# National Institute of Standards & Technology

# Certificate of Analysis

## Standard Reference Material® 1976c

### Instrument Response Standard for X-Ray Powder Diffraction

This Standard Reference Material (SRM) consists of a sintered alumina disc intended for the 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 any variability in intensity measurements introduced by the sample loading procedure. A unit of SRM 1976c 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 electronic components. The alumina powder used as the precursor for these substrates was of high phase purity (corundum structure) with a platelet particle morphology. The platelets were 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. The compacts were liquid-phase sintered using a small percentage of an anorthite glass phase. No crystalline impurities have been detected. The glass phase involved in the liquid-phase sintering effectively prevents inter-particle contact and relaxes during the cooling of the pieces from the sintering temperature. This leads to a minimal development of micro-strain and its associated line broadening; though some micro-strain is detectable as Gaussian broadening with a tanθ dependence. Given this, and the essential absence of crystallite size broadening, SRM 1976c can be used to obtain an approximation of the instrument profile function (IPF). Use of SRM 1976c is not recommended, however, for quantitative microstructure analyses. The discs comprising the feedstock of this SRM were manufactured in a single, dedicated production run to ensure consistency of microstructure with respect to grain size, shape, micro-strain, and texture.

**Certified Values:** A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or taken into account. The measurands are the certified values for relative intensity (dimensionless ratios) shown in Table 1, and the lattice parameters, shown in Table 2. Metrological traceability is to the SI units for the relative intensity values are the dimension of one, and for lattice parameters the dimension is length (expressed as nanometers). The certified values and uncertainties were calculated according to the method described in the ISO/JCGM Guide [1].

**Information Values:** The analyses associated with certification of SRM 1976c included the computation of the diffraction line positions shown in Table 3. In order to use SRM 1976c on diffraction equipment of various optical configurations, the effects of polarization must be taken into account. The values shown in Table 4 include a bias applied to the certified values to account for this effect. The data of Tables 3 and 4 are presented as information values. An information value is considered to be a value that will be of interest to the SRM user, but insufficient information is available to assess the uncertainty associated with the value. Information values cannot be used to establish metrological traceability.

**Expiration of Certification:** The certification of **SRM 1976c** is valid indefinitely, within the measurement uncertainty specified, provided the SRM is handled and stored in accordance with instructions given in this certificate (see "Instructions for Storage and Use"). Periodic recertification of this SRM is not required. The certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Overall coordination and technical direction of the certification were performed by J.P. Cline of the NIST Materials Measurement Science Division.

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Certificate Issue Date: 02 April 2019

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Preparation, measurements and data analyses were performed by J.P. Cline, M.H. Mendenhall and D. Black of the NIST Materials Measurement Science Division and A. Henins of the NIST Quantum Measurement 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 Office of Reference Materials.

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

## INSTRUCTIONS FOR STORAGE AND USE

**Storage:** SRM 1976c consists of a sintered alumina substrate that is essentially identical to NIST SRMs that have been available since 1991. While no long-term stability studies have been performed, we have no evidence of any degradation of the diffraction properties of this SRM when used under laboratory conditions. Furthermore, alumina is known to be a highly stable oxide. Contamination of the surface with other crystalline materials may result in impurity lines in the data. Discoloration may occur from exposure to X-rays; this does not affect the certification.

**Use (Mounting of SRM 1976c):** The disc format of the SRM was chosen to be amenable to many sample holder geometries. Diffraction data should only be collected from the side opposite the label. The stamping operation used to make the disc during manufacture resulted in the edge 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 (see also "Use of SRM 1976c for Testing of Instrument Sensitivity").

## SOURCE, PREPARATION, AND ANALYSIS[1]

**Materials:** The alumina discs used for this SRM were manufactured by International Business Machines Corporation, East Fishkill, NY.

**Certification Method:** Certification was performed using data from a NIST-built diffractometer [2] that includes several advanced design features. The optical layout is that of a conventional divergent-beam diffractometer of Bragg-Brentano geometry, equipped with a Johansson incident beam monochromator (IBM), sample spinner, and a silicon strip position sensitive detector (PSD). Data analyses were via the fundamental parameters approach (FPA) [3] using the Pawley method [4]. These analyses were used to verify homogeneity, certify both the relative intensities of 13 lines and the lattice parameters. Use of the Johansson IBM simplified the IPF of the machine aiding in the accurate fitting of the profiles; this was particularly important in the certification of the relative intensity values. Furthermore, the residual errors to the fits were analyzed for systematic offsets in the intensity determination, with reported intensities then being compensated for said offsets [5]. The linkage of the certified lattice parameter values to the fundamental unit of length, as defined by the International System of Units (SI) [6], was established with use of the emission spectrum of Cu Kα radiation as the basis for constructing the diffraction profiles. With the use of the FPA, diffraction profiles are modeled as a convolution of functions that describe the wavelength spectrum, the contributions from the diffraction optics, and the sample contributions resulting from microstructural features. Analysis of data from a divergent-beam instrument requires knowledge of both the diffraction angle and the effective source-sample-detector distance. Two additional models are therefore included in the FPA analyses to account for the effect of the sample height and attenuation. Certification data were analyzed in the context of both Type A uncertainties, assigned by statistical analysis, and Type B uncertainties, based on knowledge of the nature of errors in the measurements, to result in the establishment of robust uncertainties for the certified values.

**Certification Procedure:** Twenty units of SRM 1976c were selected in a stratified random manner from the population of units being certified. The 1.5 kW copper tube of standard fine-focus geometry was operated at a power of 1.2 kW during certification measurements. The source size was approximately 8 mm × 0.04 mm. The variable divergence incident slit was set to 0.9°. A 1.5° Soller slit was located in front of the PSD window to limit axial divergence, no Soller slits were used in the incident beam. The goniometer radius was 217.5 mm. Samples were spun at 0.5 Hz during data collection. The PSD was scanned using a variable window length and a combination of coarse and fine steps in θ and 2θ was used that allowed for timely data to be collected at high resolution [7]. The response

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of the PSD was measured with a scan of the attenuated direct beam to obtain a flat field correction; this ensured the uniformity in the measurement of X-ray intensity across the active area of the PSD. The machine was equipped with an automated anti-scatter slit, located above the specimen, that blocked air scatter of the incident beam from entering the PSD, where it would otherwise contribute to the low angle background level. The machine was located within a temperature-controlled laboratory space where the nominal short-range control of temperature was $\pm$ 0.1 K. The temperature was monitored using two 10 k$\Omega$ thermistors with a Hart/Fluke BlackStack system that was calibrated at the NIST temperature calibration facility [8] to $\pm$ 0.002 °C. The source equilibrated at operating conditions for at least an hour prior to recording any certification data. The performance of the machine was qualified with the use of SRM 660c *Line Position and Line Shape Standard for Powder Diffraction* [9] and SRM 676a *Alumina Powder for Quantitative Analysis by X-Ray Diffraction* [10] using procedures discussed by Cline *et al.* [2].

**Data Analysis:** The certification data were analyzed using the FPA method with Pawley refinements as implemented in TOPAS [11]. Mendenhall *et al.* [12] verified that TOPAS operated in accordance with published models for the FPA. The analysis used energies of the Cu K$\alpha$ emission spectrum as characterized by Mendenhall *et al.* [13]. The optics of the Johansson IBM were modeled using dynamical scattering from the monochromator in conjunction with the powder sample as per the optics of a 2-crystal monochromator. The resulting "band pass" model provides a function that effectively cuts off the Lorentzian tails of the native copper emission lines, providing good agreement with the shape of the tails of the diffraction peaks. It also adds a dispersion term to the FPA emission model which adds to the width of the modeled lines, further improving the fit to the observation [14]. Parameters associated with the bandpass model, as well as others of the IPF, the incident slit angle and the Soller slit angles of the "full" axial divergence model [15] were refined using scans from SRM 660c. They were then fixed at the SRM 660c values for the analyses of SRM 1976c. Other refined parameters included the intensity values, 11 Chebyshev polynomial terms for modeling of the background, the lattice parameters, specimen displacement and attenuation terms and a term for Lorentzian size and Gaussian strain broadening. The refined lattice parameters were adjusted using the CTE values found in Miyake *et al*, [16] to values at 22.5 °C.

The relative intensity values were computed in a manner that avoided error correlation difficulties when the values are based on the 100 % line alone. Each line was compared with the sum of the intensity values for all lines and then this ratio was re-scaled to yield the correct relative intensity values. Thus, the relative intensities were determined with a comparison of each given line intensity, x, to the total intensity of 14 lines measured from each sample. With the number of samples being 20, $n(s) = 20$, and the number peaks being 14, $n(p) = 14$, we have for the $j^{th}$ peak of the $i^{th}$ sample:

$$y_{ij} = \frac{x_{ij}}{\sum_{j=1}^{n(p)} x_{ij}} \tag{1}$$

We then scale this value to the 100% line by multiplying it by the average, over the 20 specimens, of the total line intensity, relative to the average of the total intensity of the 100 % line:

$$z_{ij} = 100 \, y_{ij} \, \frac{\frac{1}{n(s)} \sum_{i=i}^{n(s)} \sum_{j=1}^{n(p)} x_{ij}}{\frac{1}{n(s)} \sum_{i=1}^{n(s)} x_{i(100\%)}} \tag{2}$$

Where z is the relative intensity value that is not corelated to an error in the measurement of the 100 % line alone. The relative intensities of SRM 1976c and their expanded uncertainties, using the $k = 2$ factor, are shown in Table 1.

A statistical analysis of the data indicated that the means of the measurements were a = 0.475 909 20 nm and c = 1.299 336 50 nm with a $k = 2$ Type A expanded uncertainty of 0.000 000 79 nm and 0.000 000 99 nm for a and c respectively. However, a Type B uncertainty due to systematic error must be incorporated into the uncertainty bounds of the certified lattice parameter. Data were considered in the context of the uniformity in lattice parameter as a function of 2$\theta$ angle; this, in turn, would reflect the functionality of the FPA model. This consideration leads to an assignment of a Type B uncertainty that is roughly an order of magnitude larger than the Type A. The certified lattice parameters and their expanded uncertainties, Type A compounded with Type B, are shown in Table 2. Peak positions were computed from the certified lattice parameters for Cu K$\alpha$ Radiation, $\lambda$ = 0.154 059 29 nm, and are shown in Table 3 as information values.

Table 1.  Certified Relative Intensity Data for SRM 1976c

| Reflection, (hkl) | Relative Intensity | Expanded Uncertainty ($k = 2$) |
|---|---|---|
| (012) | 23.62 | ± 0.21 |
| (104) | 100.00 | ± 0.34 |
| (113) | 37.16 | ± 0.23 |
| (024) | 20.68 | ± 0.15 |
| (116) | 87.83 | ± 0.22 |
| (300) | 12.43 | ± 0.15 |
| (1.0.10) & (119) | 72.00 | ± 0.49 |
| (0.2.10) | 13.42 | ± 0.06 |
| (226) | 8.22 | ± 0.05 |
| (2.1.10) | 16.65 | ± 0.06 |
| (324) & (0.1.14) | 26.37 | ± 0.16 |
| (1.3.10) | 15.29 | ± 0.05 |
| (146) | 13.05 | ± 0.07 |
| (4.0.10) | 11.04 | ± 0.06 |

Table 2.  Certified Lattice Parameters for SRM 1976c

| | Lattice Parameter (nm) | Expanded Uncertainty ($k = 2$) |
|---|---|---|
| a | 0.475 909 2 | ± 0.000 008 0 |
| c | 1.299 337 | ± 0.000 015 |

Table 3. Peak Position Information Values for SRM 1976c,
Lines Listed with a Relative Intensity >5 %, Computed Using Cu Kα Radiation, λ = 0.154 059 29 nm

| Reflection, (hkl) | Peak Position (2θ, degrees) |
|---|---|
| (012) | 25.575 |
| (104) | 35.148 |
| (110) | 37.776 |
| (006) | 41.673 |
| (113) | 43.352 |
| (024) | 52.549 |
| (116) | 57.495 |
| (018) | 61.297 |
| (214) | 66.515 |
| (300) | 68.207 |
| (1.0.10) | 76.866 |
| (119) | 77.229 |
| (0.2.10) | 88.989 |
| (0.0.12) | 90.699 |
| (226) | 95.243 |
| (2.1.10) | 101.066 |
| (324) | 116.093 |
| (0.1.14) | 116.588 |
| (1.3.10) | 127.670 |
| (3.0.12) | 129.863 |
| (2.0.14) | 131.083 |
| (146) | 136.066 |
| (1.1.15) | 142.292 |
| (4.0.10) | 145.154 |
| (1.2.14) | 150.082 |
| (1.0.16) | 150.380 |
| (330) | 152.406 |

**Use of SRM 1976c for Testing of Instrument Sensitivity:**  The relative intensities reported for SRM 1976c are to be used for the basis of a calibration of an instrument for diffraction intensity as a function of 2θ angle, or instrument sensitivity.  The $k = 2$ expanded uncertainties, shown in Table 1, represent our degree of confidence in the reported relative intensity values; they do not play any role in a judgment concerning the qualification of a test instrument.  It is the responsibility of the end user, in conjunction with the instrument vendor, to determine the acceptance criteria for their specific instrument.  Such acceptance criteria may be based on a number of factors concerning random and systematic influences on the measurement method.  The "method" in this case refers to the entire suite of hardware, software, and procedures used to obtain the results under consideration.  In the determination of an acceptance criterion, it may be appropriate to perform an extensive study of the measurement method itself; such a study would have to include the sensitivity of the results on such environmental factors as power fluctuations, laboratory temperature variations, etc.

The determination of accurate intensity values is, to say the least, complicated by the accurate determination of the background.  Complete scans of the entire 2θ range and the use of "whole pattern" data analysis methods are recommended when the profile shape may include a significant Lorentzian component.  Lorentzian profiles exhibit considerable intensity far from the peak center.  Given the Lorentzian nature of atomic emission lines, any machine not equipped with an IBM would exhibit such profiles.  Experiments comparing results from limited scans to those of "whole pattern" methods may be used to validate the more timely, limited region methods.  Use of a sample spinner will improve particle counting statistics.  Graphical evaluation of the ratio of these test data to the certified values vs. 2θ 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 and in the context of testing for a slope in the data.  A few outliers do not constitute a failure.

The use of SRM 1976c for the calibration of X-ray diffraction equipment of differing optical configurations may require that a bias be applied to the certified values to render them appropriate for the machine to be qualified.  This bias is needed to account for differences in the polarization effects from the presence, absence, and character of crystal monochromators.  The polarization factor for a diffractometer that is not equipped with a monochromator is, from Guinier [17]:

$$\frac{1 + \cos^2 2\theta}{2} \tag{3}$$

The polarization factor for a diffractometer equipped with only an incident beam monochromator is, from Azaroff [18]:

$$\frac{1 + \cos^2 2\theta_m \cos^2 2\theta}{1 + \cos^2 2\theta_m} \tag{4}$$

where $2\theta_m$ is the 2θ angle of diffraction for the monochromator crystal.  The polarization factor for a diffractometer equipped with only a diffracted beam, post monochromator is, from Yao & Jinno [19]:

$$\frac{1 + \cos^2 2\theta_m \cos^2 2\theta}{2} \tag{5}$$

where, again, $2\theta_m$ is the 2θ angle of the monochromator crystal.  Equations 4 and 5 are considered appropriate when the crystal is of an "ideal mosaic" structure, i.e., the diffracting domains are uniformly small and, therefore, the crystal is diffracting in a kinematic context.  This is in contrast to a "perfect" crystal, which would diffract in accordance with dynamical scattering theory.  The use of equations 4 and 5 was evaluated with the diffractometer used in the certification of SRM 1976c.  With the Johansson IBM, as per Equation 4, a Ge crystal (111) reflection ($2\theta_m = 27.3$ degrees) was used.  With respect to Equation 5, a pyrolytic graphite crystal (0002) basal plane reflection ($2\theta_m = 26.6$ degrees) as a diffracted beam, post monochromator was used.  Rietveld analyses of data from SRMs 660b, 1976c, and 676a that included a refinement of the polarization factor, modeled as per Equations 4 and 5 in TOPAS, indicated that Equations 4 and 5 are appropriate for these crystals and configurations.  Given that the certification data of SRM 1976c were collected using a Johansson IBM, the ratio of values computed from Equations 3, 4, and 5 were used to bias the certified values to correspond to those of alternative configurations.  The results are shown in Table 4.  The user may select the set of relative intensity values from Table 4 that are appropriate for the configuration of the instrument to be qualified and proceed accordingly.  Use of SRM 1976c for additional configurations may require computation of biases alternative to those presented herein.

Table 4.  Information Values for Biased Relative Intensity Data for SRM 1976c

| Reflection, (hkl) | Relative Intensity | |
|---|---|---|
| | No Monochromator | Graphite Post Monochromator |
| (012) | 23.88 | 23.63 |
| (104) | 100.00 | 100.00 |
| (113) | 36.70 | 37.13 |
| (024) | 20.08 | 20.64 |
| (116) | 84.40 | 87.61 |
| (300) | 11.68 | 12.38 |
| (1.0.10) & (119) | 66.62 | 71.65 |
| (0.2.10) | 12.29 | 13.34 |
| (226) | 7.54 | 8.17 |
| (2.1.10) | 15.35 | 16.57 |
| (324) & (0.1.14) | 25.00 | 26.28 |
| (1.3.10) | 14.85 | 15.27 |
| (146) | 12.88 | 13.04 |
| (4.0.10) | 11.04 | 11.04 |

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