Addressing the Amorphous Content Issue in Quantitative Phase Analysis: The Certification of NIST SRM 676a

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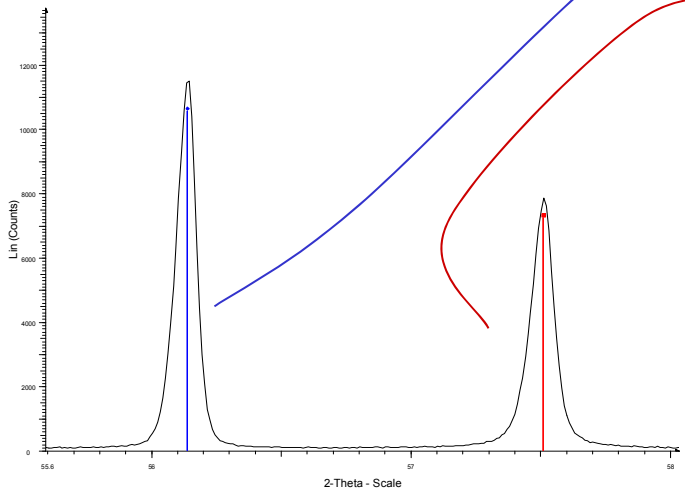
NIST SRMs for X-ray Wavelength Metrology

Diffraction Application	SRM	Composition (Powder)	Unit Size, g
Line Position	640d	Silicon	*7.5*
Line Position	675	Mica	7.5
Line Position	2000	Si (100)with Si/Ge epilayer	2.5 cm sq.
Line Shape	660b	LaB_6	6
Line Shape	1979	ZnO, 25 nm & 75 nm	*3 (each)*
Instrument Response	1976b	Sintered Alumina Plate	2.6 cm disc. x 0.2 cm
Quantitative Analysis	676a	Alumina (corundum)	20
Quantitative Analysis	674b	ZnO, TiO_2, CeO_2, & Cr_2O_3	10 (each)
Quantitative Analysis	1878b	Respirable Quartz	5
Quantitative Analysis	1879a	Respirable Cristobalite	5
Quantitative Analysis	656	Silicon Nitride: α & β phases	10 (each)

Quantitative Analysis via Powder Diffraction

It's been around for a while



$$\frac{I_\alpha}{I_s}\left(\frac{I_{js}^{rel}}{I_{i\alpha}^{rel}}\right) RIR_{\alpha,s} = \frac{X_\alpha}{X_s}$$

Reference Intensity Ratio, RIR, (Internal Standard) Method

RIR: Innate characteristic of the two materials being considered

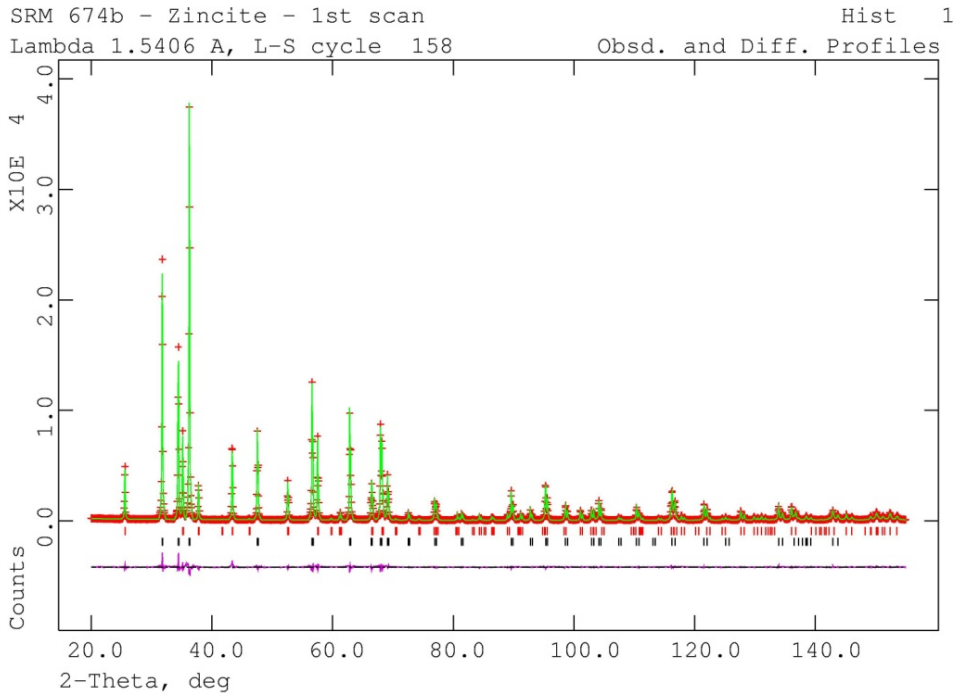
Chung (1974) "adiabatic" method

Snyder (1992) "normalized RIR"

$$\frac{X_\alpha}{X_\beta} = \frac{I_\alpha}{I_\beta}\frac{RIR_{\beta,s}}{RIR_{\alpha,s}} \qquad \sum_{k=1}^{n} X_k = 1$$

Quantitative Rietveld Analysis, QRA

Apparent standardless quantitative analyses



Quantification via GSAS:

$$\frac{X_\alpha}{\sum_{k=1}^{n} X_k} = \frac{S_\alpha Z_\alpha w_\alpha}{\sum_{k=1}^{n} S_k Z_k w_k}$$

X_α is the mass fraction of phase α
S_k are the scale factors
w_k are the molecular weights
Z_k are the number of formula weights per unit cell

$$\sum_{k=1}^{n} X_k = 1$$

Suitable Standard: $X_s = X_{s(xtal)} + X_{s(amor)}$ Yields:

$$\frac{X_{s(xtal)}}{\sum X_{u(xtal)} + X_{s(xtal)}} = \frac{S_s Z_s w_s}{\sum S_k Z_k w_k}$$

$$\sum X_{u(xtal)} + X_{u(amor)} = 1 - X_s$$

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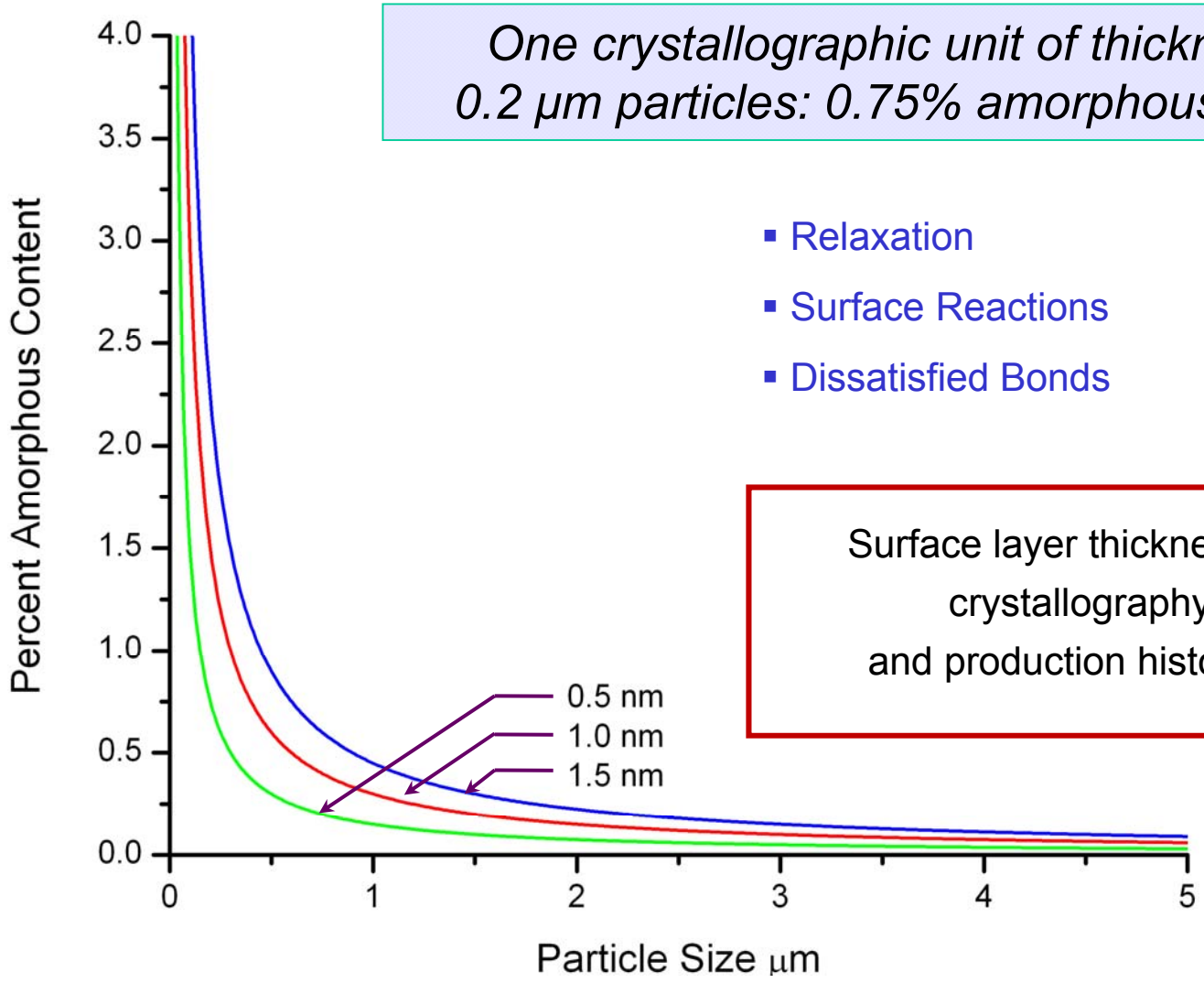
Amorphous Component of Finely Divided Crystalline Solids

One crystallographic unit of thickness on 0.2 μm particles: 0.75% amorphous content



- Relaxation
- Surface Reactions
- Dissatisfied Bonds

Surface layer thickness determined by crystallography, chemistry and production history of the powder

Selection of an Alumina Powder for use as an Internal Intensity (Quantitative Analysis) Standard

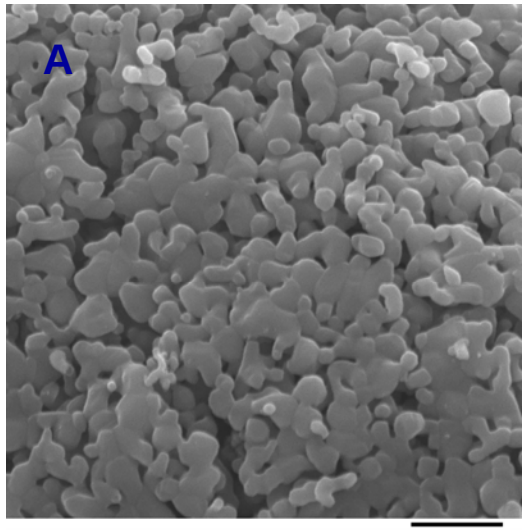
I/I_c Proposed by Visser and deWolff (1964)

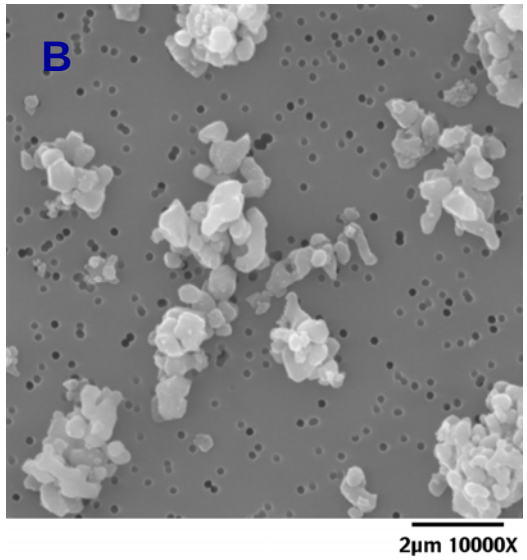
Property included in ICDD database; hence SRM 676(x)

Desired characteristics of SRM feedstock

- strong lines over a wide d-space range
- stability
- inertness
- equi-axial (non-orienting) particles
- particle size in the one micrometer range: microabsorption (Brindley, 1945)
- small diffracting domains: primary extinction (Zachariasen, 1945)

Selection of an Alumina Powder for use as an Internal Intensity Standard





Commercial Alumina Production

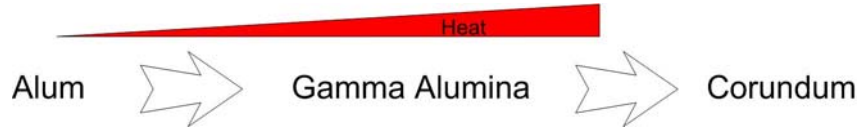
95% via Bayer process:

Low T: Transition alumina impurities "Active Alumina"

High T: Platelike coarse grains "Tabula Alumina"

Material not well suited for use as a standard

Dynys and Halloran (1982) :



Low T: Phase pure alumina w/ "sponge" microstructure **A**

With comminution: Equiaxial fine grains **B**

Material quite well suited for use as a standard

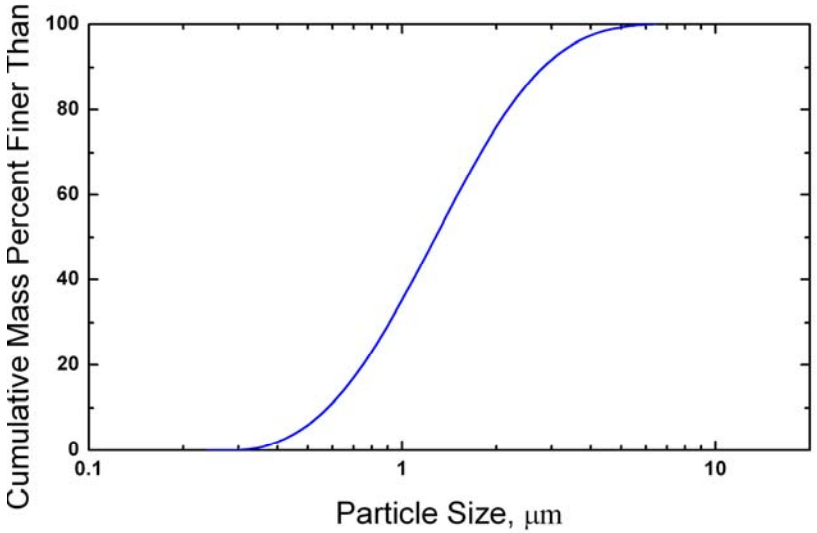
SRM 676a Feedstock Consists of Baikalox* CR1

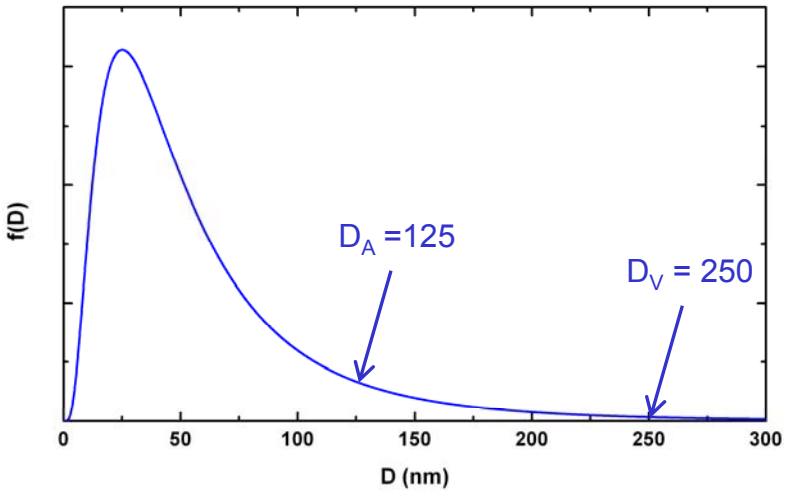
Alum process *Calcined to 1400°C* *Jet milled*

Particle size via laser scattering

%<	µm
10	0.58
50	1.28
90	2.82

*Baikowski Chimie, France





Crystallite size via profile broadening

Data from 11 BM, APS, SRMs 660a & 676a

Analysis via TOPAS

Distribution via Krill & Birringer (1998)
Popa & Balzar (2002)

Implementation via P. Whitfield

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Determination of Amorphous Fraction I

Diffraction experiment: crystalline fraction only
Weighing operation: all constituents

Experimental Design

No possibility for phase pure reference material

Vary impurity level in systematic manner

Engineer microstructure so as to ensure said variation

Single crystal reference material; as per silicon of SRM 640c

Amorphous material restricted to surface (oxide) layer

Surface layer of uniform thickness, invariant with respect to particle size

Variation of particle size / surface area in series of single crystal powders

Diffraction experiments on series of two phase mixtures, reference vs. test

Extrapolate diffraction results to reference phase of “zero” amorphous content

Compare diffraction result from test phase to mass fraction of weighing operation

Determination of Amorphous Fraction II

Execution

Comminute silicon to broad size distribution & anneal

Fractionate into five lots from 5 - 25 micrometers

Measure surface area & particle size

Prepare 4 X 50-50 mixtures, plus SRM 640c

Accurate diffraction experiments

Multiple diffraction methods/facilities

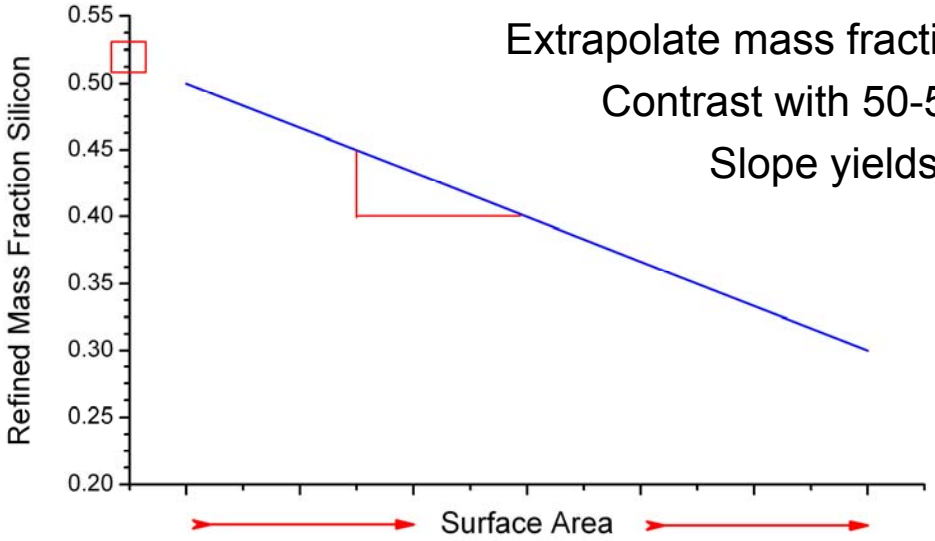
Address extinction effects within QRA

Plot refined mass fraction silicon vs. surface area

Extrapolate mass fraction trend to a silicon with “zero” surface area

Contrast with 50-50 mass fraction: phase purity of SRM 676a

Slope yields oxide layer thickness on silicon



Microstructure Data on the Five/Six Lots of Silicon

Sieve Fraction	SRM 640c	< 5 μm	5 < 10 μm	10 < 15 μm	15 < 20 μm	20 < 25 μm
Particle Size, μm	4.44	5.28	9.81	14.47	19.24	23.98
Surface Area, m^2/g	1.40	1.50	0.70	0.41	0.31	0.27

Annealed in gettered argon at 1000°C for 2 h, van Berkum, et al. (1995)

Electro-deposited sieves, 5,10,15,20 & 25 μm

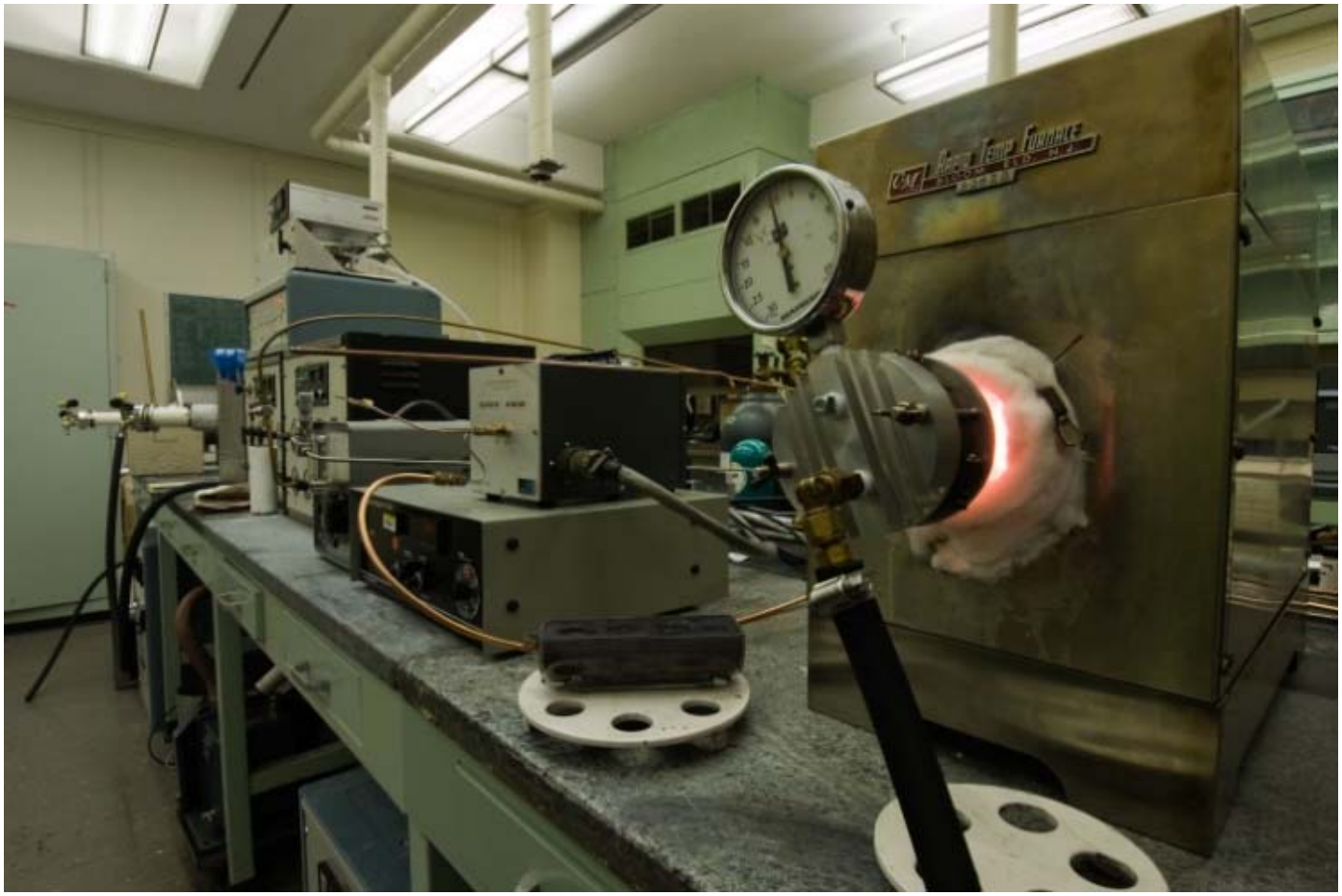
Sieved in anhydrous isopropyl alcohol, wash w/ dilute nitric acid

Size distribution via laser scattering

Surface area via BET adsorption, krypton

Image of Equipment Used for Annealing of Silicon in ultra-low P_{O_2} Ar

Silicon oxide surface layer reduced to elemental silicon



Primary Extinction

Dynamical scattering theory

Reduction in intensity due to destructive interference of standing waves

Zachariasen: R = Q f(A)

R diffraction intensity
Q intensity per unit volume
f(A) diffraction geometry

$$A = \frac{e^2 \lambda F t}{m c^2 V}$$

λ wavelength
F structure factor
T nominal crystal/domain dimension
V unit cell volume

Neutron Time-of-Flight: refine extinction parameter via Sabine model (1985)

High-energy X-ray diffraction: no extinction???

Data Collection

Neutron Time-of-Flight

SEPD, IPNS

Exposed for 2 h at 13 μA and 30Hz, d-space range: 0.05 nm to 0.39 nm

25 keV X-ray

32 IDB, APS, eight detector machine, 0.8 mm spun kapton capillary

6° to 51° 2Θ, 0.0005° sw, 1 s ct, d-space range: 0.058 nm to 0.474 nm

67 keV X-ray

X17B1, NSLS, focusing optics, 1.0 mm spun glass capillary

2.7° to 12° 2Θ, 0.001° sw, 1 s ct, d-space range: 0.0890 nm to 0.393 nm

8 keV Laboratory X-ray

Siemens D500, Ge focusing IBM, sample spinner & PSD

20° to 154° 2Θ, 0.75° /min, d-space range: 0.079 nm to 0.44 nm

Data Analysis: Rietveld code GSAS

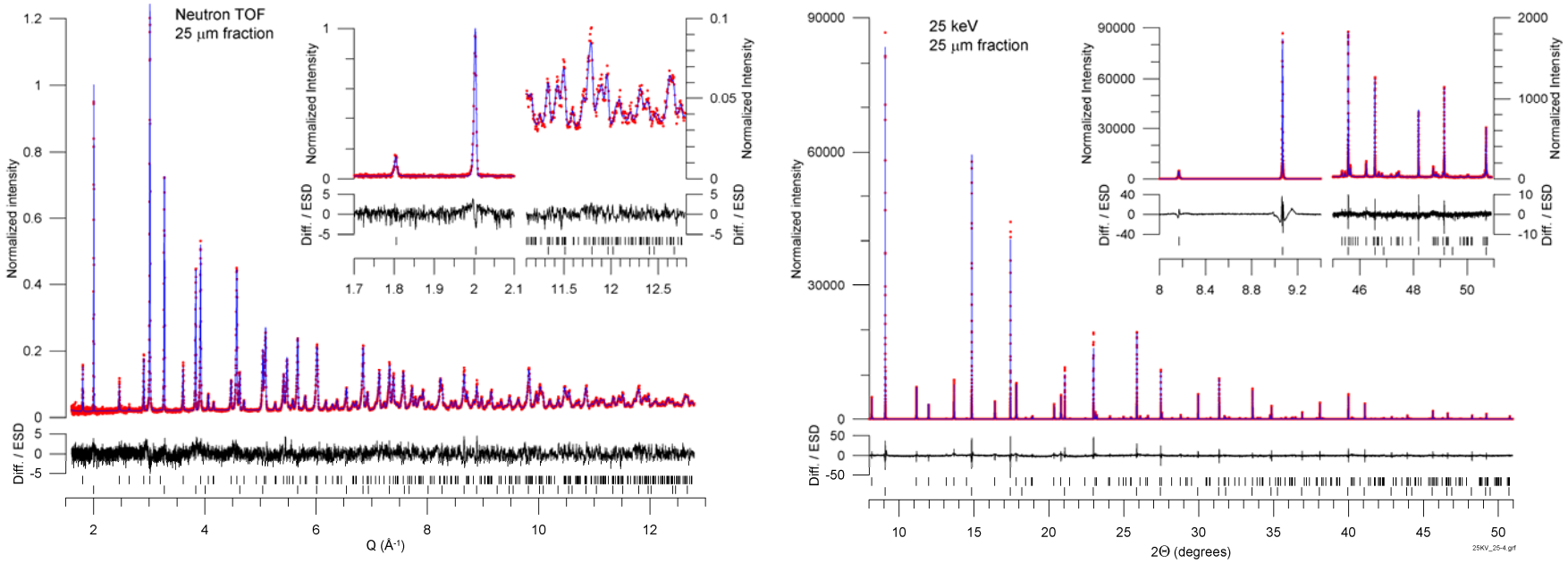
Minimize number of refined parameters

Four joint refinements

Constrain structural parameters across 24 specimens

Microstructural parameters constrained for alumina

Microstructural & extinction parameters constrained within each lot of silicon



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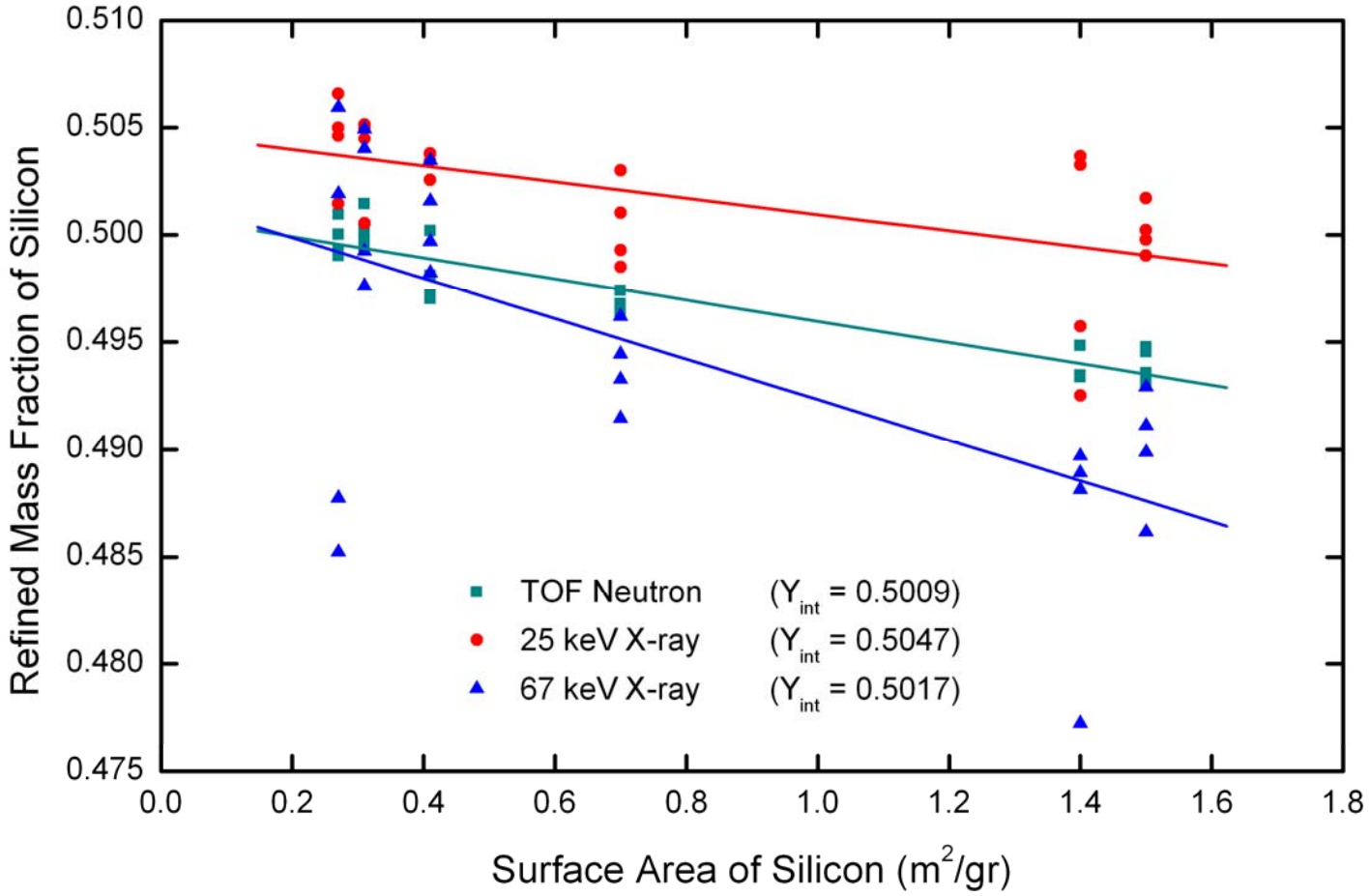
SRM 676a Certification Data

SRM 676a 99.02% ±1.11% phase pure alumina



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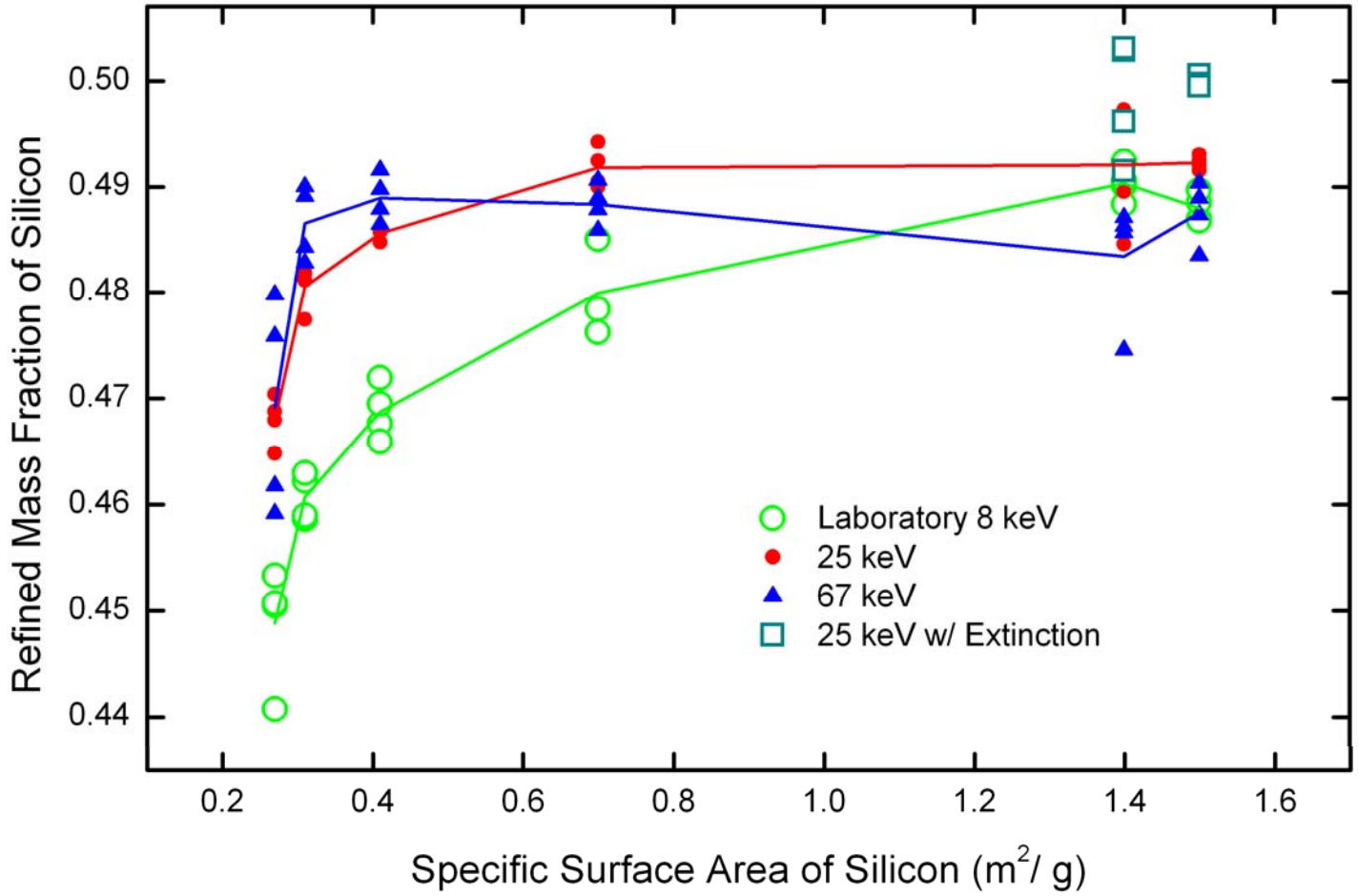
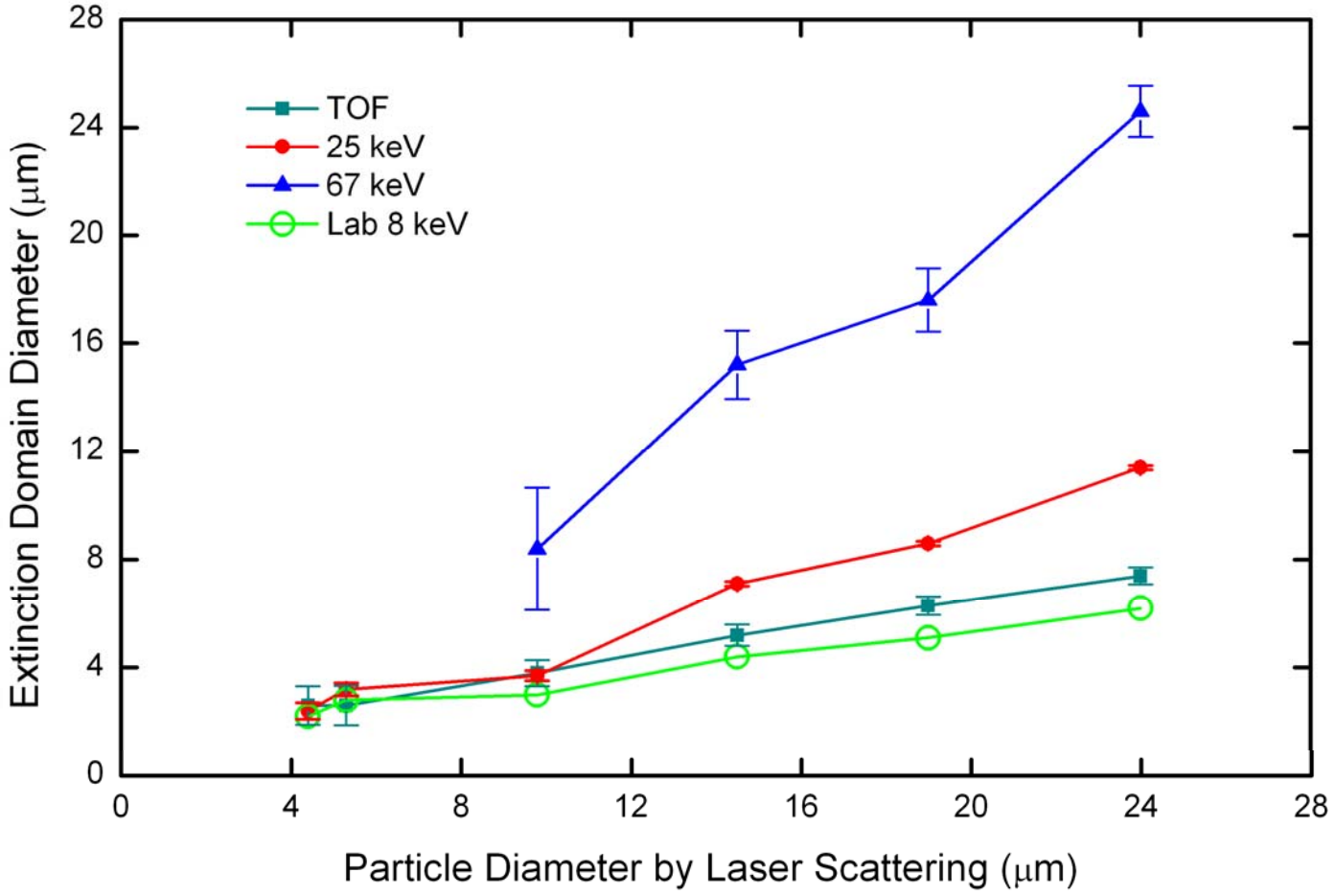
X-ray Data With / Without Extinction Correction

Extinction effects illustrated at < 5 μm particle size range & 67 keV



Refined Extinction Domain Sizes

Consistent within each method
Inconsistent between methods



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Thickness of Oxide (Gunk) Layer on Silicon Powder

Computed from line slope of certification data

Slope = Δ mass of Si displaced by SiO_2 / Δ surface area of Si

= 0.0061 g/m^2 (average slope of TOF, 25 & 67 keV data sets)

Density of SiO_2 = 2.2 g/cm^3 = 0.45 cm^3/g

Layer thickness = 0.0061 (g/m^2) * 0.45 (cm^3/g) * 10^{-6} (cm^3/m^3)

= 0.0028 (cm^3/m^2) * 10^{-6} (cm^3/m^3)

Layer thickness = 2.8 * 10^{-9} m = 2.8 nm

Generally accepted value for thickness of self-limiting oxide layer on silicon under ambient conditions is 1.5 nm

Conclusions

NIST quantitative analysis SRM 676a certified for amorphous content

SRM 676a now permits measurement
of layer thickness or amorphous content in unknowns

Extinction affects diffraction intensity measurements
with both small domain sizes and high energy radiation

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"Addressing the Amorphous Content Issue in Quantitative Phase Analysis:
The Certification of NIST SRM 676a",
Acta Crystallographica Section A, **A67**, 357–367 (2011)