STANDARD REFERENCE MATERIAL™ (SRM 1990) FOR SINGLE CRYSTAL DIFFRACTOMETER ALIGNMENT

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ABSTRACT
Through extensive international collaborations, a Standard Reference Material™, SRM 1990 (a set of ≈3500 units of Cr-doped Al₂O₃, or ruby spheres) for single crystal diffractometer alignment has been certified at NIST after a successful international round-robin project. The results of the round robin project confirmed that well-aligned diffractometers are important for obtaining accurate lattice parameters, and that the ruby spheres satisfy the criteria required of a standard reference material. During the lattice parameters certification process, a total of 39 ruby spheres were measured using four single crystal diffractometers. These rubies are rhombohedral, with space group R3c. The certified mean unit cell parameters are \( a = 4.76080 \pm 0.00029 \text{ Å} \) (expanded uncertainties), and \( c = 12.99568 \pm 0.00087 \text{ Å} \). Five samples of powdered rubies were measured on a Guinier-Haagg transmission camera, giving good agreement with the values obtained from the single crystal spheres (\( a = 4.7610 \pm 0.0013 \text{ Å} \), and \( c = 12.9954 \pm 0.0034 \text{ Å} \)). The chromium mole fraction composition was found to be relatively homogenous (\( 0.42 \pm 0.011 \% \)) (expanded uncertainty). The auxiliary data on the chromium content will also be useful for microanalytical calibrations. Various systematic corrections associated with measurement and diffractometer alignment were also investigated. Among them, thermal expansion and refraction corrections were applied.

INTRODUCTION
In order to provide industrial, academic and government laboratories with a Standard Reference Material™ (SRM) for the alignment of single crystal diffractometers, an international project was completed which involved two major undertakings: an international round robin to demonstrate the viability of the selected standard, and the certification of the lattice parameters of the standard. Presently, other than a few commercially available crystals from various manufacturers and materials that have been prepared locally at individual laboratories, no certified standard material is available. A set of 3500 units of ruby spheres (\( 0.42 \pm 0.011 \% \)) (expanded uncertainty) of Cr-doped Al₂O₃ spheres was acquired from the Acranum Corporation to be a potential SRM. The high hardness of ruby allows the grinding of 150 \( \mu \text{m} \) diameter spheres (sphericity 0.0013 mm), which produces strong reflections at high angles for copper as well as for molybdenum radiation. These materials are nontoxic and have high symmetry (rhombohedral, R3c). From well-centered reflections at high angles, high precision lattice parameters can be obtained. This SRM is intended to improve the accuracy of lattice parameter determinations, and to evaluate the state of the instrument employed at each local laboratory. The project was supported by NIST, International Union of Crystallography (IUCr), and...
The American Crystallographic Association (ACA). This report highlights the critical results of the round robin and the certification projects. Details of the study will be published elsewhere [1].

INTERNATIONAL ROUND ROBIN

In 1994, fifty sets of ruby spheres and reference crystals (synthetic zeolite, Si_{36}O_{72}·2(C_2H_5N)·2HF, with a plate-like morphology) were distributed from the Hauptman-Woodward Medical Research Institute to laboratories around the world. The main goals of the round robin project were to determine realistic limits on the precision and accuracy of lattice parameters using various commercial diffractometers, to assess the x-ray technique and the state of the instrument employed at each local laboratory, and to evaluate the usefulness of the rubies as a NIST SRM for diffractometer alignment. Scientists were asked to determine the lattice parameters of the ruby and the zeolite crystals by standard laboratory procedures in use in their facilities, and provide information concerning their equipment, and lattice parameter determination software. The algorithms recommended were those described by Hamilton in the International Tables for Crystallography [2], by Busing and Levy [3], and also by King and Finger [4].

A total of 45 sets of reports for the ruby spheres and zeolite crystals respectively were received from 32 laboratories (incomplete sets of data from two laboratories). More than 10 different types of diffractometers were employed by these participants. All except one participants collected their data within the ambient temperature range. A correction of the lattice parameters to room temperature of 25 °C was made before comparison. Within the range of 0 °C to 100 °C the α-Al₂O₃ was found to expand approximately linearly and anisotropically [5, 6]. Under these conditions, the corrections were calculated according to the following expression: a (25 °C) = a' [1+αₐ(25-T)], where αₐ = 5.0 x 10⁻⁶ and c (25 °C) = c' [1+αₙ(25-T)], where αₙ = 6.66 x 10⁻⁶. Another correction that was applied was the refraction correction [7]. In the equation, δd/d = (1-n)/n, where n is the refractive index, we found that for Mo radiation the value of (1-n) = 2.69 x 10⁻⁶, and for Cu radiation, the value of (1-n) = 1.27 x 10⁻⁵.

The mean values of the lattice parameters of the ruby spheres are: a = 4.7608 Å ± 0.0062 Å, c = 12.9979 Å ± 0.020 Å (95% interval on mean of laboratories). Figures 1 displays the histograms of the results of lattice parameters a (upper graph) and c (lower graph) of 30 laboratories providing complete round robin reports. For the lattice a, the results of the laboratories are centered on the certified value (discussed later) and are symmetric around this value. For the lattice parameters c, there are three results that are somewhat separated from the others. The spread of the results for the c parameter (standard deviation = 0.010) is greater than that for the a parameter (standard deviation = 0.0031). In general, one also observed that for data sets with large deviations of cell data from that of the SRM value, the corresponding cell data of the zeolite crystals also show similar magnitude of deviations from the known values, suggesting improved alignment using the SRM will increase the accuracy of a laboratory unknown.
CERTIFICATION OF SRM 1990

The lattice parameters of SRM1990 were certified by using four well-aligned commercial single crystal diffractometers, three at Lucent Technology and one at NRC of Canada (three Enraf-Nonius CAD4 diffractometers and one Picker diffractometer). A second method, the Guinier-Hagg transmission technique, was employed to corroborate the single crystal lattice parameter data. Statistical analysis of the resulting data was carried out in collaboration with the NIST Statistical Engineering Division. Auxiliary data such as the quantity of chromium in these crystals were analyzed using the electron microprobe, and also by the scanning electron spectroscopy/energy dispersive x-ray (SEM/EDS) technique.

Single Crystal Diffractometer Studies and statistical Analysis

A total of 45 sets of 4-circle diffractometer data were measured corresponding to four subsets of data. Set 1 (fifteen measurements) was studied using CuKα radiation at the NRC of Canada on a CAD4 diffractometer. Set 2 (four measurements) was also investigated at NRC Canada using Mo Kα radiation, but with a Picker diffractometer. Set 3 (fifteen measurements) and Set 4 (eleven measurements) were measured at Lucent Technology with two CAD4 diffractometers; one with Cu radiation, and one with Mo radiation. The diffractometer control program, DIFRAC (National Research council of Canada) [8], which has the state-of-the-art data collection and data reduction routines was employed for all sets. This program can be adapted to machines with different geometry, including the Kappa geometry used by the CAD4 diffractometers. X-ray wavelengths used for all calculations were taken from Hartwig et al. [9] and from Cohen and Taylor [10]. The value for Cu Kα, maximum is 1.54059292 (45) Å, and for Mo Kα, radiation the maximum is 0.70931631 (84) Å.

Systematic corrections investigated include thermal expansion, absorption and eccentricity, horizontal divergence, vertical divergence, and refraction. Among them, only thermal expansion and refraction corrections were applied. Other corrections were too small to be considered. Data collection of these experiments took place within a range of 19 °C to 26 °C and corrections to 25 °C have been applied.

The certified values of the lattice parameters (a and c) of SRM 1990 and their uncertainties represent a consensus of the four sets of measurements. Each of the four sets of measurements for a particular lattice parameter is reduced to a mean value, and the certified value for the lattice parameter is the mean of the resulting four mean values. The certified value of the lattice parameters are a = 4.76080 Å ± 0.00029 Å (expanded uncertainty), and c = 12.99568 Å ± 0.00087 Å. The standard uncertainty of the certified value is the standard error of the mean, which is equal to the sample deviation of the four mean values divided by the square root of 4. The associated degree of freedom is 3 and the corresponding uncertainties is equal to the standard uncertainty times the coverage factor. The

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1 Certain trade names and company products are mentioned in the text or identified in illustrations in order to adequately specify the experimental procedure and equipment used. In no case does such identification imply recommendation or endorsement by NIST.
Fig. 1. Distribution of the international round robin results of the lattice parameters $a$ (upper) and $c$ (lower) of SRM 1990, with certified values and their expanded uncertainties shown.

uncertainty interval contains the lattice value with a 95% level of confidence. Readers are to refer to reference [11, 12] for details on the procedure and terminology of the expression of uncertainty in measurement. These certified lattice parameters fall well within the results of the those obtained from the international round robin study ($a = 4.7608 \pm 0.0062 \text{ Å}$, $c = 12.9979 \pm 0.020 \text{ Å}$). Figure 2 displays the four sets of measurements, the certified value, and the expanded uncertainty for the lattice parameters $a$ and $c$, respectively. For both lattice parameters, the expanded uncertainty interval contains the means of the four sets of measurements.

**Guinier-Hägg Transmission powder technique**

The Guinier-Hägg transmission camera technique was used as a second method for determining the lattice parameters. Prior to the measurements of the samples, the camera was aligned and calibrated. The powder pattern of silicon x-ray diffraction SRM 640b [13] was measured to check the cylindrical form and the adjustment of the camera. Five samples were prepared for this study. In each of five preparations, about 12 spheres were crushed in a small agate mortar under toluene. The powdered material (about 5 mg) was transferred to the planchet and mixed with Si powder. Various possible errors involved with the Guinier-Hägg technique that may affect the accuracy of cell parameters include errors due to x-ray beam divergence, film shrinkage and thermal expansion. Thermal expansion corrections were applied. Other problems caused by specimen displacement, transparency effect, and absorption can mostly be compensated by using the Si internal standard. The mean values of these lattice parameters are $a = 4.7610 \pm 0.0013 \text{ Å}$ (expanded uncertainty), and $c = 12.9954 \pm 0.0034 \text{ Å}$. The Guinier-Hägg powder data support the single crystal data well.
Fig. 2. Four sets of lattice parameters $a$ (Å, upper graph) and $c$ (Å) as measured from (1) NRC Canada, CAD4 diffractometer (Cu Kα), (2) NRC Canada, Picker diffractometer (Mo Kα radiation, (3) and (4) Lucent Technology, CAD4 diffractometers, Cu Kα and Mo Kα radiation, respectively.

**Measurement of the Cr content**

A total of 15 spheres was studied. One of the spheres was randomly selected to study in detail using the electron microprobe technique for determining the Cr concentration, and to study whether Cr is relatively uniformly distributed in the sphere. After the Cr content was obtained (mass fraction of 0.44 % Cr$_2$O$_3$), this sphere was in turn used as a secondary standard for the rest of the 14 spheres by using an SEM/EDS broadbeam technique. The spheres were prepared by potting in epoxy and polishing. The final polishing step was completed using 0.1 μm diamond abrasive. A polished cross section of the spheres for analysis was thereby obtained. During analysis, the beam was rastered over an area $\approx 100 \mu$m x 100 μm in size. Data was reduced using the conventional analysis methods with the aid of the DTSA software package [14]. The Cr composition was found to be relatively
homogenous throughout the 14 samples, and had a mole fraction estimated to be 0.42% ± 0.011% (expanded uncertainty).

**SUMMARY**

X-ray structural determinations using automatic data collection and structure solution schemes require accurate initial cell parameter data. Until now, no certified standard was available for the evaluation of the diffractometer condition, alignment and interlaboratory comparison of data. The set of SRM 1990 ruby spheres utilizes a stable material and with high symmetry; these spheres are easy to handle and to perform both optical and diffractometer alignment. The certified lattice parameters for SRM 1990 are consistent with both the results of the international round robin and also with those from Guinier-Hagg transmission powder diffraction of crushed rubies. Further, the small variation in Cr composition is sufficiently small to affect the accuracy of the certification. The expanded uncertainties and the number of significant digits reported for the certified values are much smaller than those obtained in typical laboratories (round robin results). This batch of ruby spheres therefore will serve well as a diffractometer alignment standard and a good standard for interlaboratory comparison of data. The result of this work is expected to have a significant impact on accurate scientific investigations using single crystal diffractometers.

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