National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 676

Alumina Internal Standard
for Quantitative Analysis by X-ray Powder 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 676 consists of approximately 20 g of powder bottled in an argon atmosphere.

Material Description: The powder consists of sub-micrometer equi-axial alumina grains that have been de-aggregated and calcined. 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 lattice parameters determined from X-ray powder diffraction data indicated that the SRM material was homogeneous with respect to diffraction properties.

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

Crystalline Alumina: 91.75 % $\pm$ 1.52 %

The interval defined by the certified value and its uncertainty represents an expanded uncertainty using $k = 2$, in the absence of systematic error [3,4].

Expiration of Certification: The certification of this SRM is valid indefinitely within the stated uncertainties, provided the SRM is stored and handled in accordance with the "Storage" section of this certificate.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive 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. Winburn of Minot State University, Minot, ND; R.B. Von Dreele of Argonne National Laboratory, Argonne, IL; A. Huq and P.W. Stephens of State University of New York, Stony Brook, NY, and National Synchrotron Light Source, Brookhaven, NY.

Statistical analysis was provided by S.B. Schiller, H-k. Liu, and J.J. Filliben of the NIST Statistical Engineering Division.

The 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: 20 September 2005

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

See Certificate Revision History on Last Page

Materials: The material used for this SRM was donated to NIST by Union Carbide Corporation, Specialty Powders, Indianapolis, IN[1]. The material was de-aggregated and calcined courtesy of Trans-Tec Inc., Adamstown. MD.

Certification: This SRM was originally certified in 1992, with the certification for amorphous content being completed in 2005. Provided that the SRM has been handled in accordance with the "Storage" section of this certificate, the certified value for amorphous content is valid retroactively to the previously released units of this SRM. The SRM material was selected as a result of an extensive study that determined the character of an alumina powder optimal for accurate and precise X-ray powder diffraction intensity measurements. The certification procedure 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 of the reported lattice parameters and the X-ray emission spectrum of Cu, establishing a qualified traceability to the International System of Units (SI) [5]. The SRM was certified with respect to the mass fraction of material that exhibits Bragg scattering in correspondence to that of alumina with a Rietveld analysis [6] (for a complete discussion of the Rietveld method [7,8]) of neutron time-of-flight (TOF) and high energy X-ray powder diffraction (HE-XRPD) data.

Phase Purity: A long-count-time X-ray powder diffraction pattern of SRM 676 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. Furthermore, in the case of alumina, the surface impurities may include residual transition alumina precursor phases [9]; though the Bragg diffraction resulting from them may be sufficiently diffuse so as to be largely indiscernible. While the 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. The characterization of "phase purity" or "amorphous content" discussed herein is not in the context of a phase that is mechanically separable from the alumina powder of the SRM, but it is a microstructural characteristic innate to the production history of the alumina powder used as the feedstock.

The amorphous content was certified through an analysis of the discrepancy between the results of powder diffraction experiments, which measure the mass 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 676 and hyper-pure silicon powder. Embodied in the experimental design were the assumptions that the mass of 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 effected 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 that lead to distortions in observed diffraction intensity were addressed with use of the TOF and HE-XRPD powder diffraction, 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 silicon sample that would have "no" specific surface area, and, therefore, "no" amorphous content yielded the mass fraction of SRM 676 that exhibited Bragg diffraction. A publication is in progress concerning the aforementioned method for absolute amorphous content determination.

The silicon was obtained from the dedicated production run of intrinsic, float zone material that was used as the feedstock for SRM 640c [10]. The boules were crushed and jet milled to yield a powder of a relatively broad size distribution. This powder was then fractionated into five lots of varying particle size. The powders were then annealed under gettered Ar at 1000 °C for two hours to remove microstructural defects that resulted from the comminution [11]. 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 adsorbent at 77 K in accordance to German Standard DIN 66131 [12]. Ten randomly selected bottles of SRM 676 were pulled from the population for this certification. Mixtures of 50 % silicon, from each lot and SRM 640c, and 50 % alumina from SRM 676 were prepared.

---

[1]Certain 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.

The TOF data were collected on the High Intensity Powder Diffractometer (HIPD) at the Manuel Lujan, Jr., Neutron Scattering Center (LANSCE), Los Alamos National Laboratory. The samples were contained in 9.5 mm diameter by 50 mm long vanadium cans during the analysis. Each sample was exposed to the neutron beam for 1.3 h with the LANSCE source operating at 70 µA proton beam current. Data used for this certification were obtained from detector banks positioned at ± 153° 2Θ covering a d-spacing range of 0.05 nm to 0.48 nm. The run order was randomized on an informal basis. The HE-XRPD data were collected at National Synchrotron Light Source, beamline X17B1, at a nominal energy of 67 keV in Debye-Scherrer, capillary geometry. The 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 in step-scan mode, 0.001 degree step width, at a rate of approximately one second per point, over an angular range of 2.7° 2Θ to 12° 2Θ. Samples were loaded in 1-mm capillaries that were spun at ≈2 Hz during data collection. The diffracted signal was normalized to the incident beam intensity, as monitored by an ion chamber between the monochromator and sample. These data were collected from two samples of each size fraction of silicon, run order being informally randomized.

The Rietveld analyses of the data were performed using General Structure Analysis System, GSAS [13]. Two refinements were performed, one for each of the complete suite of histograms collected from each of the two data collection methods. The refined parameters for both refinements included: scale factors, lattice parameters of the SRM 676 alumina phase with those of the silicon fixed at the certified value of SRM 640c, an absorption term, atomic position and isotropic thermal parameters, and terms of a background function describing the effects of thermal diffuse scattering and air scattering (incoherent) of the incident beam. Parameters specific to the TOF data included: extinction domain size, a profile shape function term representing Lorentzian peak broadening [14], and a term for the diffractometer (DIFC). Parameters specific to the HE-XRPD data included: crystallite size and strain broadening as represented by the GU, LX, and LY terms of the Thompson-Cox-Hastings, profile model [15], wavelength, diffractometer zero angle, and a peak asymmetry parameter of the Finger model [16]. The wavelength and asymmetry were constrained to be the same for all samples. The peak shapes in both refinements were constrained to be the same for the alumina in all samples and for each size fraction of silicon. The sample absorption term for HE-XRPD data was set at the computed value for the capillary dimension at 50 % packing density. The Sabine [17] model was used for analysis of the extinction domain sizes. They were refined only in the TOF data set, and were constrained within each size fraction of silicon

A linear least squares fit to the mass fraction silicon vs. silicon surface results from the TOF and HE-XRPD data was used to extract the y-intercept and the standard deviation of the y-intercept, $SD_{intercept}$ values. These were, for the TOF method: y-intercept = 0.522 891, $SD_{intercept}$ = 0.001 438, and for the HE-XRPD method: y-intercept = 0.520 152, $SD_{intercept}$ = 0.002 730. The y-intercept values of the two 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 $SD_{intercept}$ information, while the second method utilized it. The first approach is appropriate when the two values differ significantly, while the second procedure is appropriate when the two 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.

Laboratory X-ray Diffraction Data: Certified intensity data were collected from 2 samples taken from each of 15 randomly selected SRM bottles on a modernized "classic" Philips diffractometer equipped with 12-millimeter optics, incident beam Sollar slits, graphite diffracted beam monochromator, and scintillation detector. The incident beam was 0.93° in divergence (locked theta compensating slits), the receiving slit was 0.066°. Data were collected and processed with the Siemens Diffrac5000 version of NBS*Quant [18]. This algorithm scans specific peaks for an integrated intensity measurement, with extended count times for each of ten points on either side of the scan range. The step width was 0.01°. Scan time was nominally 30 min per peak. Starting and ending scan angles are indicated with the certified relative intensity data shown in Table 1. These data were corrected for aberrations in instrument response with the use of SRM 1976 [19]. Data from four SRM 1976 samples were averaged in the computation of a correction curve that was then applied to raw intensity data from the thirty SRM 676 samples. The uncertainties listed in Table 1 are the half-width of a 95 % confidence interval for the mean. They incorporate the imprecision of the measurements as well as the uncertainty of the instrument correction based on SRM 1976.

Lattice parameters were determined from a second set of 30 samples from the aforementioned fifteen bottles by means of least squares refinement [20] from 40 peak positions ranging from 22° 2Θ to 152° 2Θ. Measurements were made on a Siemens D500 diffractometer equipped with a focusing Ge incident beam monochromator, sample spinner, and a position sensitive proportional detector. The wavelength of CuKα_1 radiation used in the refinements was 0.154 062 9 nm (1.540 629 Å) [21]. Peak positions were determined with a second derivative algorithm, with the exception of the silicon (620) and alumina (1.3.10) reflections that, due to peak overlap, were determined by profile fitting. Peak positions were corrected for optical aberrations of the diffractometer with the use of SRM 640b [22] silicon powder admixed with each sample to generate a 2nd order polynomial internal standard correction curve. Certified lattice parameters are shown in Table 2. The standard deviation reported reflects only the variation in the measurements on SRM 676 and not the variability of SRM 640b used as the d-spacing standard.

Table 1. Certified Relative Intensity Data

Reflection	Scan Angles		Relative Intensity		
(hkl)	Low	High	Value		Uncertainty
012	23.9°	27.1°	57.96	±	1.80
104	33.8°	36.5°	87.40	±	0.65
110	36.5°	38.8°	36.32	±	0.19
113	42.0°	45.0°	100.0	±	----
024	50.7°	54.0°	47.18	±	0.41
116	55.7°	58.9°	95.59	±	1.21
124	65.1°	67.2°	36.02	±	0.78
030	67.2°	69.6°	55.75	±	1.26

Table 2. Certified Lattice Parameters of SRM 676

Lattice Parameter	nm	Å
a	0.475 919 ± 0.000 044	4.759 19 ± 0.000 44
c	1.299 183 ± 0.000 017 4	12.991 83 ± 0.000 174

Storage: SRM 676 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.

Acknowledgements

REFERENCE

[1]   Visser, J.W.; deWolff, P.M.; *Absolute Intensities*; Report No. 641.109; Technisch Physische Dienst: Delft, The Netherlands (1964).

[2]   Snyder, R.L.; *The Use of Reference Intensity Ratios in X-ray Quantitative Analysis*; Powder Diff. J., Vol. 7, No. 4, pp. 186–192 (1992).

[3]   ISO; G*uide to the Expression of Uncertainty in Measurement*; ISBN 92-67-10188-9, 1st ed.; International Organization for Standardization: Geneva, Switzerland (1993).

[4]   Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297; U.S. Government Printing Office: Washington, DC (1994); available at http://physics.nist.gov/Pubs/.

[5]   *International System of Units (SI)*, 7th edition, Bureau International des Poids et Mesures, Sèvres, France (1998).

[6]   Rietveld, H.M.; *Line Profiles of Neutron Powder-Diffraction Peaks for Structure Refinement*; Acta Crystallogr., Vol. 22, pp. 151–152 (1967); and Rietveld, H.M.; *A Profile Refinement Method for Nuclear and Magnetic Structures*; J. Appl. Crystallogr., Vol. 2, pp. 65–71 (1969).

[7]   *The Rietveld Method*; Young, R.A., Ed.; Oxford University Press: New York (1993).

[8]   *Modern Powder Diffraction*; Bish, D.L.; Post, J.E., Eds.; Rev. Mineral., Vol. 20, p. 369 (1989).

[9]   Dynys, F.W.; Halloran, J.W.; *Alpha Alumina Formation in Alum-Derived Gamma Alumina*; J. Am. Ceram. Soc., Vol. 65, pp. 42–448 (1982).

[10]   SRM 640c; *Silicon Powder Line Position and Line Shape Standard for Powder Diffraction;* National Institute of Standards and Technology; U.S. Department of Commerce: Gaithersburg, MD (2000).

[11]   van Berkum, J.G.M.; Sprong, G.J.M.; de Keijser, Th.H.; Delhez, R.; Sonneveld, E.J.; *The Optimum Standard Specimen for X-ray Diffraction Line-Profile Analysis*; Powder Diff. J., Vol. 10, No. 2, pp. 129–139 (1995).

[12]   German Standard DIN 66131; supperceeded by DIN ISO 9277: *Determination of the Specific Areas of Solids by Gas Adsorption UsingBrunauer, Emmett, Teller (BET) Method* (2003).

[13]   Larson, A.C.; Von Dreele, R.B.; *General Structure Analysis System (GSAS)*; Report LAUR 86-748; Los Alamos National Laboratory: Los Alamos, NM (2003).

[14]   Von Dreele, R.B.; Jorgensen, J.D.; Windsor, C.G.; *Rietveld Refinement with Spallation Neutron Powder Diffraction Data*; J. Appl. Crystallogr., Vol. 15, pp. 581–589 (1982).

[15]   Thompson, P.; Cox, D.E.; Hastings, J.B.; *Rietveld Refinement of Debye-Scherrer Synchrotron X-ray Data from Al_2O_3*; J. Appl. Crystallogr., Vol. 20, pp. 79–83 (1987).

[16]   Finger, L.W.; Cox, D.E.; Jephcoat, A.P.; *A Correction for Powder Diffraction Peak Asymmetry due to Axial Divergence*; J. Appl. Crystallogr., Vol. 27, pp. 892–900 (1994).

[17]   Sabine, T.M.; *Extinction in Polycrystalline Materials*; Aust. J. Phys., Vol. 38, Issue 3, pp. 507–518 (1985).

[18]   Snyder, R.L.; Hubbard, C.R.; *NBS*Quant84: A System for Quantitative Analysis by Automated X-ray Powder Diffraction*; NBS Special Publication; U.S. Government Printing Office: Washington, DC, p. 101 (1984).

[19]   SRM 1976; *Instrument Sensitivity Standard for X-ray Powder Diffraction*; National Institute of Standards and Technology; U.S. Department of Commerce: Gaithersburg, MD (1991).

[20]   Appleman, D.E.; Evans, H.T., Jr.; Report No. PB216188; U.S. Dept. of Commerce, National Technical Information Center: Springfield, VA (1973).

[21]   Richard Deslattes, personal communication.

[22]   SRM 640b; *Silicon Powder 2θ/d-Spacing Standard for X-ray Diffraction*; National Institute of Standards and Technology; U.S. Department of Commerce: Gaithersburg, MD (1987).

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.