National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 1976a

Instrument Response Standard for X-Ray Powder Diffraction

This Standard Reference Material (SRM) consists of a sintered alumina disc intended for use in calibration of X-ray powder diffraction equipment with respect to line position and intensity as a function of 2Θ angle. The solid form of the SRM eliminates variability imposed by sample loading procedure from intensity measurements. A unit of SRM 1976a consists of a sintered alumina disc approximately 25.6 mm in diameter by 2.2 mm in thickness

Material Description: The manufacturing process used to produce this SRM was developed for the production of substrates for electronics. The manufacture of the starting powder involved calcination to a temperature sufficient to yield a high purity (corundum structure) alumina with platelet grain morphology. The platelets are typically 5 μm to 10 μm in diameter by 2 μm to 3 μm in thickness. The compaction procedure for the discs resulted in an axisymmetric texture with the basal planes tending towards parallelism with the surface of the disc. This axisymmetric character of the texture permits sample mounting in any orientation about the surface normal and allows the use of a sample spinner during data collection. The compacts were liquid-phase sintered using a small percentage of a glass phase. No crystalline impurities have been detected. The glass phase involved in the liquid-phase sintering allows for relaxation of strain by preventing inter-particle contact, while the crystallite size is larger than that which can be discerned with conventional equipment; therefore, SRM 1976a can be used to obtain an approximation of the instrument profile function (IPF). This SRM was manufactured in a single, dedicated production run to offer consistency of microstructure with respect to grain size, shape, micro-strain, and texture.

Expiration of Certification: The certification of SRM 1976a is valid indefinitely, within the measurement uncertainties specified, provided the SRM is 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 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 overall coordination of the preparation and the technical measurements leading to certification were performed by J.P. Cline of the NIST Ceramics Division.

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.

INSTRUCTIONS FOR USE

Storage: SRM 1976a consists of sintered alumina. Although there have been no long-term stability studies on this SRM, alumina is known to be a stable oxide. Contamination of the surface with other crystalline materials may result in impurity lines in the data, though simple discoloration poses no issue.

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SOURCE, PREPARATION, AND ANALYSIS

Materials[1]**:** The alumina discs used for this SRM were manufactured by International Business Machines Corporation, East Fishkill, New York.

Technical Issue: The need for this SRM was delineated by a round robin study pursued through the International Centre for Diffraction Data, ICDD [1]. The round robin tested instruments in the field for diffraction intensity as a function of 2Θ angle, or instrument sensitivity. In order to eliminate the variable of sample loading procedure, sintered alumina plates, virtually identical to those used for this SRM, were used as the test specimens. Variations in instrument sensitivity were observed between instruments that would be unfavorable to continued improvement of the ICDD database. However, these variations could be quantified and corrected through conventional, single peak data analyses methods in conjunction with a suitable NIST SRM.

Certification Procedure: The certification procedure utilized laboratory, divergent beam X-ray powder diffraction (XRPD) methods for determination of relative intensity and lattice parameter data. 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) [2].

XRPD data for relative intensity determinations were collected from 20 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 0.67° while the receiving angle of the PSD was nominally 4.5°. The PSD was also fitted with a 2° Soller slit. Calibration of the equipment was performed using SRMs 660a and 676 [3-5]. Data were collected from 20° to 154° 2Θ 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 method was to fit the profiles using the split Pearson VII function as implemented within TOPAS [6]. The second involved Rietveld [7,8] analyses via GSAS [9] (for a complete discussion of the Rietveld method see [10,11]). 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, GU, GV, GW, LX and LY terms of the Thompson-Cox-Hastings [12] "type 3" profile shape model representing instrumental, crystallite size, and strain broadening, sample shift and transparency terms, and structural parameters. One of the peak asymmetry parameters of the Finger [13] model, S/L, was refined, while the second, H/L, was fixed such that the two terms were nearly equal. Temperature parameters, U_{iso}, were set to 0.005 and 0.004 for the Al and O atoms respectively. These values were obtained from consideration of the high q range experiments performed in the certification of SRM 676a [14].

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. Discrepancies between the relative intensity data from the two methods were typically within 1%, 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 1976a and their expanded uncertainties, using the $k = 2$ factor, are shown in Table 1. Such uncertainty values represent our degree of confidence in the reported relative intensity values in the absence of systematic error [15,16]. The $k = 2$ tolerance intervals of the twenty data points themselves represent a prediction interval for a single future measurement made in the field on equipment of similar performance to that used to collect the certification data.

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 Kα 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 [17] for Rietveld analyses as implemented in TOPAS. Calibration of the equipment was performed using SRM 660a. Calibration 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. [18] with a satellite component [19]. The refined parameters included the scale factors, linear background terms, the lattice parameters, the intensities

[1]Certain commercial equipment, instruments, or materials are identified in this certificate in order to adequately specify 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.

and position of the $K\alpha_2$ and satellite components of the Cu Kα emission spectrum, terms indicating the position and intensity of the "tube tails" [20], a Soller slit value in the "full" axial divergence model [21,22], 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 1976a were collected for 20 randomly selected samples with two sets of run time parameters: from 22° to 80° 2Θ with a step width of 0.014° 2Θ and a 4 s count time, and from 80° to 155° 2Θ with a step width of 0.02° 2Θ 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 twenty analyses. However, the intensities and position of the $K\alpha_2$ and satellite components were fixed at the values obtained from the analysis of SRM 660a. Two background functions were used; these were represented by fifth order Chebyshev polynomials with $1/x$ terms. The lattice parameters of SRM 1976a 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 lattice parameters. The $k = 2$ tolerance intervals of the twenty data points themselves represent a prediction interval for a single future measurement made in the field.

Table 1. Certified Relative Intensity Data for SRM 1976a.

Reflection (hkl)	Relative Intensity	Expanded Uncertainty ($k = 2$)	Tolerance Interval ($k = 2$)
(012)	24.37	± 0.197	± 0.858
(104)	100.0[(a)]	---	---
(113)	38.09	± 0.328	± 1.430
(024)	21.43	± 0.165	± 0.720
(116)	88.73	± 0.293	± 1.278
(300)	12.88	± 0.179	± 0.781
(1.0.10) & (119)	73.56	± 0.717	± 3.126
(0.2.10)	13.88	± 0.090	± 0.395
(226)	8.61	± 0.070	± 0.305
(2.1.10)	17.21	± 0.057	± 0.248
(324) & (0.1.14)	27.07	± 0.279	± 1.217
(1.3.10)	15.78	± 0.117	± 0.511
(146)	13.55	± 0.123	± 0.534
(4.0.10)	11.39	± 0.076	± 0.332

[(a)] Value not certified

Table 2. Lattice Parameters of SRM 1976a

	Lattice Parameter, nm	Expanded Uncertainty ($k = 2$)	Tolerance Interval ($k = 2$)
a	0.4758877	± 0.00000113	± 0.00000480
c	1.2992877	± 0.00000164	± 0.00000693

Mounting of SRM 1976a: The disc format of the SRM was chosen to be amenable to many sample holder geometries. The SRM can be cut to fit if necessary, but diffraction data should only be collected from the side opposite the label. The cutting operation used during manufacture resulted in the edge region of the disc surface being depressed by approximately 10 μm relative to the center. While this is not regarded as a significant difficulty due to the low attenuation of X-rays by alumina, height justification during mounting should be with respect to the center of the disc.

Use of SRM 1976a for Testing of Instrument Sensitivity: Accurate integrated intensity values, in correspondence to those of the certification, should be collected from the test equipment using established and reliable procedures. Use of a sample spinner will improve particle counting statistics. Care should be taken to ensure proper modeling of the background in data analysis procedures. Graphical evaluation of the ratio of these test data to the certified values vs. two theta will allow for an appropriate judgment as to the condition of the test equipment. The desired result would consist of unity values across the two theta range. However, data should be considered as a whole in the context of observed trends; a few outliers do not constitute a failure. Furthermore, the bounds on the certified values indicated

by the $k = 2$ Tolerance Intervals of Table 1 constitute those obtained from equipment equipped with both a sample spinner and a PSD. These two features will reduce the spread in the data due to improved counting statistics realized through their use. Therefore, the intervals of Table 1 are specific to high-performance instruments and are narrow relative to those which would be encountered with typical equipment. Should the data indicate a failure, options include the calculation of and application of a correction curve or an investigation into the performance of the test equipment itself.

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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.