National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 1878a

Respirable Alpha Quartz
(Quantitative X-Ray Powder Diffraction Standard)

This Standard Reference Material (SRM) is intended for use in preparation of calibration standards for quantitative analyses of α-quartz by X-ray powder diffraction in accordance to National Institute for Occupational Safety and Health (NIOSH) Analytical Method 7500 [1] (or equivalent). A unit of SRM 1878a consists of approximately 5 g of powder bottled in an argon atmosphere.

Material Description: The SRM material was prepared from electronic grade, single crystal nodules of Brazilian quartz obtained from the National Defense Stockpile, which were crushed and jet milled to a median particle size of 1.6 µm. The resulting powder was then washed in hydrofluoric acid and hydrochloric acid, rinsed, ignited at 500 °C, and bottled.

An analysis of the quantitative results from Rietveld analyses of 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:

93.7 % ± 0.21 % (crystalline α-quartz)

The interval defined by a value and its uncertainty is expressed as a 95 % confidence interval in the absence of systematic error [2,3].

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. This material degrades with exposure to humidity. If excessive exposure is suspected, discontinue use.

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 and R.B. Von Dreele of Argonne National Laboratory, Argonne, IL. The jet milling operation was performed by D. Ramsey and J. McLaurin, NIOSH, Cincinnati, OH.

Statistical analysis was performed by 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: 21 September 2005
See Certificate Revision History on Last Page

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

The acid washing was performed by MV Laboratories, Inc., Frenchtown, NJ.[1].

Certification: This SRM was certified in 1999 with respect to the mass fraction of material that exhibits Bragg scattering in correspondence to that of α-quartz, or phase purity. The certification procedure utilized Quantitative Rietveld Analyses (QRA) [4] (for a complete discussion of the Rietveld method [5,6]) of neutron time-of-flight (TOF) diffraction measurements in conjunction with the use of SRM 676 [7] as the internal standard. This procedure referenced the phase purity of SRM 1878a against that of SRM 676. The basis of the method rests on 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 phase purity of SRM 1878a, as certified in 1999, reflected our approximate knowledge of the phase purity of SRM 676 in 1999 [8]; however, SRM 676 was certified with respect to phase purity in 2005. Therefore, the certified phase purity of SRM 1878a was revised in 2005.

A long-count-time X-ray powder diffraction pattern of a given powder sample may offer data consistent with a high purity powder, i.e., no impurity phases and a background that is consistent with contributions of air scatter from the incident beam and thermal diffuse scatter from the sample. 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 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 is not in the context of a mechanically separable impurity phase, but it is a microstructural characteristic innate to the chemistry of SiO_2 and the production history of the SRM feedstock.

The QRA of laboratory, divergent beam X-ray powder diffraction (XRPD) data displayed a systematic bias of less than 2 %; however, these results were as precise as those determined from the TOF data. Therefore, the certified phase composition was determined from the TOF data while the homogeneity of the SRM material was verified with Rietveld analyses of XRPD data. It should be noted that the mechanism inducing this bias is not operative in Reference Intensity Ratio (RIR) based methods [9] (for a complete discussion of RIR methods, see [10]). The reported, non-certified, lattice parameters were from the aforementioned Rietveld analyses of the XRPD data. 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) [11].

Five randomly selected samples from the SRM 1878a material were admixed with SRM 676 at the 50 % level for TOF neutron diffraction analysis. TOF data were obtained on the High Intensity Powder Diffractometer (HIPD) at the Manuel Lujan, Jr., Neutron Scattering Center (LANSCE), Los Alamos, NM. 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 ± 90° and ± 153° 2Θ. The ± 90° banks covered a d–spacing range of 0.05 nm to 0.63 nm, while the ± 153° banks covered 0.05 nm to 0.48 nm. Rietveld refinements using the General Structure Analysis System (GSAS) [12] of the phases in these samples included: scale factors, lattice parameters, atomic positional and thermal parameters, crystallite size and microstrain [13] parameters, an absorption factor, and six terms of a background function describing the effects of thermal diffuse and incoherent scattering for each data set.

X-ray diffraction data for homogeneity testing and lattice parameter determination were collected on two specimens removed from each of ten randomly selected bottles of the SRM material; these 10 bottles included those from which the TOF specimens were prepared. These specimens also had known amounts of SRM 676 admixed with them. These XRPD data were collected on a Siemens D500 diffractometer equipped with a focusing Ge incident beam monochromator, sample spinner, and a scanning position sensitive detector. Copper $K\alpha_1$ radiation $\lambda = 0.154\,059\,45$ nm [14] was used. The scan range was from 18° to 154° 2Θ. GSAS was used for a Rietveld refinement of the two phases as outlined in reference [15]. Refined parameters included scale factors, crystallite size and strain induced broadening terms of the pseudo-Voigt profile function [16], one of the two parameters of the Finger [17] model for profile asymmetry, lattice parameters, sample shift and transparency terms, atomic thermal and position parameters, and five terms of a background function describing the effects of thermal diffuse scattering and

---

[1] Certain commercial materials, services and equipment are identified in order to adequately specify the experimental procedure. Such identification does not imply a recommendation or endorsement by NIST, nor does it imply that the materials or equipment are necessarily the best available for the purpose.

air scattering (incoherent) of the incident beam. Gaussian U, V, and W terms [18] were presumed to be instrumental in origin and fixed at those obtained from a refinement of SRM 660 [19].

Storage: SRM 1878a was bottled under argon to protect against humidity. When not in use, store the unused portion of this powder tightly capped in the original bottle or in a manner with similar or greater protection against humidity.

Information Values and Uncertainties: NIST information values are considered to be of interest to the SRM user, but are not certified because the measurements are not traceable to the SI, or only a limited number of analyses were performed which disallowed imparting plausible uncertainties to the measured values. The information values for lattice parameters, as determined from the aforementioned Rietveld analysis of the XRPD data, and the particle size distribution, as determined by laser scattering, are given in Table 1 and Figure 1, respectively. The interval defined by a value and its uncertainty is a 95 % confidence interval for the true value of the mean in the absence of systematic error.

Table 1. Information Values for Lattice Parameters

	Lattice Parameter (nm)
a	0.491 386 7 ± 0.000 001 6
c	0.540 561 0 ± 0.000 001 7

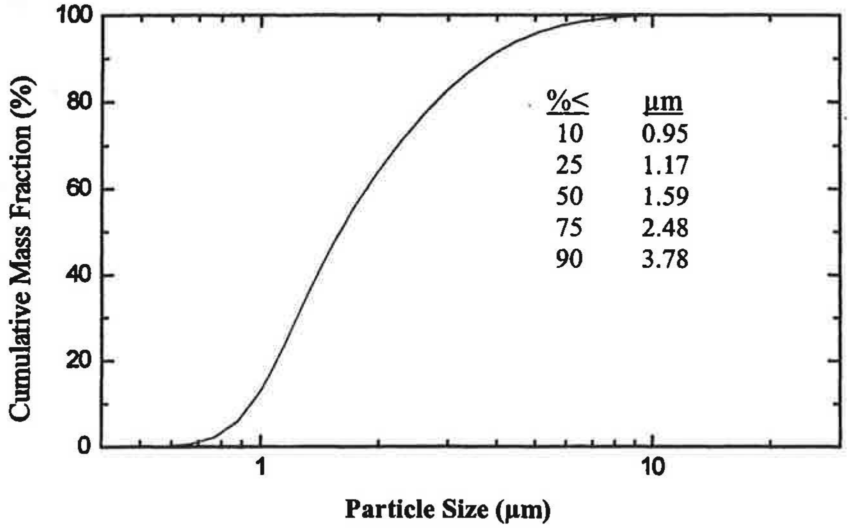

Figure 1. Typical Particle Size Distribution by Laser Scattering

REFERENCES

[1] *NIOSH Manual of Analytical Methods (NMAM)*, 4th ed.; DHHS (NIOSH) Publication No. 94-113; Eller, P.; Cassinelli, M., Eds. (1994).

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

[3] 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/.

[4] 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).

[5] *The Rietveld Method*; Young, R.A., Ed.; Oxford University Press (1993).

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

[7] SRM 676; *Alumina Internal Standard for Quantitative Analysis by X-ray Powder Diffraction*; National Institute of Standards and Technology; U.S. Department of Commerce: Gaithersburg, MD (2005).

[8] Von Dreele, R.B.; Cline, J.P.; *The Impact of Background Function on High Accuracy Quantitative Rietveld Analysis (QRA): Application to NIST SRM 676 and 656*; Adv. X-ray Anal., Vol. 38, pp. 59–68 (1994).

[9] Chung, F.H.; *Quantitative Interpretation of X-Ray Diffraction Patterns. I. Matrix-Flushing Method of Multi-Component Analysis*; J. Appl. Crystallogr., Vol. 7, pp. 519–525 (1974); and Chung, F.H.; *Quantitative Interpretation of X-ray Diffraction Patterns. II. Adiabatic Principle of X-ray Diffraction Analysis of Mixtures*; J. Appl. Crystallogr., Vol. 7, pp. 526–531 (1974).

[10] 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).

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

[12] Larson, A.C.; Von Dreele, R.B.; *General Structure Analysis System (GSAS)*; Report LAUR 86-748; Los Alamos National Laboratory: Los Alamos, NM (1994).

[13] 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).

[14] Cline, J.P.; *NIST XRD Standard Reference Materials: Their Characterization and Uses*; In Proceedings of the International Conference: Accuracy in Powder Diffraction II, NIST Special Publication 846; U.S. Government Pringing Office: Washington, DC (1992).

[15] Cline, J.P.; *NIST Standard Reference Materials for Characterization of Instrument Performance*; Industrial Applications of X-ray Diffraction; Chung, F.H.; Smith, D.K., Eds.; Marcel Dekker, Inc.: New York, pp. 903-917 (1999).

[16] 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).

[17] 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).

[18] Caglioti, G.; Pauletti, A.; Ricci, F.P.; *Choice of Collimators for a Crystal Spectrometer for Neutron Diffraction*; Nucl. Instrum., Vol. 3, pp. 223–226 (1958).

[19] SRM 660; *Instrument Line Position and Profile Shape Standard for X-Ray Powder Diffraction*; National Institute of Standards and Technology; U.S. Department of Commerce: Gaithersburg, MD (1989).

Certificate Revision History: 21 September 2005 (This revision reflects a change in the certified value for crystalline α-quartz resulting from the improved characterization of phase purity as provided in SRM 676); 31 August 1999 (Original certificate date).

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; email srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.