

**X-ray Diffraction Methods Subcommittee
International Centre for Diffraction Data
Minutes of the Meeting of 13 March 2013**

Dr. Papoular called the meeting to order at 10:00 am.

Attending: List of attendees list was circulated.

M. Suchomel appointed meeting secretary.

Previous minutes from March 2012 are discussed, and approved.

BoD report: J Rius has no report from the board, as there were no motions in 2012.

New Business:

1) Standard reference materials for powder diffraction:

J. Cline was scheduled to give overview talk on the importance of standard reference materials (SRM) for powder XRD and discuss appropriate SRMs. Jim could not make the meeting – his talk may be postponed to next year.

(Note 1: after the meeting was over, Jim kindly volunteered the slides for his talk and the latter are linked to this box and attached at the end of these minutes. Additional information taken from his NIST website completes the latter and renders it self-contained.)

Topics that could be addressed include - which are the best standards (only NIST ones?) Different standards are best for different samples and problems. Could this info be added to the database and/or recommendations (best practices?) posted for the ICDD community on this topic? *(Note 2: there was further discussion on this topic later in the meeting as noted below)*

2) Extraction of Powder Diffraction (PD) Intensity for Structure Solution

J. Rius presents a talk about PD intensity clustering for structure determination (SD)

- Effective use of direct methods (DM) attempts at PDSO can be limited by a combination of data resolution & fitting peak overlap.
- Traditional DM only uses low angle data - with no overlap.
- A 'cluster' method approach can use resolved peak cluster info at higher 2theta angles
- How to define the cluster? Using the "coincidence" & "residual" functions are defined.
- New program (DAJUST) produces these cluster lists – then use these lists with XLENS, a direct methods program based on the modulus sum function:
- Also presented; TALP – a new program from J Rius for direct space method powder SD, other programs similar include FOX, DASH, ESPOIR, PSSP, TOPAS, PowderSolve.
- Explanation of new TALP program, showing also how the molecular model and restraints are defined in the program GUI.

Discussion point (R. Papoular): Would it be possible to use this program to back calculate atomic coordinates in the ICDD database from old datasets?

Discussion point (R. Papoular): is it possible to establish criteria which predict if a PD pattern is suitable for a smooth crystal structure determination by direct methods?

Discussion point: Is it possible to provide an analysis tool (or some guidelines) for users to predict if their data has a chance to be solved by direct methods?

No motions or further discussion on this topic.

3) Standard reference materials for powder diffraction (Part 2):

Discussion leads by R. Papoular:

- Should more information about standards and/or calibrating samples be deposited (when available) with data added into the ICDD database?
- Could/Should data on the lab instruments alignment be required for GiA and/or voluntary submissions?
- ICDD editors do ask this already from new GiA [S. Misture].
- This is a grant-in-aid requirement – for new GiA – and at the start of new cycles each GiA must submit new data on a SRM. [S Kabekkodu].
- However - ICDD does not always get this information from GiA [S Kabekkodu]
- Fawcett has done a cluster analysis on GiA SRM data sets to roughly check if instrument is "OK" – also they have other checks to catch 'bad' data from submitted entries (compare lattice, volume, DI list, etc.)
- ICDD has hundreds of old SRM data sets; also some years ago (2004?) J. Faber *et al* published an IUCr paper of ~ 30 SRM datasets from 5 years – showing the average and spread. Might be repeated with newer datasets.
(Note: *J. Appl. Cryst.* (2004). 37, 635-642)
- M Leoni suggests that Si (or other standard data) should be asked each time
- T. Fawcett replies this is not always possible, and states that other checks mentioned above are in place at the review and editorial stages, and work well. Some GiA investigators go on probation if data sets are bad or suspicious.
- ~ 50% or more of GiAs submit SRMs data with patterns - but it is especially stressed for new GiAs
- About instrument profile terms – S. Kabekkodu says that these are not included in database, but much of these data are stored.

No motions or further discussion on this topic.

4) Total scattering (Pair-Distribution Function) data in the ICDD:

Short note by T. Fawcett: Valeri Petkov continues to work with ICDD staff on this topic; it is complicated with many elements to consider. Despite some recent ICDD staff losses which will delay the project – it is still active, and anyone who wants to help should get in touch with Fawcett or Kabekkodu.

The meeting was adjourned at 11:00 AM.



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

James P. Cline

**Robert B. Von Dreele¹, Ryan Winburn²,
Peter W. Stephens³ and James J. Filliben**

National Institute of Standards and Technology
Gaithersburg MD, USA

¹Argonne National Laboratory
Argonne, IL

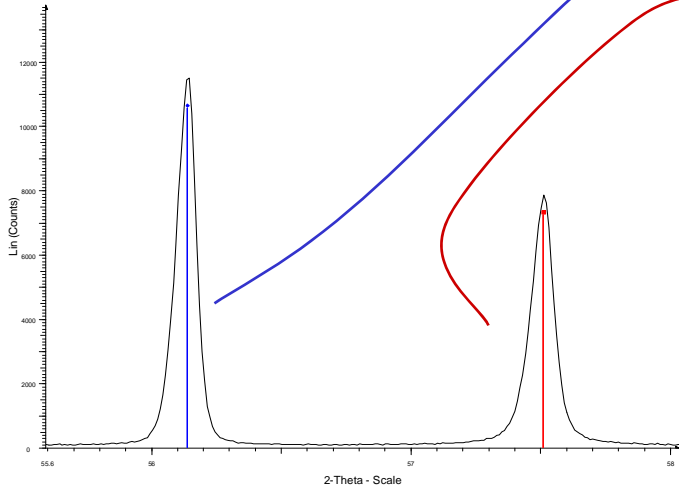
²Minot State University
Minot, ND

³State University of New York at Stony Brook
Stony Brook, NY



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

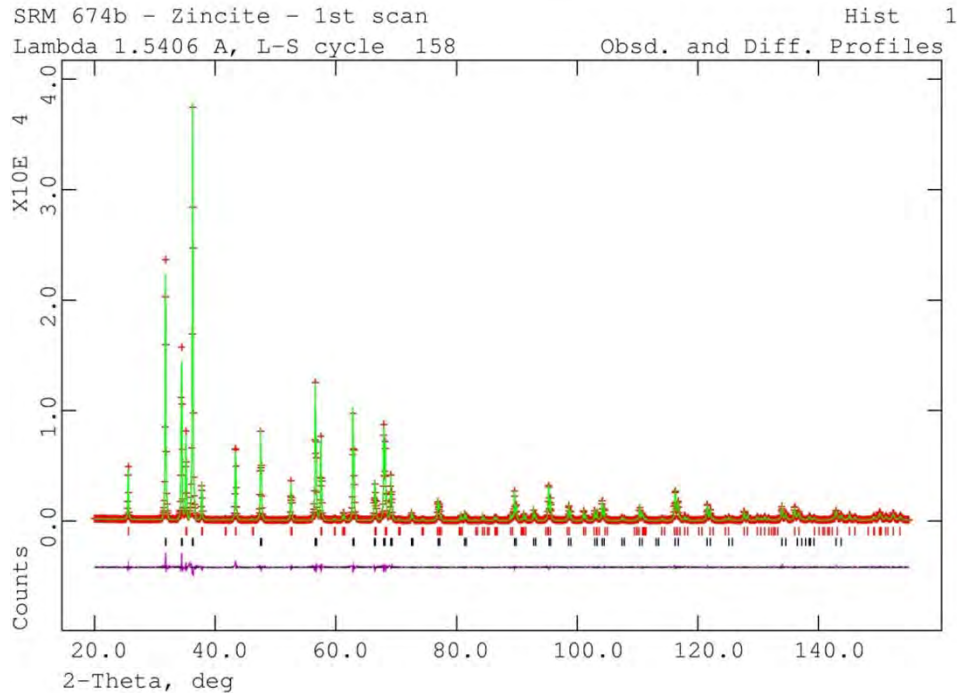
Chung (1974) “adiabatic” method
Snyder (1992) “normalized RIR”

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



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: $X_s = X_{s(\text{xtal})} + X_{s(\text{amor})}$ Yields:

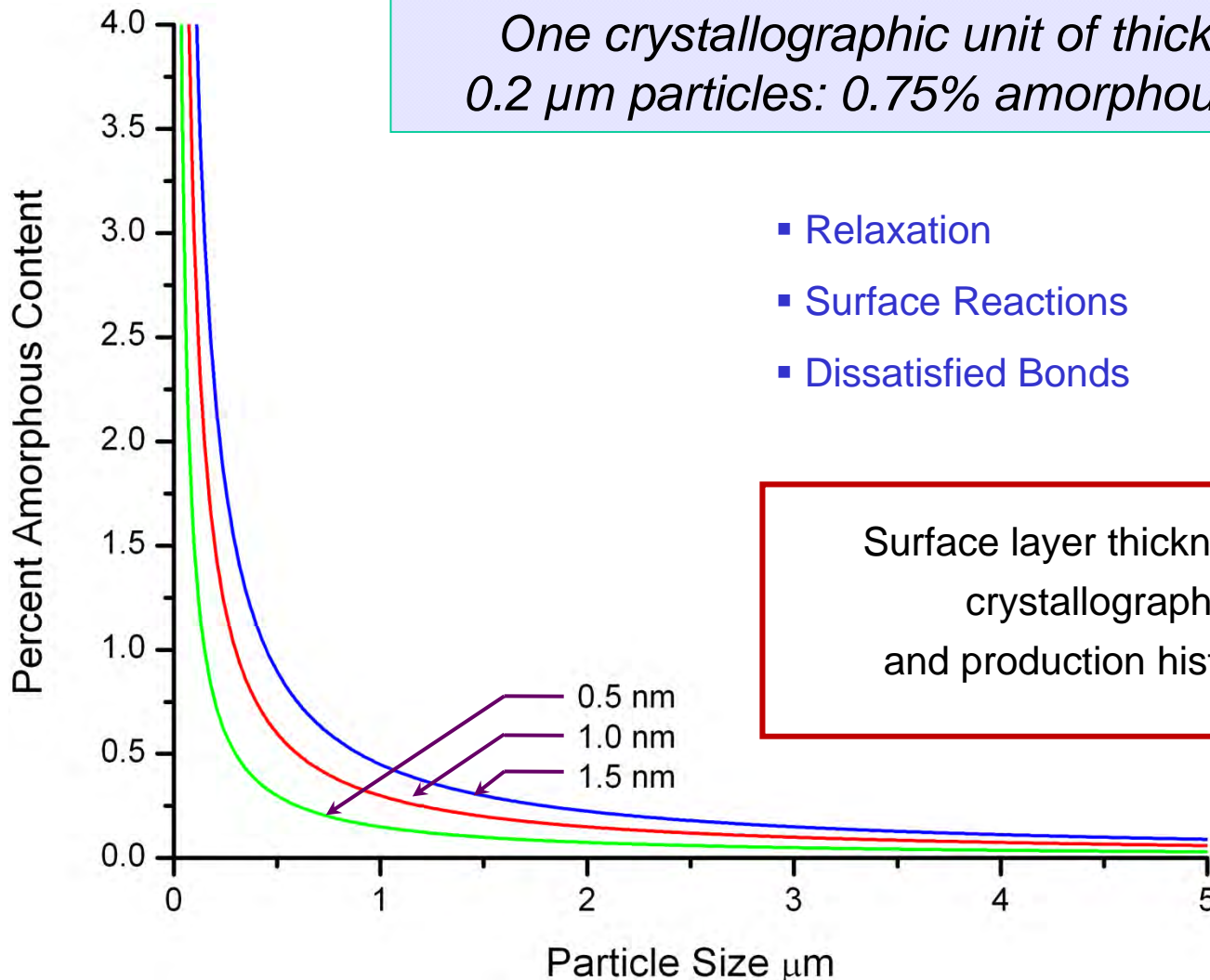
$$\frac{X_{s(\text{xtal})}}{\sum X_{u(\text{xtal})} + X_{s(\text{xtal})}} = \frac{S_s Z_s w_s}{\sum S_k Z_k w_k}$$

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



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

I/I_c Proposed by Visser and deWolff (1964)

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

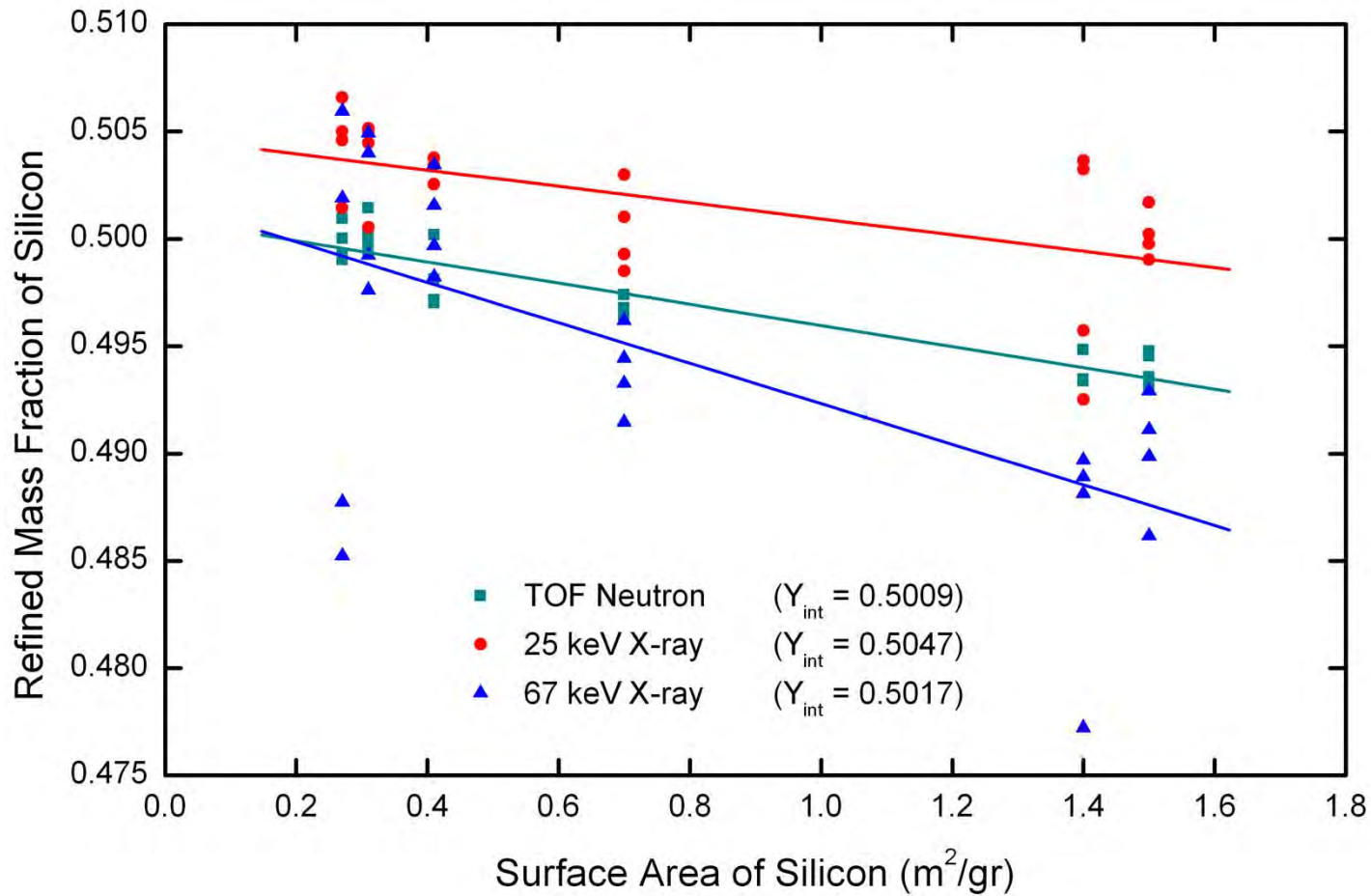
Desired characteristics of SRM feedstock

- 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)



SRM 676a Certification Data

SRM 676a 99.02% \pm 1.11% phase pure alumina





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

"Addressing the Amorphous Content Issue in Quantitative Phase Analysis:
The Certification of NIST SRM 676a",
J.P. Cline, R.B. Von Dreele, R. Winburn, P.W. Stephens and J.J. Filliben,
Acta Crystallographica Section A, **A67**, 357–367 (2011)



The Calibration of Laboratory X-Ray Diffraction Equipment Using NIST Standard Reference Materials

**James P. Cline, David Black,
Donald Windover, Albert Henins,**

National Institute of Standards and Technology, Gaithersburg MD, USA

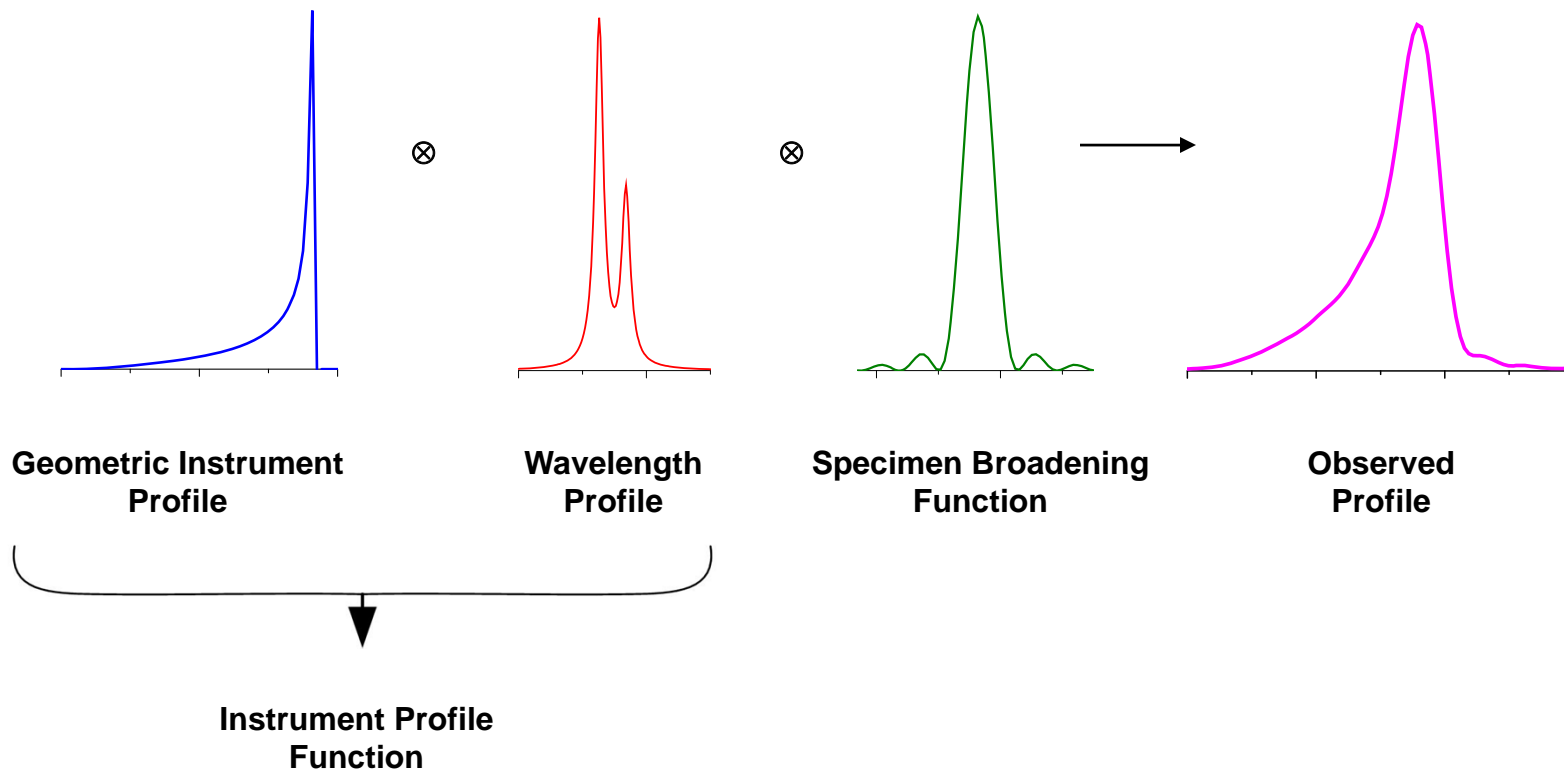
Robert W. Cheary

Richard D. Deslattes



Convolution of Functions to Synthesize Observed Profile Shape

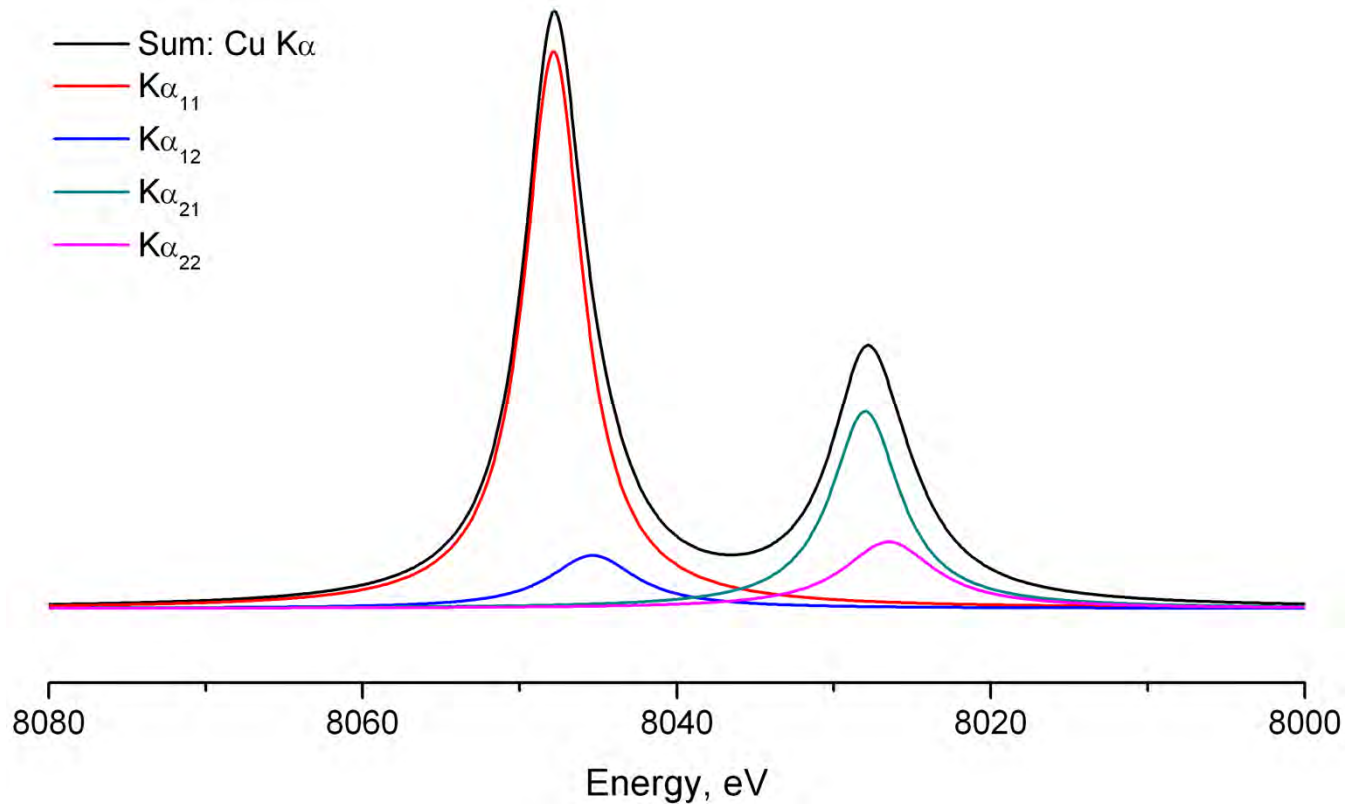
Constant wavelength powder diffractometer





Current Emission Spectra Characterization

Hölzer, *et al.*, Phys. Rev. A (1997)



Four Lorentzian profiles used for analytical representation of the CuK α spectrum



Aberrations Contributing to Geometric Component

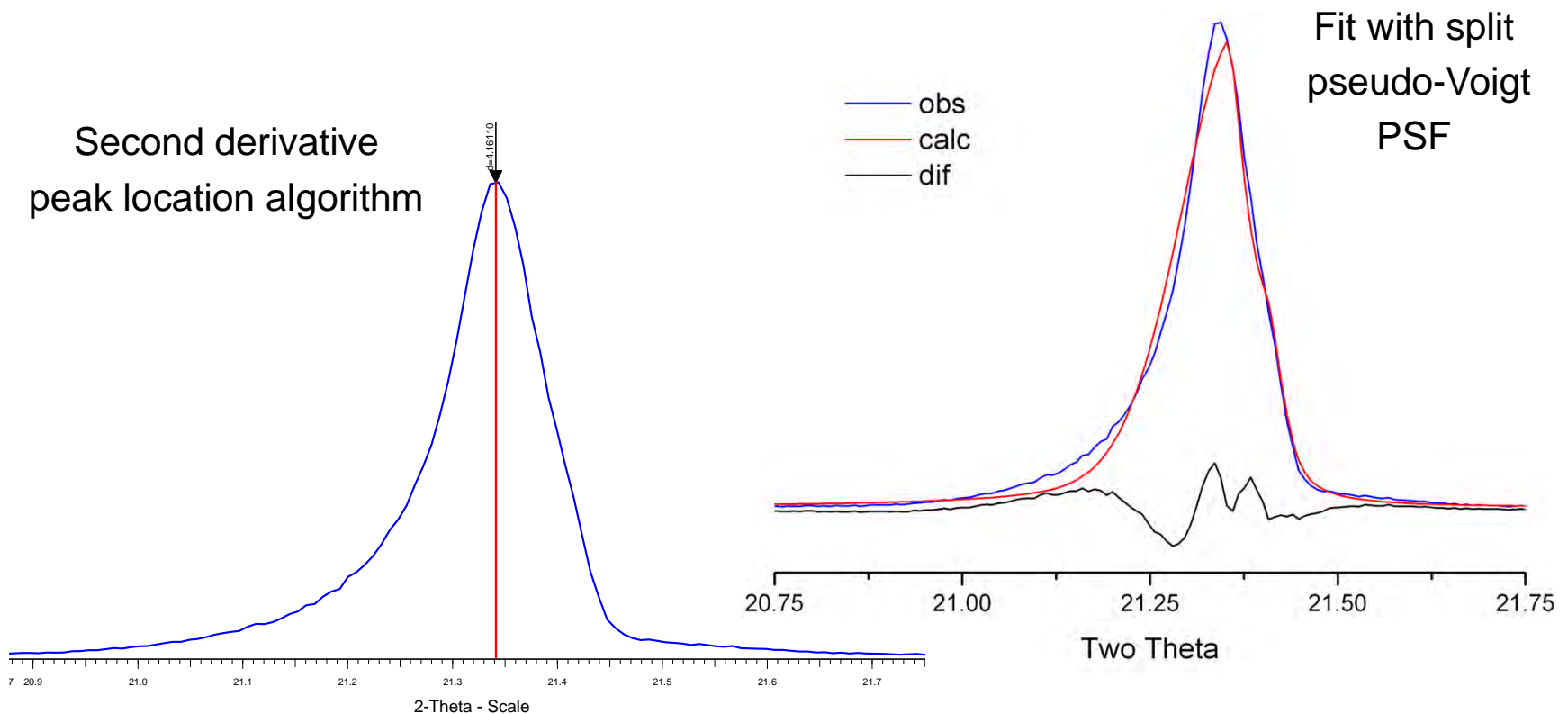
May affect both profile shape and position

Aberration	Controlling parameters	Impact
X-ray Source Width (w_x)	Angle subtended by source: $\frac{w_x}{R}$	Symmetric broadening
Receiving Slit Width (w_r)	Angle subtended by slit: $\frac{w_r}{R}$	Symmetric broadening
Flat Specimen Error / Equatorial Divergence	Angle of divergence slit: α	Asymmetric broadening to low 2θ , with decreasing 2θ
Axial Divergence Case 1: No Soller slits Case 2: Soller slits define divergence angle	Axial lengths of the x-ray source (L_x) sample (L_s) & receiving slit (L_r) relative to goniometer radius (R) Acceptance angles Δ_I and Δ_D of the incident and diffracted beam Soller slits	Below $\approx 110^\circ$: Asymmetric broadening to low 2θ , with decreasing 2θ Else to high 2θ , with increasing 2θ
Specimen transparency	Penetration factor relative to diffractometer radius $\frac{1}{\mu R}$	Asymmetric broadening to low 2θ , with $\text{Sin}(\theta)$
Specimen Displacement Z height	Displacement of specimen surface from goniometer rotation axes	Displacement of profiles with $1/\text{Cos}(\theta)$



Second Derivative vs. Profile Fitting for Determination of Peak Location

Profile fitting may yields results that are in error by 0.015° while 2nd derivation methods are precise to 0.0025°

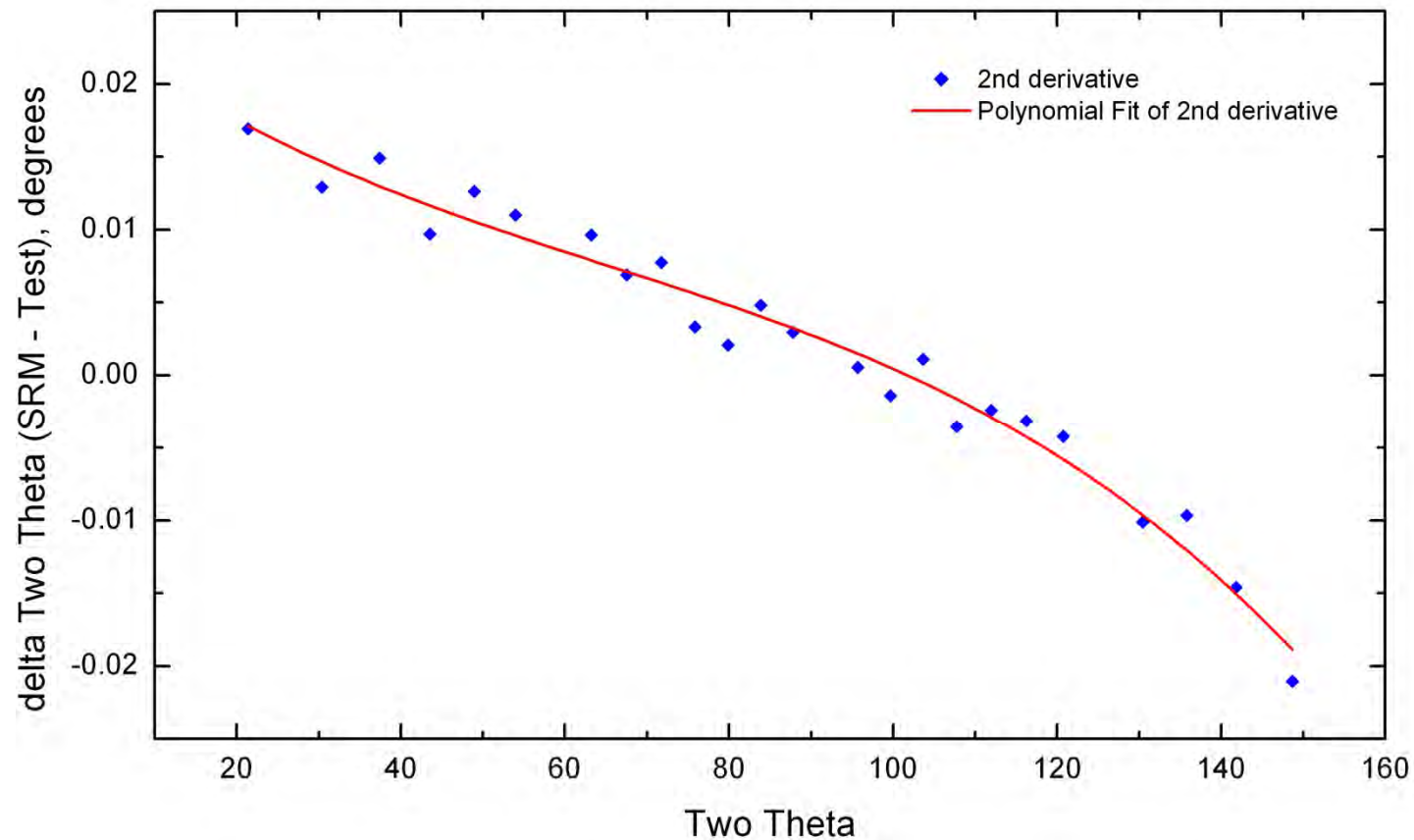


Complex XRD profile shape can not be fit accurately with analytical PSF



Delta Two-Theta Curve via SRM 660b

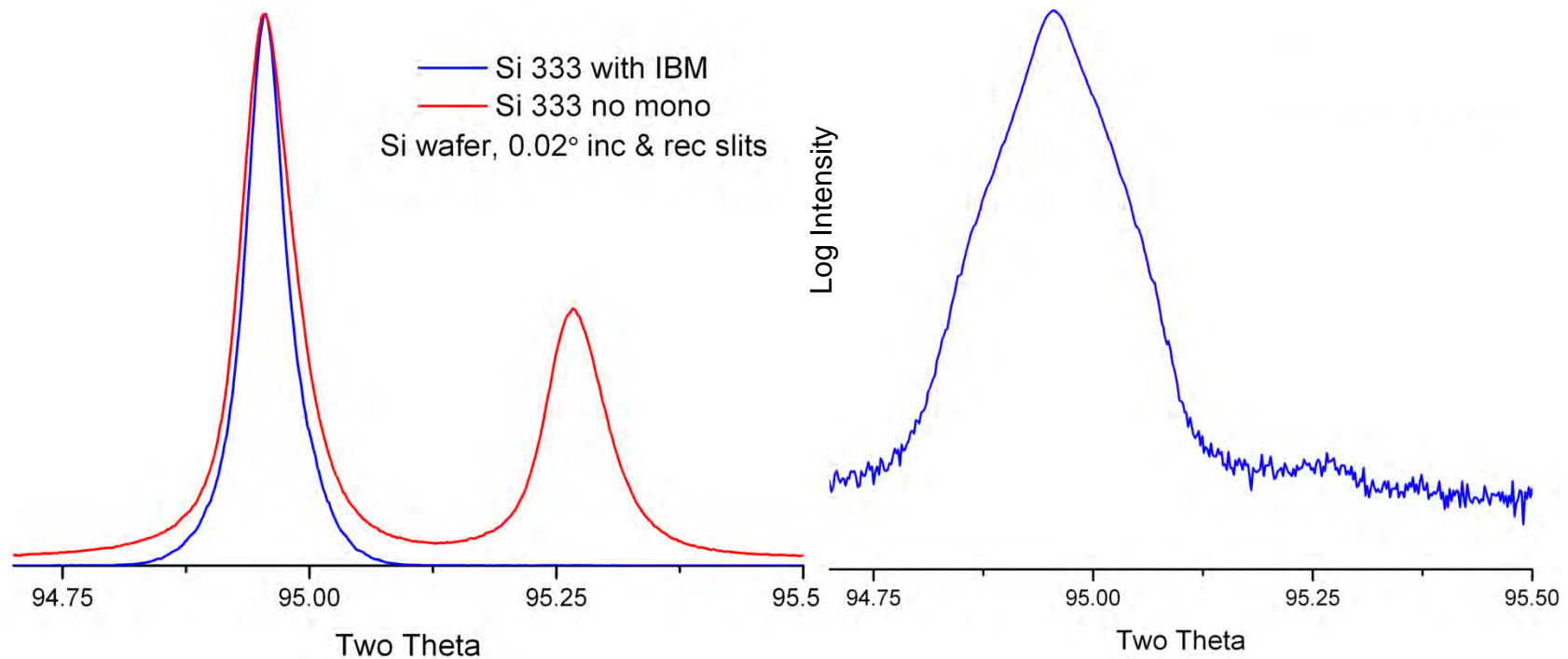
Deviations in position of peak maxima are consistent with expectations as per contributions from Geometric and Wavelength Profiles





Performance of Johansson Incident Beam Monochromator (IBM)

Crismatec (Saint Gobain) Johansson optic Ge 111



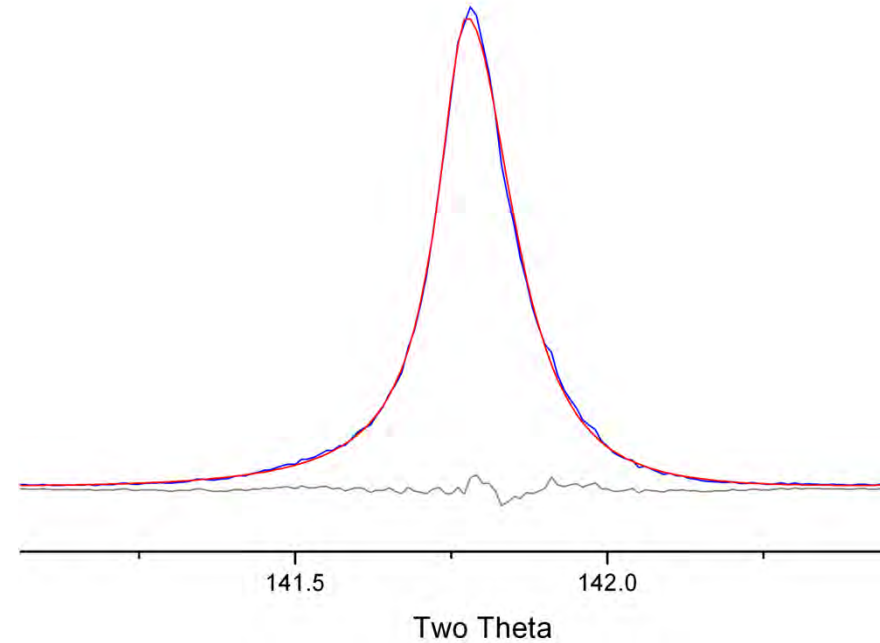
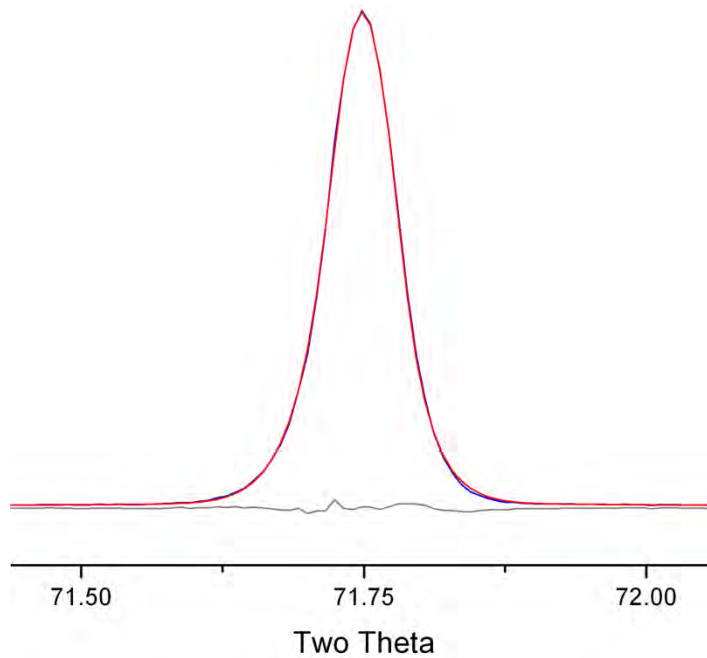
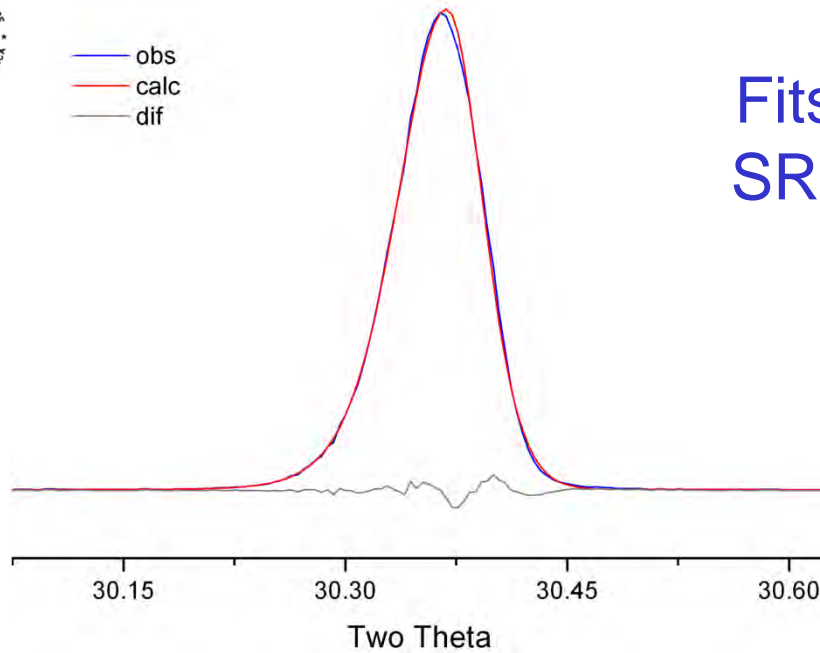
Simplified XRD profile shape



— obs
— calc
— dif

Fits of LaB_6 100, 310 & 510 lines, SRM 660b, Split Pearson VII PSF Johansson IBM

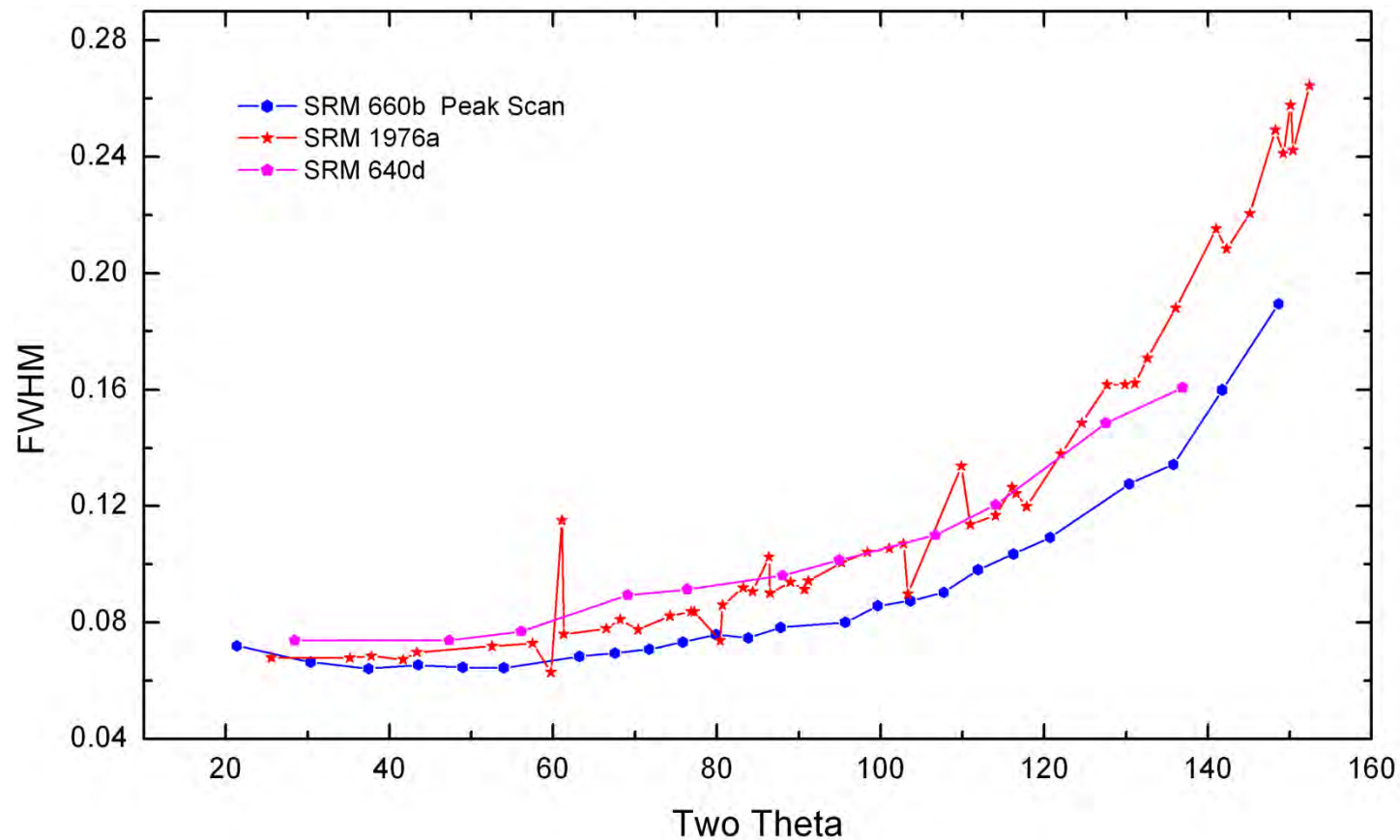
*Excellent fit with analytical
profile shape functions*





FWHM data from SRMs 640d, 660b and 1976b

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





Conclusions

SRM 660b is the optimal standard for use in characterization of the IPF;
SRMs 640d and 1976b can be used to obtain qualitative results

Care must be exercised when interpreting results from profile fitting using
analytical profile shape functions

Proper use of SRMs can verify that equipment is operating in conjunction with
expectations, as per a knowledge of the Geometric and Wavelength Profiles

“The Calibration of Laboratory X-Ray Diffraction Equipment
Using NIST Standard Reference Materials”

James P. Cline, David Black, Donald Windover, and Albert Henins

Modern Diffraction Methods

Edited by Eric J. Mittemeijer and Udo Welzel

Wiley-VCH Verlag & Co., Germany (2013)

Diffraction Metrology and Standards

Objective

Our objective is the development of Standard Reference Materials (SRMs) and quantitative, reproducible, and accurate measurement methods for characterization of any structure possessing spatial order on the scale of X-ray wavelengths. Such SRMs and measurement methods will aid in the development of new crystalline materials and devices made from them. Therefore, the impact of this project includes pharmaceuticals, ceramics, metals, semiconductors, and polymers.



Impact and Customers

- Our primary impact is the enhancement of the measurement capability of the laboratory X-ray diffractometer; there are 20,000 in use worldwide.
- Two of the three major instrument vendors supply NIST Diffraction Metrology SRMs with the equipment they sell. One vendor includes SRM 1976 with every instrument and, as a result, has been able to improve their angular resolution three times over the previous value.
- Calibration of equipment with NIST Diffraction Metrology SRMs is requisite for ISO certification.
- Primary customers are the International Center for Diffraction Data (ICDD) and X-ray instrument vendors (BEDE, Bruker AXS, Jordan Valley, PANalytical, Rigaku and Technos).

SRM	Material / Format	Diffraction Application	Unit Size (g)
640c	Silicon Powder	Line Position & Line Profile	7.5
675	Mica Powder	Line Position, Low 2 θ	7.5
2000	Silicon 100 Wafer with SiGe epi-layer	Hi-Resolution Line Position & Reflectometry	2.5 cm sq
660a	LaB ₆ Powder	Line Position & Line Profile	6
1979	CeO ₂ & ZnO Powders	Line Profile	New, In Prep
1976a	Sintered Alumina Plate	Instrument Response	2.6 cm disc x 0.2 cm
676a	Alumina (corundum) Powder	Quantitative Analysis	20
674b	Powder Set: ZnO, TiO ₂ , CeO ₂ , & Cr ₂ O ₃	Quantitative Analysis	10 (each)
1878a	Respirable Quartz Powder	Quantitative Analysis	5
1879a	Respirable Cristobalite Powder	Quantitative Analysis	5
656	Silicon Nitride: α & β Powders	Quantitative Analysis	10 (each)

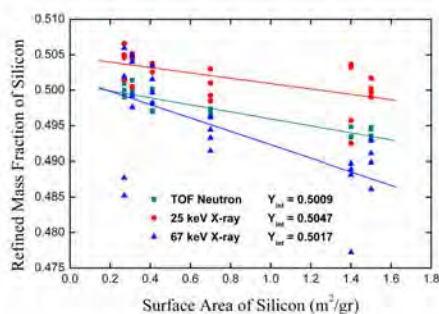
Approach

Diffraction techniques can provide data on a number of sample characteristics. Therefore, the method of certification and the artifact itself are chosen to address a specific measurement issue pertinent to a diffraction experiment. NIST diffraction SRMs may be divided into five groups: Line Position, for calibration of the angle two-theta; Line Profile, for microstructure analysis; Instrument Response, for calibration of angle and intensity; Quantitative Analysis, for measurement of phase abundance; and Thin Film SRMs for measurement of thickness, surface roughness, and density of layered structures. The most common use of NIST SRMs is for calibration of diffraction line position. This requires that the SRM is certified with respect to lattice parameter. This length must be measured in a manner that is traceable to the International System of Units (SI) meter through a robust and transparent measurement chain. A major component of our effort consists of developing the capability for performing traceable measurement of lattice parameters for thin films and powders.



Accomplishments

The measurement technology associated with the certification procedures for the entire suite of diffraction metrology SRMs is continuously being improved. Three SRMs were recently certified, and a fourth is due for release early in 2009. SRM 676a is the renewal of SRM 676, an alumina powder certified for quantitative analysis of multiphase mixtures. Improvements in SRM 676a include an alumina powder (feedstock) of higher phase-purity, as well as a more accurate certification of its phase content. The new SRM 1976a is the successor to SRM 1976, which, since its introduction in 1991, has become the best selling of the diffraction metrology SRMs. SRM 1976a features a more uniform microstructure that, in turn, results in reduced error bounds on the certified values. The new SRM 2000 is the first thin-film, high-resolution diffraction SRM. It consists of 25 mm x 25 mm pieces of a silicon wafer with a Si-Ge epilayer. The SRM is certified with respect to the lattice parameter of the Si substrate. SRM 640d is also a renewal; SRM 640, silicon powder, was the first NIST SRM for powder diffraction and has traditionally been very popular. One of the leading instrument companies uses this SRM for ISO certification of equipment used in the pharmaceutical industry.



Refined diffraction data for SRM 676a

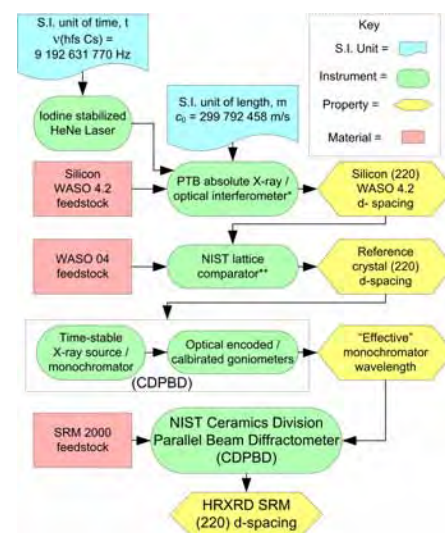
While diffraction is commonly used for quantification of multiphase mixtures, using it to quantify the amorphous-component fraction of unknown samples has only become possible with the certification of NIST SRMs for absolute phase purity. NIST's method for certification of phase content has been developed over the course of ten years and uses both synchrotron and neutron powder diffraction methods. The method's first application was in the recertification of SRM 676. With SRM 676a, further improvements to the experimental design realized the convergence of three measurement methods (neutron time-of-flight scattering and X-ray diffraction on two different synchrotron beamlines, at energies of 25 and 67 KeV); this allowed certification of SRM 676a with reduced error bounds. SRM 676a will also enable accurate measurement of the thickness of disordered surface layers, which is of particular importance for nanoscale materials with surface-dependent properties.

SRM 1976 was originally certified in response to a round robin study done by the International Centre for Diffraction Data in preparation for a new database format. A conclusion of the study was that an SRM was needed that allowed for the calibration of both line position and intensity as a function of two-theta angle (instrument response) using conventional data analysis methods. Based upon customer feedback on SRM 1976, the new SRM 1976a was manufactured in a single production run in order to significantly reduce the error bounds in the relative intensity data.

SRM 2000 provides the high-resolution X-ray diffraction (HRXRD) community with either wavelength or angle calibration through certification of the Si (220) lattice spacing

of the artifact. This SRM also provides certification of the Si wafer miscut (angle from surface to crystal plane) for sample rotation axis and sample holder alignment. Future recertification of this SRM will involve modeling HRXRD reflection data to provide customers with epitaxial layer structural information.

The silicon used for SRM 640d was obtained from intrinsic, float-zone boules that were crushed and jet-milled to a narrow particle size distribution centered at 5 micrometers. The powder was then annealed to remove crystallographic defects caused by comminution. This preparation procedure yields a powder that is optimal for powder diffraction measurements. The certification measurements were performed on the newly commissioned Ceramics Division Divergent Beam Diffractometer (CDDBD).



SI traceability chart for SRM 2000

Learn More

Donald Windover
Albert Henins
David Gil
David Black

James P. Cline
 (Ceramics Division)
 (301) 975-5793
 jcline@nist.gov
 www.nist.gov/ceramics

Publications

SRM 676a; *Alumina Powder for Quantitative Analysis by X-ray Powder Diffraction*; National Institute of Standards and Technology; U.S. Department of Commerce: Gaithersburg, MD (2008)

SRM 1976a; *Instrument Response Standard for X-ray Powder*; National Institute of Standards and Technology; U.S. Department of Commerce: Gaithersburg, MD (2008)

SRM 2000; *Calibration Standard for High-Resolution X-ray Diffraction*; National Institute of Standards and Technology; U.S. Department of Commerce: Gaithersburg, MD (2008)

209.1 X-Ray Diffraction (powder and solid forms)

SRMs 656, 676, 674b, 1878a and 1879a consist of high phase purity materials for use in the quantitative analysis of samples by the internal standard method. SRM 656 consists of 2 silicon nitride powders, one high in α , the other high in β . SRMs 640c, 660a, 675, and 1976 consist of materials with select crystallographic and microstructure properties used in the evaluation of diffraction equipment for the following variables; 1) d-spacing or line position, 2) line or instrument intensity, and 3) instrumental or sample contributions to the shape of reflection profiles. SRM 1976, a sintered alumina plate, is also certified with respect to lattice parameters as well as 12 relative intensity values from 25° to 145° 2θ (Cu K_α). SRM 1990 is certified for lattice parameter. SRM 1994 is certified for miss orientation of the crystal axis relative to the surface normal. SRM 2910 is a high purity synthetic calcium hydroxyapatite for which line profile, relative intensity, lattice parameter, and crystallographically disordered material fraction reference data have been provided.

Technical Contact: james.cline@nist.gov Technical Contact: eric.benck@nist.gov for SRM 1994

PLEASE NOTE: The tables are presented to facilitate comparisons among a family of materials to help customers select the best SRM for their needs. For specific values and uncertainties, the certificate is the only official source.

SRM	Description	XRD Application	Lattice Parameters (in nm)	Unit Size (in g)
640c	Silicon Powder $2\theta/d$ -Spacing	Line Position	(0.54311946 \pm 0.00000092)	7.5
656	Silicon Nitride	Quantitative Analysis	α -(0.7752630 / 0.5619372) β -(0.7602293 / 0.2906827)	10 10
660a	Lanthanum Hexaboride Powder	Line Position	(0.41569162 \pm 0.00000097)	6
674b	X-Ray Powder Diffraction Intensity Set	Quantitative Analysis		
	CeO ₂ (fluorite structure)		(0.541651)	10
	Cr ₂ O ₃ (corundum structure)		(0.4950979 / 1.359592)	10
	TiO ₂ (rutile)		(0.4593927 / 0.2958875)	10
	ZnO (wurtzite structure)		(0.3249897 / 0.520653)	10
675	Mica	Line Position - Low 2θ	0.998104	7.5
676a	Alumina Powder for Quantitative Analysis by X-ray Diffraction	Quantitative Analysis	0.47590914 / 1.2991779	20
1878a	Respirable Alpha Quartz	Quantitative Analysis		5
1879a	Respirable Cristobalite	Quantitative Analysis		5
1976	XRD Instrument Sensitivity, Alumina Plate	Instrument Response	0.4758846/1.299306	4.5 x 0.16cm
1990	Single Crystal Diffractometer Alignment Standard	Quantitative Analysis		3 Spheres
1994	Standard Silicon Single Crystal Wafer for Crystalline Orientation	Crystalline Orientation		100-mm wafer
2910	Calcium Hydroxyapatite	Quantitative Analysis	(a-0.942253) (c-0.688501)	2

Values in parentheses are not certified but are provided as reference values or are given for information only.