National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material 1976

Instrument Sensitivity Standard for X-ray Powder Diffraction

This Standard Reference Material (SRM) consists of a sintered alumina plate, approximately 45 mm on a side by 1.6 mm in thickness, intended for use in calibration of powder X-ray equipment for diffraction intensity as a function of 2Θ angle (instrument sensitivity). The form of the SRM serves to eliminate the variability of sample loading procedure from intensity measurements. This SRM material was chosen for consistency of microstructure with respect to grain size, shape, micro-strain and orientation. The platelets comprising this microstructure are 3 to 7 µm in diameter by 1 to 2 µm in thickness and are highly oriented with the basal plane parallel to the surface of the plate. Some amount of amorphous phase is present though no crystalline impurities could be detected.

The proper use of this SRM requires the measurement of intensity values from test equipment in a manner analogous to either of the two measurement methods used for certification. The certified parameters consist of absolute variation in intensity, 12 relative intensity values calculated from integrated intensity and peak height measurements from 25.5 to 145 degrees 2Θ, and the lattice parameters. Graphical evaluation of the ratio of data from the test equipment to the certified values will allow for an appropriate judgment as to the condition of the test equipment. This may be followed by the calculation of a correction curve, yielding standardization of instrument sensitivity and thus more accurate inter-laboratory comparisons of data involving X-ray diffraction intensity measurements.

The overall coordination of the preparation and the technical measurements leading to certification was performed by J.P. Cline of the NIST Ceramics Division. The project was the result of a round robin study carried out by R. Jenkins and W. Schreiner of the International Centre for Diffraction Data, Swarthmore, Pennsylvania.

The alumina substrates for this SRM were donated to NIST by International Business Machines Corporation, East Fishkill, New York, through the efforts of R. Anderson.

Statistical analysis was provided by S.B. Schiller and K.R. Eberhardt of the NIST Statistical Engineering Division.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Standard Reference Materials Program by N.M. Trahey.

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Certified intensity data were collected from 25 randomly selected samples on a Philips[1] diffractometer using an AEG[1] long fine-focus Cu X-ray tube operated at 1800 watts with a constant potential generator. The diffractometer was equipped with incident and diffracted beam sollar slits, graphite diffracted beam monochromator in anti-parallel geometry, and scintillation detector. The incident beam slits were of the theta compensating type, locked such that the illumination area was 12.5 mm wide at 25 degrees 2Θ. This corresponds to a slit size of 0.93 degrees; the receiving slit was 0.066 degrees. The take-off angle was 4 degrees. Samples were spun at approximately 52 rpm during data collection.

Data were collected and processed with the Siemens Diffrac500[1] version of NBS*Quant. This algorithim scans specific peaks for an integrated intensity measurement, with extended count times for each of ten points on either side of the scan range. Scan angles are indicated in Table 1; the step width was 0.005 degrees. Scan time ranged from 30 to 90 minutes per peak, for a total of 16 hours per sample. The seventh and eleventh scan ranges actually include two peaks, as noted by the two sets of miller indices listed for them in Table 1. The use of two peaks in these scan ranges ensured that intensity data were reported evenly through the desired 2Θ range.

Peak height values were manually determined, with a background subtraction, from the same scans as were the integrated intensity data. Five background data points from each end of the scan range were averaged to determine the background value. Peak height values were determined from an average of the three most intense points for data below 55 degrees 2Θ; four data points were used for the remainder of the data. Due to the proximity of the two reflections used in the seventh and eleventh relative intensity values, peak height values for these data reflect the superposition of the Cu $K\alpha_1$ and $K\alpha_2$ peaks. Thus, peak height data for these two pairs of reflections will be valid only with the use of Cu $K\alpha$ radiation.

Lattice parameters were determined from the 25 samples by means of least squares refinement from 47 peak positions determined with the spline method, ranging from 22 to 152 degrees 2Θ. Peak positions were corrected for optical aberrations with the use of SRM 640b silicon powder, to generate a 2nd order polynomial external standard correction curve which was applied to peak location determinations. Measurements were made on a Siemens D500[1] diffractometer equipped with a focusing Ge incident beam monochromator, sample spinner, and a position sensitive proportional detector. Copper $K\alpha$ radiation was used. Measurements were made within a period of 48 hours during which operating conditions were maintained. The machine was stabilized under such conditions for several days prior to measurements.

The intensity measurements from the SRM material are expected to show heterogeneity due to variations in preferred orientation. The heterogeneous nature of the samples requires a certification of a population of true relative intensities rather than the average relative intensity for each peak. The preferred orientation will uniformly effect the variability of all the peaks so analysis of the data assumed the intensity measurements have the same true relative variance. This allowed for pooling of the variances for both absolute and relative intensities. The exception to this assumption is the (300) peak; the crystallites in the diffracting position for this reflection must be perpendicular to the preferred orientation direction. Increased variability of intensity from this reflection is thus expected. The nominal value of the relative intensity is reported for information only; it was not used in subsequent analysis.

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[1] Certain manufacturers are mentioned for informative purposes only and do not represent an endorsement by NIST.

ABSOLUTE VARIATION IN INTENSITY

Analysis of the raw integrated intensity values indicated a drift in the instrument. This drift was modeled with a quadratic equation and removed from subsequent analyses. The relative standard deviation of the raw counts, pooled from the 13 peaks is:

RSD (raw counts) = 2.21%

This value incorporates both material variability and machine imprecision. This parameter can be used to determine differences in absolute sensitivity with different SRM samples.

RELATIVE INTENSITY VARIATION

The relative intensity values displayed no drift. The pooled relative standard deviation from integrated intensity measurements of the 12 peaks is:

RSD (integrated area, relative intensity) = 2.06%

The pooled relative standard deviation of the relative intensity values determined from peak height measurements is:

RSD (peak height, relative intensity) = 2.62%

The total relative uncertainty is a multiple of the relative standard deviation. For each relative intensity, this value is:

Total Uncertainty (integrated intensity) = 6.12%
Total Uncertainty (peak height) = 7.85%

This uncertainty is the half-width of a 90% confidence, 95% coverage tolerance interval. With 90% confidence, 95% of the true relative intensities for all of the peaks of this SRM should fall within the uncertainty of the certified values.

Each SRM plate is sintered to a relatively low density allowing it to be scored and broken easily into a desired size. Care should be taken to ensure that the side opposite the label is illuminated; otherwise, results are invalid. Each plate is cylindrically symmetrical, thus orientation of the plate is not of concern. However, errors due to particle counting statistics will be reduced if a sample spinner is used. Consistency in the degree of size and micro-strain induced peak broadening of the SRM allow for the use of peak heights as a substitution for integrated intensity measurements, though precision is seen to suffer as a result. The ratio of experimental data to the certified values should be plotted as a function of 2Θ angle. If this data is patternless, and if all of the ratios fall within the total uncertainty (0.0612/0.0785) of 1, then the test equipment is in control. However, if there is a clear pattern in the data, or if the ratio for at least one peak is more than 0.0612/0.0785 from 1, then the system is out of control (see Appendix).

Table 1

Reflection(s) (hkl)	Scan Angles (low/high) 2Θ		Relative Intensity	
			Integrated Area	Peak Height
(012)	24.7	26.2	32.34	33.31
(104)	34.0	36.2	100.0	100.0
(113)	42.4	44.2	51.06	49.87
(024)	51.8	53.3	26.69	25.17
(116)	56.0	59.0	92.13	83.6
(300)	67.4	69.0	19.13	16.89
(1.0.10) (119)	75.7	78.2	55.57	34.61
(0.2.10)	88.1	89.7	11.76	8.99
(226)	94.3	96.0	10.14	7.25
(2.1.10)	100.1	102.0	16.13	10.94
(324) (0.1.14)	115.4	117.4	20.86	10.09
(1.3.10)	126.8	128.95	15.58	7.56
(146)	135.2	137.4	15.47	6.55
(4.0.10)	144.3	146.7	11.29	4.06

LATTICE PARAMETERS

The certified lattice parameters, from the mean of the 25 samples are:

$$a = 0.4758846 \text{ nm } (4.758846 \text{ Å})$$

$$\sigma = 0.0000109 \ (0.000109)$$

$$c = 1.299306 \text{ nm } (12.99306 \text{ Å})$$

$$\sigma = 0.0000238 \ (0.000238)$$

where λ ($CuK\alpha_1$) = 0.1540629 nm (1.540629Å)

Appendix: How to assess and correct instrument bias using this SRM

When looking for instrumental problems, the peaks should be considered jointly, not individually. First, plot control bands as $1 \pm U$ over the range of 2Θ, where U is the relative uncertainty ($U = 0.0612$ if peak areas were used, or 0.0785 if peak heights were used). Next, plot the ratio of each new measurement to the certified value on the vertical axis against the 2Θ peak location on the horizontal axis. As long as these ratios fall within the control bands and are patternless, the system cannot be labelled "out of control."

However, if there is a pattern in the ratios, then the device is introducing a systematic error, even if all of the ratios fall within the control bands. This systematic error should be corrected by modelling the ratios as a function of peak location and using the model to correct future observations on unknowns.

Let the measured relative intensities on the 12 peaks be y_i and the certified values be c_i, so the ratios to model are

$$r_i = \frac{y_i}{c_i}.$$

Fit a simple model, using ordinary least squares regression, which describes these ratios adequately as a function of peak location (x_i). The fitted model has m parameters: m=1 for a horizontal straight line, m=2 for a slanted straight line, m=3 for a quadratic, etc. The residual sum of squares from the fit, plus an allowance for the uncertainty in the certified values on the certificate, is:

$$RSS_{full} = \sum_{1}^{n} (r_i - \hat{r}_i)^2 + (n-m)\frac{(RSD)^2}{25}$$

and the residual degrees of freedom for this "full" model are n - m. The RSD = 0.0206 if peak areas were used, or 0.0262 if peak heights were used. The residual sum of squares for the horizontal line at 1 (which describes "ideal" data), plus an allowance for the uncertainty in the certified values on the certificate, is:

$$RSS_1 = \sum_{1}^{n} (r_i - 1)^2 + (n-1)\frac{(RSD)^2}{25}$$

and the residual degrees of freedom are n - 1. Then if the test statistic

$$F = \frac{\left\{RSS_1 - RSS_{full} + (m-1)\frac{(RSD)^2}{25}\right\} / (m-1)}{\left\{RSS_{full} + (n-m)\frac{(RSD)^2}{25}\right\} / (n-m)}$$

is larger than the upper 0.05 percentage point from the F distribution with m-1 numerator and n-m denominator degrees of freedom (commonly provided in table form in introductory statistics texts), the correction model is needed.

To use the correction model: A new peak angle x* and a new relative intensity y* are measured on an unknown sample. If $\hat{r}^*$ is the predicted value of the fitted model at x*, the corrected relative intensity for the new peak angle on the unknown sample is

$$\text{corrected relative intensity} = \frac{y^*}{\hat{r}^*}.$$