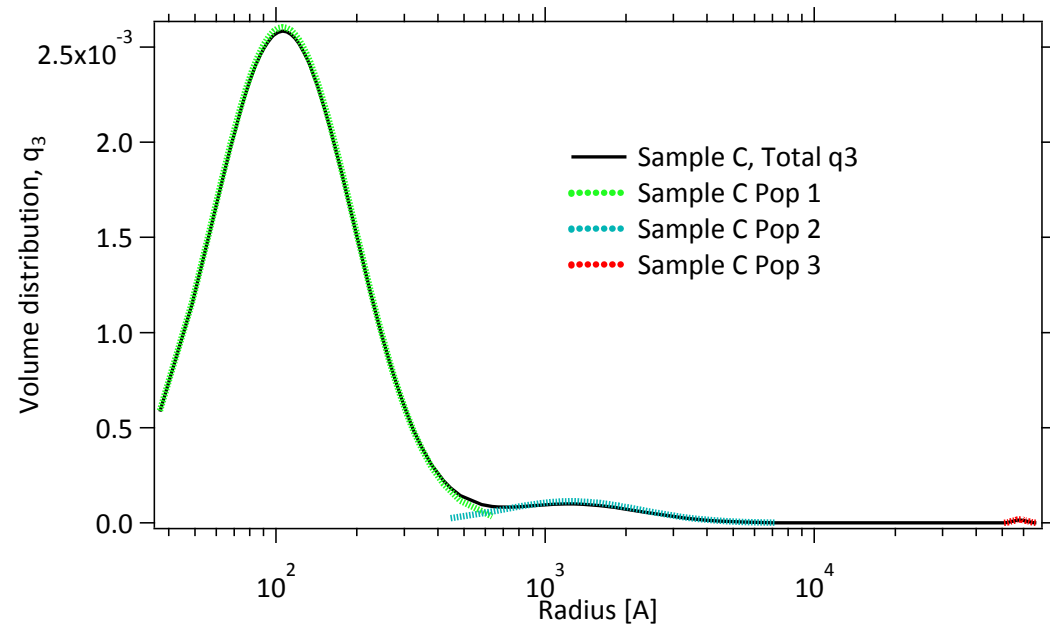
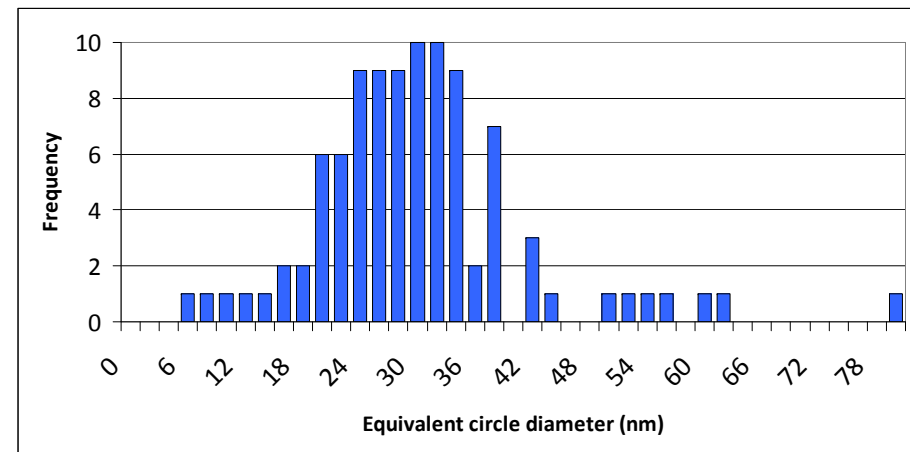
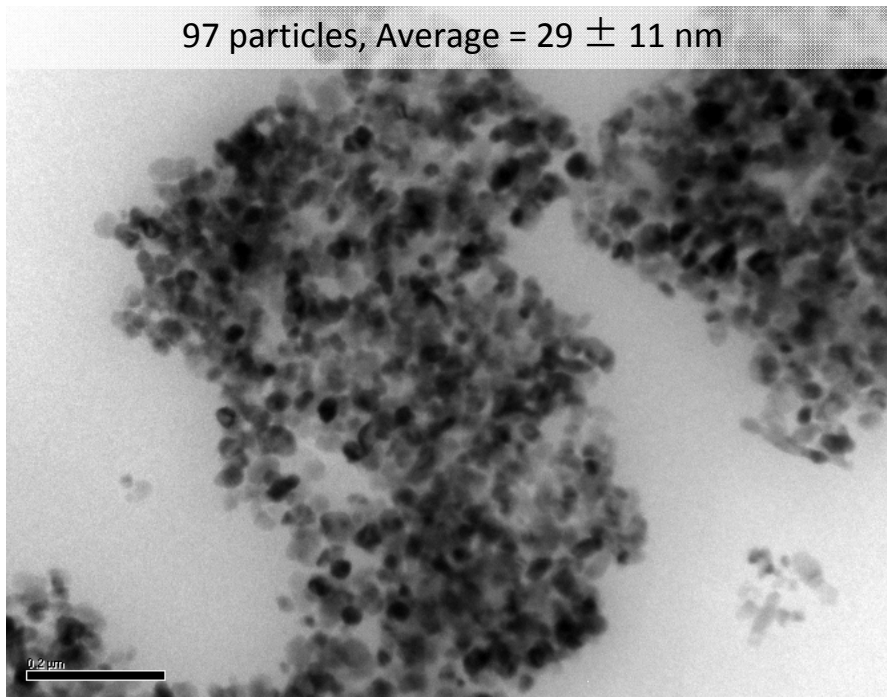


Table of results

	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

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)

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.



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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

