



National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material[®] 676a

Alumina Powder for Quantitative Analysis by X-ray Diffraction

This Standard Reference Material (SRM) consists of an alumina powder (corundum structure) intended primarily for use as an internal standard for quantitative analysis and I/I_c [1] (for a complete discussion of I/I_c , see [2]) determinations by X-ray powder diffraction. A unit of SRM 676a consists of approximately 20 g of powder bottled in an argon atmosphere.

Material Description: The alumina powder has been calcined to 1400 °C and jet milled to a fully de-aggregated state. The alumina grains are sub-micrometer in size and equi-axial in shape. The high calcination temperature ensures high phase purity while the isometric form of the grains effectively eliminates preferred orientation effects in this powder. The de-aggregated state of this material ensures the homogeneity of test mixtures prepared by conventional methods.

An analysis of the phase fractions determined from X-ray powder diffraction data from mixtures of SRM 676a and silicon powder, SRM 640c [3], indicated that the SRM material was homogeneous with respect to diffraction properties.

Certified Value: The certified phase purity of the material expressed as a mass fraction is:

Crystalline Alumina: 99.02 % \pm 1.11 %

The interval defined by the certified value and its uncertainty represents an expanded uncertainty using $k = 2$, in the absence of systematic error [4,5]. The error bounds define a range about the certified value that is in excess of 100% phase purity, a physical impossibility.

Expiration of Certification: The certification of SRM 676a is valid indefinitely, within the measurement uncertainties specified, provided the SRM is stored and handled in accordance with instructions given in this certificate (See "Instructions for Use"). The certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

The material preparation, measurements, and data analysis leading to the certification of this SRM were provided by J.P. Cline of the NIST Ceramics Division; R.B. Von Dreele of Argonne National Laboratory, Argonne, IL; R. Winburn of Minot State University, Minot, ND; P.W. Stephens of State University of New York, Stony Brook, NY, and the National Synchrotron Light Source, Brookhaven, NY.

Statistical analysis was provided by J.J. Filliben of the NIST Statistical Engineering Division.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Measurement Services Division.

Debra L. Kaiser, Chief
Ceramics Division

Gaithersburg, MD 20899
Certificate Issue Date: 28 January 2008

Robert L. Watters, Jr., Chief
Measurement Services Division

INSTRUCTIONS FOR USE

Storage: SRM 676a was bottled in an argon atmosphere to protect against humidity. Although there have been no long-term stability studies on this SRM, alumina is known to be a stable oxide. It is therefore believed that this SRM is stable after exposure to atmosphere. However, the unused portion of this powder should be stored, tightly capped, in the original bottle or in a manner with similar protection against humidity.

SOURCE, PREPARATION, AND ANALYSIS

Materials¹: The material used for this SRM was obtained from Baikowski International Corporation, 6601 Northpark Blvd Suite H, Charlotte, NC 28216-2385.

Certification Characteristics: The SRM material has the characteristics of an alumina powder judged optimal for accurate and precise X-ray powder diffraction intensity measurements. The SRM was certified with respect to the mass fraction of material that exhibits Bragg scattering in correspondence to that of alumina, corundum structure. This was accomplished with a Rietveld analysis [6] (for a complete discussion of the Rietveld method see references 7 and 8) of neutron time-of-flight (TOF) powder diffraction data and two sets of high energy X-ray powder diffraction (HE-XRPD) data. The certification procedure also utilized laboratory, divergent beam X-ray powder diffraction (XRPD) to verify the material's homogeneity, provide seven relative intensity values, and determine the lattice parameters. While the XRPD data suffer from centration and penetration errors and, therefore, are not metrological in nature; a linkage is nonetheless established between the reported lattice parameters and the X-ray emission spectrum of Cu, establishing a qualified traceability to the International System of Units (SI) [9].

Phase Purity: A long-count-time X-ray powder diffraction pattern of SRM 676a will offer data consistent with a high purity alumina powder. However, the surface region of any crystalline material will not diffract as the bulk due to relaxation of the crystal structure and inclusion of surface reaction products. While this disordered, amorphous surface layer may only be on the order of a few crystallographic units in thickness, in a finely divided solid it can easily account for several percent of the total mass. Phase purity as discussed herein is a microstructural characteristic innate to a finely divided crystalline solid and influenced by the production history of the alumina powder used as the feedstock.

Certification Method: The phase purity was certified through an analysis of the discrepancy between the results of powder diffraction experiments, which measure the mass ratio of material exhibiting Bragg diffraction, relative to weighing operations, which include all components. The procedure involved a comparison of the phase abundance measured from a series of mixtures of SRM 676a and hyper-pure silicon powder. Embodied in the experimental design were the assumptions that the non-Bragg-diffracting material associated with the silicon powder was confined to the crystallite surface, and that this amorphous layer thickness was invariant with respect to crystallite size. Systematic variation in the amorphous content of the silicon was then affected within the aforementioned series of mixtures by the selection/variation of the particle size (hence specific surface area) of the silicon powder. The effects of extinction in the silicon, which lead to distortions in observed diffraction intensity, were addressed with use of the neutron TOF powder diffraction and multiple energies, 25 keV and 67 keV, of HE-XRPD, in conjunction with the Rietveld data analysis method. The mass fractions of crystalline silicon, determined from the Rietveld refinements, were plotted relative to the surface areas of the silicon of each sample. An extrapolation of these data to a hypothetical (and physically impossible) silicon sample that would have no specific surface area and, therefore, no amorphous content yielded the mass fraction of SRM 676a that exhibited Bragg diffraction.

Certification Procedure: The silicon was obtained from the dedicated production run of intrinsic, float zone material that was used as the feedstock for SRM 640c. The boules were crushed and jet milled to yield a powder of a relatively broad size distribution. The powder was then annealed under gettered Ar at 1000 °C for two hours to remove microstructural defects that resulted from the comminution [10]. This powder was then fractionated into five lots of varying particle size. The powder of SRM 640c was prepared in an analogous manner, except that it was jet milled to a narrow size distribution initially. The surface area of each lot, and SRM 640c, was measured via a multipoint Brunauer-Emmett-Teller (BET) adsorption using krypton as the adsorbent². Ten randomly selected bottles of SRM 676a were pulled from the population for this certification. Four 4 g specimens were prepared using

¹Certain commercial equipment, instruments, or materials are identified in this certificate in order to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

²Laboratory Services, Quantachrome Instruments, 1900 Boyton Beach Drive, Boyton Beach, Florida 33426

each lot of silicon and SRM 640c, for a total of 24 specimens, at the 50/50 mass ratio.

The TOF data were collected on the Special Environment Powder Diffractometer at the Intense Pulsed Neutron Source, Argonne National Laboratory. The nominally 4 g samples were contained in vanadium cans during the analysis. Each sample was exposed to the neutron beam for 2 h with the source operating at 13 μ A and 30Hz. Data used for this certification were obtained from detector banks positioned at $\pm 144^\circ 2\Theta$ covering a d-space range of 0.05 nm to 0.39 nm. The run order was randomized on an informal basis on all data collection. The 25 keV synchrotron data were collected at the Advanced Photon Source on an 8 detector/analyzer machine located at beamline 32IDB. The incident beam monochromator was a two-crystal diamond (111) while the analyzers consisted of silicon (111). The data were collected in $0.0005^\circ 2\Theta$ steps with a 1 s count time. The 8 individual scans, separated by $2^\circ 2\Theta$, were summed to give a total angular range of 6° to $51^\circ 2\Theta$, with a d-space range of 0.058 nm to 0.474 nm. The 67 keV synchrotron data were collected at National Synchrotron Light Source, beamline X17B1. The incident beam was defined by a bent Laue Si (113) focusing monochromator and the diffracted beam analyzed by a slightly strained Laue Si (220) analyzer. Data were collected with a step width of $0.001^\circ 2\Theta$, a nominal count time of 1 s, over an angular range of 2.7° to $12^\circ 2\Theta$, for a d-space range of 0.0890 nm to 0.393 nm. Both X-ray diffractometers were set up in Debye-Scherrer, capillary geometry with a beam size of approximately 1 mm x 2 mm for the 25 keV machine and 1 mm x 1 mm for the 67 keV equipment. Samples were loaded into 0.8 mm Kapton capillaries for 25 keV, and 1 mm glass capillaries for 67 keV. Capillaries were spun at ~ 2 Hz during data collection. The diffracted X-ray data were normalized to the incident beam intensity, as monitored by an ion chamber between the monochromator and sample.

The Rietveld analyses were performed using General Structure Analysis System (GSAS) [11]. Refined parameters were constrained with respect to uniformity in physical parameters across the 24 specimens. The analyses were performed with three refinements, one for each diffraction method. This approach constrained the refined lattice parameters, crystal structure, and temperature parameters within each diffraction method. Profile shape terms were constrained across the alumina phase and within each lot of silicon. Profile shape parameters used with the alumina included terms to describe strain broadening and anisotropic particle shape present in this phase but absent in the silicon. The Sabine [12] model was used to address the effects of extinction; the refined extinction domain size parameters were constrained within each lot of silicon.

The sample absorption term in the TOF experiment, used to correct for the absorption effect of the vanadium rod used in the incident spectrum calibration run, was constrained throughout. Profile positions and instrumental factors affecting them were effectively constrained by the inclusion of SRM 640c in the specimens. Lattice parameters of the silicon were fixed to the certified values of SRM 640c. Therefore, the TOF detector bank parameters which affect profile position, DIFC, DIFA and Zero, were refined independently to correct for slight variations in effective sample center location. Likewise, the refined X-ray diffractometer constants of wavelength and zero angle were refined independently to account for slight instabilities in the equipment. The profile asymmetry parameters, S/L and H/L, of the Finger model [13] were initially set to values determined from the geometry of the two instruments. Late in the analyses the term S/L was refined with full constraints applied. This was done, however, for a limited number of cycles in order to test for the plausibility of the values without destabilizing the refinement.

The refined parameters common to all refinements included: scale factors, lattice parameters of the SRM 676a alumina phase, 8 parameters of a shifted Chebyshev background function, atomic position and isotropic thermal parameters. The profile shape function “type -3” within GSAS was used to fit the TOF data [14]. Refined parameters represented Gaussian and Lorentzian size broadening, and anisotropic Lorentzian size broadening. Only the Gaussian term was used for the silicon, while the aforementioned three were used with the alumina phase. The profile shape function used to fit the synchrotron X-ray data were the “type 3” which included instrumental, crystallite size and strain broadening as represented by GU, GV, GW, LX and LY terms of the Thompson-Cox-Hastings profile shape model [15]. The profile shape terms GU, GV and GW were constrained throughout in both analyses of X-ray data. For the 25 keV refinement, the additional profile shape terms included LX and LY for both phases and the anisotropic size and strain terms, ptec and stec respectively, for the alumina phase. For the 67 keV refinement, the additional profile shape terms included LX and LY for the alumina phase, with LY alone for the silicon phase.

A linear least squares fit to the mass fraction silicon vs. silicon surface area results from the TOF and two HE-XRPD data sets was used to extract the y -intercept and the standard deviation of the y -intercept, $SD_{\text{intercept}}$ values. These are shown in Table 1.

Table 1. y -intercept and $SD_{\text{intercept}}$ values from least squares fits

	Neutron TOF	25 keV X-ray	67 keV X-ray
y -intercept	0.5009	0.5047	0.5017
$SD_{\text{intercept}}$	0.00039	0.00099	0.00208

The y -intercept values of the three diffraction techniques were averaged to yield the certified phase purity. The standard deviation of the mean was estimated with two procedures; the first ignored the $SD_{\text{intercept}}$ information, while the second method utilized it. The first approach is appropriate when the three values differ significantly, while the second procedure is appropriate when the values do not differ significantly, as was the case here. Although justification exists for choosing the latter method, a more conservative statistical approach, which provides further protection from unforeseen sources of variation, is to utilize the results from both methods in a root-mean-squares fashion. Such was done here so as to yield the final reported value for the standard deviation of the mean.

Ancillary Laboratory X-ray Diffraction Data: XRPD data for relative intensity determinations were collected from 10 randomly selected specimens on a Siemens D500 diffractometer. This machine was equipped with a focusing Ge incident beam monochromator, sample spinner/changer, and a quartz wire position sensitive proportional detector (PSD). The divergence slit was of 0.67° while the receiving angle of the PSD was nominally 4.5° . The PSD was also fitted with a Soller slit of 2° . Calibration of the equipment was performed using SRMs 660a and 676 [16-18]. Data were collected from 20° to $154^\circ 2\theta$ with a step width of 0.01° and a scan rate of 1° per minute. Data were analyzed with two methods using two software packages, though the results from only one are reported. The first procedure was to fit the profiles using the split Pearson VII function as implemented within TOPAS [19]. The second involved Rietveld analyses via GSAS. The background in both analyses was represented by a tenth order Chebyshev polynomial with a $1/x$ term. The refined parameters of the Rietveld analyses included the scale factors, Gaussian and Lorentzian crystallite size and strain broadening as represented by the GP, LX and LY terms of the Thompson-Cox-Hastings “type 3” profile shape model, the “type 1” polarization factor, sample shift and transparency terms, and structural parameters. Profile terms GU, GV, GW and the peak asymmetry parameters of the Finger model were fixed at values obtained from an analysis of SRM 660a. Relative intensity data were extracted with the GSAS utility REFLIST which uses the observed structure factors, corrected for multiplicity and Lorentz-polarization factor, to compute relative intensity values. Relative intensity data correlated to better than 1% between the two methods which served to validate the results. Data are reported from the Rietveld analyses as these are judged more accurate due to the lack of a profile shape model. The relative intensities of SRM 676a and their expanded uncertainties, using the $k = 2$ factor, are shown in Table 2. Such uncertainty values represent our degree of confidence in the reported relative intensity values. The $k = 2$ tolerance intervals of the ten data points themselves represent a prediction interval for a single future measurement made in the field.

Table 2. Relative Intensity Data from SRM 676a

Reflection (hkl)	Relative Intensity	Expanded Uncertainty ($k = 2$)	Tolerance Interval ($k = 2$)
(012)	57.06	± 0.122	± 0.385
(104)	88.41	± 0.254	± 0.803
(110)	37.75	± 0.112	± 0.353
(024)	47.33	± 0.075	± 0.238
(116)	95.78	± 0.250	± 0.789
(124)	37.74	± 0.101	± 0.319
(030)	57.49	± 0.157	± 0.500

XRPD data for the determination of lattice parameters were collected on a Siemens D5000 X-ray diffractometer of theta-theta geometry. It was equipped with a sample spinner/changer, graphite post monochromator, and scintillation detector. Cu $K\alpha$ radiation was used with an incident slit of 0.8° and a receiving slit of 0.05° . Both incident and receiving Soller slits of 2.3° were used. All data were analyzed with the Fundamental Parameters Approach convolution algorithm [20] for Rietveld analyses as implemented in TOPAS. Calibration of the equipment was performed using SRM 660a: These data were collected in selected regions straddling each profile with the run time parameters optimized for each scan. The 24 scans so collected were analyzed with a joint refinement. The analysis used the Cu $K\alpha_1/K\alpha_2$ emission spectrum as characterized by G. Hölzer, et. al. [21] with a satellite component [22]. The refined parameters included the scale factors, linear background terms, the lattice parameters, the intensities and position of the $K\alpha_2$ and satellite components of the Cu $K\alpha$ emission spectrum, terms indicating the position and

intensity of the “tube tails” [23], a Soller slit value in the “full” axial divergence model [24], specimen displacement, an absorption term, and a size broadening term of a Lorentzian profile. Refined parameters from the analyses of SRM 660a were verified to be within expected values.

Data for SRM 676a were collected for ten randomly selected samples with two sets of run time parameters: from 22° to 80° 2 θ with a step width of 0.014° 2 θ and a 4 s count time, and from 80° to 155° 2 θ with a step width of 0.02° 2 θ and count time of 8 s. The analysis of these low and high angle scans was done with a joint refinement using the aforementioned procedure, for a total of ten analyses. However, the intensities and position of the K α_2 and satellite components were fixed at the values obtained from the analysis of SRM 660a. Two background functions, represented by fifth order Chebyshev polynomials with 1/x terms, and a Gaussian profile parameter for strain broadening were also included. The lattice parameters of SRM 676a and their expanded uncertainties, using the $k = 2$ factor, are shown in Table 3. Such uncertainty values represent our degree of confidence in the reported lattice parameters. The $k = 2$ tolerance intervals of the ten data points themselves represent a prediction interval for a single future measurement made in the field.

Table 3. Lattice Parameters of SRM 676a

	Lattice Parameter, nm	Expanded Uncertainty ($k = 2$)	Tolerance Interval ($k = 2$)
a	0.47590914	± 0.00000101	± 0.00000321
c	1.2991779	± 0.00000327	± 0.0000103

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Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet at <http://www.nist.gov/srm>

Addendum

Standard Reference Material[®] 676a

Alumina Powder for Quantitative Analysis by X-ray Diffraction

Acknowledgements

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