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

<table>
<thead>
<tr>
<th>Diffraction Application</th>
<th>SRM</th>
<th>Composition (Powder)</th>
<th>Unit Size, g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Line Position</td>
<td>640d</td>
<td>Silicon</td>
<td>7.5</td>
</tr>
<tr>
<td>Line Position</td>
<td>675</td>
<td>Mica</td>
<td>7.5</td>
</tr>
<tr>
<td>Line Position</td>
<td>2000</td>
<td>Si (100) with Si/Ge epilayer</td>
<td>2.5 cm sq.</td>
</tr>
<tr>
<td>Line Shape</td>
<td>660b</td>
<td>LaB$_6$</td>
<td>6</td>
</tr>
<tr>
<td>Line Shape</td>
<td>1979</td>
<td>ZnO, 25 nm &amp; 75 nm</td>
<td>3 (each)</td>
</tr>
<tr>
<td>Instrument Response</td>
<td>1976b</td>
<td>Sintered Alumina Plate</td>
<td>2.6 cm disc. x 0.2 cm</td>
</tr>
<tr>
<td>Quantitative Analysis</td>
<td>676a</td>
<td>Alumina (corundum)</td>
<td>20</td>
</tr>
<tr>
<td>Quantitative Analysis</td>
<td>674b</td>
<td>ZnO, TiO$_2$, CeO$_2$, &amp; Cr$_2$O$_3$</td>
<td>10 (each)</td>
</tr>
<tr>
<td>Quantitative Analysis</td>
<td>1878b</td>
<td>Respirable Quartz</td>
<td>5</td>
</tr>
<tr>
<td>Quantitative Analysis</td>
<td>1879a</td>
<td>Respirable Cristobalite</td>
<td>5</td>
</tr>
<tr>
<td>Quantitative Analysis</td>
<td>656</td>
<td>Silicon Nitride: $\alpha$ &amp; $\beta$ phases</td>
<td>10 (each)</td>
</tr>
</tbody>
</table>
Quantitative Analysis via Powder Diffraction

It’s been around for a while

Reference Intensity Ratio, RIR, (Internal Standard) Method

\[ \frac{I_\alpha}{I_s} \left( \frac{I_{js}^{rel}}{I_{i\alpha}^{rel}} \right) \text{ RIR}_{\alpha,s} = \frac{X_\alpha}{X_s} \]

**RIR**: Innate characteristic of the two materials being considered

Chung (1974) “adiabatic” method
Snyder (1992) “normalized RIR”

\[ \frac{X_\alpha}{X_\beta} = \frac{I_\alpha}{I_\beta} \frac{\text{ RIR}_{\beta,s}}{\text{ RIR}_{\alpha,s}} \sum_{k=1}^{n} X_k = 1 \]
Quantitative Rietveld Analysis, QRA

**Apparent standardless quantitative analyses**

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

Yields:

\[
\frac{X_{s(xtal)}}{\sum X_{u(xtal)} + X_{s(xtal)}} = \frac{S_s Z_s w_s}{\sum S_k Z_k w_k} \quad \sum X_{u(xtal)} + X_{u(amor)} = 1 - X_s
\]

\( X_s \) is the mass fraction of phase \( \alpha \)

\( S_s \) are the scale factors

\( w_k \) are the molecular weights

\( Z_k \) are the number of formula weights per unit cell

Quantification via GSAS:

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

\( \sum_{k=1}^{n} X_k = 1 \)
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:

\[ \text{Gibbsite} \rightarrow \text{Transition Aluminas} \rightarrow \text{Corundum} \]

- **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):

\[ \text{Alum} \rightarrow \text{Gamma Alumina} \rightarrow \text{Corundum} \]

- **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

*Baikowski Chimie, France

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

### Particle size via laser scattering

<table>
<thead>
<tr>
<th>%&lt;</th>
<th>µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.58</td>
</tr>
<tr>
<td>50</td>
<td>1.28</td>
</tr>
<tr>
<td>90</td>
<td>2.82</td>
</tr>
</tbody>
</table>

### 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
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

<table>
<thead>
<tr>
<th>Sieve Fraction</th>
<th>SRM 640c</th>
<th>&lt; 5 μm</th>
<th>5 &lt; 10 μm</th>
<th>10 &lt; 15 μm</th>
<th>15 &lt; 20 μm</th>
<th>20 &lt; 25 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle Size, μm</td>
<td></td>
<td>4.44</td>
<td>5.28</td>
<td>9.81</td>
<td>14.47</td>
<td>19.24</td>
</tr>
<tr>
<td>Surface Area, m²/g</td>
<td></td>
<td>1.40</td>
<td>1.50</td>
<td>0.70</td>
<td>0.41</td>
<td>0.31</td>
</tr>
</tbody>
</table>

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

\[
A = \frac{e^2 \lambda F t}{mc^2V}
\]

- \( \lambda \): 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
SRM 676a Certification Data

SRM 676a  99.02% ±1.11% phase pure alumina
Extinction effects illustrated at < 5 μm particle size range & 67 keV
Refined Extinction Domain Sizes

Consistent within each method
Inconsistent between methods
Thickness of Oxide (Gunk) Layer on Silicon Powder

**Computed from line slope of certification data**

\[
\text{Slope} = \frac{\Delta \text{mass of Si displaced by SiO}_2}{\Delta \text{surface area of Si}}
\]

\[
\text{Density of SiO}_2 = 2.2 \text{ g/cm}^3 = 0.45 \text{ cm}^3/\text{g}
\]

Layer thickness = \[0.0061 \text{ (g/m}^2\) \times 0.45 \text{ (cm}^3/\text{g}) \times 10^{-6} \text{ (cm}^3/\text{m}^3\)\]

\[
= 0.0028 \text{ (cm}^3/\text{m}^2\) \times 10^{-6} \text{ (cm}^3/\text{m}^3\)\]

Layer thickness = \[2.8 \times 10^{-9} \text{ m} = 2.8 \text{ nm}\]

**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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