Development and Certification of NIST Standard Reference Materials for Powder Diffraction

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Calibration of Diffraction Line Position

Qualitative phase analyses:
Improved performance of search/match algorithms

Two Theta

Intensity (arb units)

ICDD “d/I” reference pattern

observed data

the “x” variable
SRM 1976b: Suitable laboratory diffractometers using conventional data analysis methods

the “y” variable

Sintered $\text{Al}_2\text{O}_3$ discs of SRM 1976b
Quantitative Phase Analyses

**SRM 676a, alumina powder, certified with respect to absolute phase purity**

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

**Reference Intensity Ratio, RIR, (Internal Standard) Method**

I/Ic, the RIR of a given phase relative to Al₂O₃ (corundum), Parameter included in ICDD database

Boundary of any crystalline solid will include an amorphous component

Ultimate measurement issue: Crystalline phase purity
Rigorous modeling of all aspects of the diffraction experiment for crystal structure analysis

Refinement of SRM 660b LaB$_6$
Microstructure Analysis via Powder Diffraction

Crystallite size and lattice defect induced broadening of diffraction profiles

- SRM 660b Instrument Profile Function
- SRM 1979 "15" nm ZnO
- SRM 1979 "60" nm ZnO

Intensity vs. Two Theta graph showing diffraction profiles.
Certification of NIST Diffraction SRMs

A technical approach with four primary facets

Calibration Artifact

- **Materials** – Stable, non-toxic, well-characterized, homogeneous, large feedstock volumes, with microstructures optimized for diffraction properties

- **Structure** – Useful, easily modeled diffraction features for instrument calibration

Instrumentation & Data Collection

- **Instrumentation** – Three NIST-constructed gizmos, angle-encoded, capable of SI traceable measurements

- **Instrument Response** – Instrument performance validated using NIST SRMs

Theory & Data Analysis

- **Theory** – Fundamental Parameters Approach to model instrument profile function and sample microstructure

- **Model Selection** – Independent evaluation of IPF parameters and feedstock character

Virtues and use of SRMs

- **Instrumentation** – Virtues and drawbacks of various optical geometries

- **Data Analysis Methods** – Cost / benefit analysis of complex vs. simple methods
# NIST SRMs for X-ray Wavelength Metrology

<table>
<thead>
<tr>
<th>SRM</th>
<th>Material / Format</th>
<th>Diffraction Application</th>
<th>Unit Size (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>640d</td>
<td>Silicon Powder</td>
<td>Line Position &amp; Line Profile</td>
<td>7.5</td>
</tr>
<tr>
<td>675</td>
<td>Mica Powder</td>
<td>Line Position, Low 2θ</td>
<td>7.5</td>
</tr>
<tr>
<td>2000</td>
<td>Silicon (100) Wafer with SiGe Epilayer</td>
<td>High-Resolution Line Position &amp; Reflectometry</td>
<td>25 mm square</td>
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<tr>
<td>660b</td>
<td>LaB$_6$ Powder</td>
<td>Line Position &amp; Line Profile</td>
<td>6</td>
</tr>
<tr>
<td>1979</td>
<td>ZnO Powders</td>
<td>Line Profile, 20 nm &amp; 70 nm</td>
<td>3</td>
</tr>
<tr>
<td>1976b</td>
<td>Sintered Alumina Plate</td>
<td>Instrument Response</td>
<td>2.5 cm disc</td>
</tr>
<tr>
<td>676a</td>
<td>Alumina (corundum) Powder</td>
<td>Quantitative Analysis</td>
<td>20</td>
</tr>
<tr>
<td>674b</td>
<td>Powder Set: ZnO, TiO$_2$, CeO$_2$, Cr$_2$O$_3$</td>
<td>Quantitative Analysis</td>
<td>10 (each)</td>
</tr>
<tr>
<td>1878a</td>
<td>Respirable Quartz Powder</td>
<td>Quantitative Analysis</td>
<td>5</td>
</tr>
<tr>
<td>1879a</td>
<td>Respirable Cristobalite Powder</td>
<td>Quantitative Analysis</td>
<td>5</td>
</tr>
<tr>
<td>656</td>
<td>Silicon Nitride: α &amp; β Powders</td>
<td>Quantitative Analysis</td>
<td>10 (each)</td>
</tr>
</tbody>
</table>
SI Traceability in Certification of Diffraction SRMs

\[ \lambda = 2d \sin \theta \]
Angle metrology
Parallel Beam Diffractometer (PBD)

**SI traceability / accuracy in wavelength and lattice parameter measurement**

Measurement capability in HRXRD, XRR, and powder diffraction

Interchangeable optics and sample stages

Vertical axes, concentrically mounted
Huber 430 rotation stages

Heidenhain RON 905 optical encoders on primary axes

Short and long range encoder calibration

SI-traceable reference crystals

Located in temperature controlled environment \( \approx \pm 0.02^\circ \text{C} \)
SI Traceable Measurement of Lattice Parameters on Powders with PBD

High-resolution Soller slit analyzer
Measure Four – Theta: “Bond method”
Collect full range of profiles
Performance of Mirror Optic Determined via Double Crystal diffraction

Reciprocal space map illustrates divergence between $K\alpha_1$ and $K\alpha_2$ beam directions
NIST – Built Divergent Beam Diffractometer (DBD)

Conventional divergent beam optics with high-performance goniometer

Second optical platform for corroboration of SI traceable measurements

Homogeneity verification
Studies of data analysis methods
Microstructure analysis

Optics from Siemens D5000 / D500
Huber 420 rotation stages
Heidenhain RON 800 series optical encoders on primary axes
Interchangeable optics,
Incident beam monochromator
Linear PSD

Located in a temperature controlled environment ≈ ±0.1° C
Overhead diagram of DBD

- X-ray source & optics mounting platform
- Counterweight
- Encoders
- Detector arm and mount
- Chassis for mounting of stages
- X-ray beam path
Stiff and Balanced Detector Arm
**Fundamental Parameter Approach (FPA) to Analysis of Powder Diffraction Data**

*Cheary & Coelho (1992,1998) as implemented in TOPAS*

Geometric instrument contribution characterized with a series of explicit physical models linking instrument geometry to the observed profile.
Current CuKα Emission Spectrum Characterization


Four Lorentzian profiles used for analytical representation of the CuKα spectrum
Observation of Tube Tails & “Kα3” Satellite Lines

Proper modeling of tube tails critical for microstructure analysis

410 reflection from SRM 660b

“Kα3” satellite lines

Two Theta

Tube Tails
Johansson Incident Beam Monochromator (IBM)

“Removes” $K\alpha_2$, $K\alpha_3$ & Tube Tails

Asymmetric Ge 111 crystal
Ground to 2R and bent to R (Rowland circle)
NIST – Built DBD Configured with Johansson IBM

Divergent beam optics with “monochromatic” source

Siemens D500 tube shield with Huber 502 optic alignment:
Features fully orthogonal adjustment capability

Modern Crismatec Johansson optic
Performance of Johansson IBM

Crismatec (Saint Gobain) Johansson optic
Ge 111 crystal bent via cementing in pre-form

Characterization of emission spectrum for FPA via convolution of Gaussian profile shape functions
Fits of Split Pearson 7 PSF to IBM data

Excellent fit quality to IBM data using analytical PSF
FWHM data from SRMs 640d, 660b and 1976b

FWHM values follow trends consistent with expectations as per contributions from Geometric and Wavelength Profiles
Parameters Affecting Geometric Profile

Divergent beam laboratory X-ray powder diffractometer
### Aberrations Contributing to Geometric Component

May affect both profile shape and position

<table>
<thead>
<tr>
<th>Aberration</th>
<th>Controlling parameters</th>
<th>Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray Source Width ($w_x$)</td>
<td>Angle subtended by source: $\frac{w_x}{R}$</td>
<td>Symmetric broadening</td>
</tr>
<tr>
<td>Receiving Slit Width ($w_r$)</td>
<td>Angle subtended by slit: $\frac{w_r}{R}$</td>
<td>Symmetric broadening</td>
</tr>
<tr>
<td>Flat Specimen Error / Equatorial Divergence</td>
<td>Angle of divergence slit: $\alpha$</td>
<td>Asymmetric broadening to low $2\theta$, with decreasing $2\theta$</td>
</tr>
<tr>
<td>Axial Divergence</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case 1: No Soller slits</td>
<td>Axial lengths of the x-ray source ($L_x$) sample ($L_n$) &amp; receiving slit ($L_r$) relative to goniometer radius ($R$)</td>
<td>Below $\approx 110^\circ$: Asymmetric broadening to low $2\theta$, with decreasing $2\theta$ Else to high $2\theta$, with increasing $2\theta$</td>
</tr>
<tr>
<td>Case 2: Soller slits define divergence angle</td>
<td>Acceptance angles $\Delta_I$ and $\Delta_D$ of the incident and diffracted beam Soller slits</td>
<td></td>
</tr>
<tr>
<td>Specimen transparency</td>
<td>Penetration factor relative to diffractometer radius $\frac{1}{\mu R}$</td>
<td>Asymmetric broadening to low $2\theta$, with $\sin(\theta)$</td>
</tr>
<tr>
<td>Specimen Displacement Z height</td>
<td>Displacement of specimen surface from goniometer rotation axes</td>
<td>Displacement of profiles with $1/\cos(\theta)$</td>
</tr>
</tbody>
</table>
Diagram of an Aligned X-ray Diffractometer

*Functionality of FPA dependent on proper alignment*

Requisite on:

1) Source-to-sample distance equals sample-to-receiving slit distance ($R_1 = R_2$)
2) X-ray line source, sample, and receiving slit centered in plane of diffraction
3) Goniometer rotation axes are co-axial
4) X-ray line source, sample surface, receiving slit, and goniometer rotation axes are co-planar, in the “zero” plane, at zero angle of theta and two-theta
5) Incident beam is centered on both equatorial and “zero” planes
Data Analysis Strategy

Determine extent and nature of flaws in FPA model

Compare refined lattice parameters from FPA Rietveld analysis with those from FPA “Profile” analysis

Always refine parameters that are indeterminate
Sometimes refine parameters that are known or essentially invariant between standards and unknowns
Never refine parameters that well known and correlate with unknowns

Always Refine:
- Axial divergence value
- Z height
- Specimen transparency
- Position & intensity of $K\alpha_2$ lines
- Structural model(s)
- Microstructure model(s)

Sometimes Refine:
- Breadth of $K\alpha_1$ and $K\alpha_2$ lines
- Inc and rec slit values
- “Tube Tail” parameters
- “$K\alpha_3$” line intensity

Never Refine:
- Zero angles
Fundamental Parameters Analysis of SRM 660b

FPA “profile” analyses: Profile positions (lattice parameters) free to refine, FPA shape parameters constrained

Plausible parameters realized throughout *
Impact of Graphite Post Monochromator on Breadth of CuKα Emission Spectrum

20% Reduction in breadth
Shift of 0.01°

Portion of Topas .inp file illustrating refinement of profile breadths
Shape of Kα₁ and Kα₂ lines constrained to that defined by Hölzer
Comparison of Lattice Parameter Data from FPA Rietveld vs. Profile

No Complaints; However, trends are indicated
Comparison of Lattice Parameter Data from FPA Rietveld vs. Profile: Certification of SRM 660b

Type A (statistical) vs. Type B (systematic) error bounds

Certification Data, ca. 2009
Finite Element Analysis of Change in Torque Moment with Rotation of Two-Theta Arm
Quantitative Rietveld Analysis, QRA

**Diffraction experiment assesses crystalline component only**

Quantification via GSAS:

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

- \(X_{\alpha}\) is the mass fraction of phase \(\alpha\)
- \(S_{\alpha}\) are the scale factors
- \(w_{\alpha}\) are the molecular weights
- \(Z_{\alpha}\) are the number of formula weights per unit cell

\[
\sum_{k=1}^{n} X_{k} = 1
\]

**Suitable Standard:**

\[
X_{s} = X_{s(xtal)} + X_{s(amar)}
\]

**Yields:**

\[
\frac{X_{s(xtal)}}{\sum X_{u(xtal)} + X_{s(xtal)}} = \frac{S_{s} Z_{s} w_{s}}{\sum S_{k} Z_{k} w_{k}}
\]

\[
\sum X_{u(xtal)} + X_{u(amar)} = 1 - X_{s}
\]
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

\[ \frac{I}{I_c} \]

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

<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>

*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

Cumulative Mass Percent Finer Than

Particle Size, µm

DA = 125

DV = 250
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

*Diffraction experiment: crystalline fraction only
  Weighing operation: all constituents*
Determination of Amorphous Fraction II

Execution

Commute 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>4.44</td>
<td>5.28</td>
<td>9.81</td>
<td>14.47</td>
<td>19.24</td>
<td>23.98</td>
</tr>
<tr>
<td>Surface Area, m²/g</td>
<td>1.40</td>
<td>1.50</td>
<td>0.70</td>
<td>0.41</td>
<td>0.31</td>
<td>0.27</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
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

![Graph showing extinction domain diameter vs. particle diameter by laser scattering](image-url)
Thickness of Oxide (Gunk) Layer on Silicon Powder

**Computed from line slope of certification data**

\[
\text{Slope} = \frac{\Delta \text{mass of Si displaced by SiO}_2}{\Delta \text{surface area of Si}} = 0.0061 \text{ g/m}^2 \text{ (average slope of TOF, 25 & 67 keV data sets)}
\]

Density of SiO\(_2\) = 2.2 g/cm\(^3\) = 0.45 cm\(^3\)/g

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

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

The divergent beam diffractometer has yielded lattice parameter values that are credible to ± 8 femtometers

We look forward to results from the parallel beam diffractometer

The *Fundamental Parameters Approach* yields the best fits to the observations and plausible refined parameters describing the experimental configuration

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