

## X-ray diffraction powder data

PETER BAYLISS

*Department of Geology, University of Calgary  
Alberta T2N 1N4, Canada*

### Abstract

The present standard of documentation of X-ray diffraction powder data is generally not adequate. Therefore suggestions for adequate documentation of X-ray diffraction powder data are tabulated.

### Introduction

When X-ray diffraction powder data are used for routine mineral identification, a reference to the unit cell constants and errors calculated therefrom, and to published comparative data—if available—is sufficient. On the other hand, powder data better than that available should be published. The suggestions that minor improvements in such data should be published only by the Joint Committee of Powder Diffraction Standards (often still incorrectly called ASTM) is unacceptable; this would restrict the published data to a copyrighted format on cards, which are not acceptable to most libraries, and would also incur a long publication delay. Therefore the data would not be exposed to critical evaluation as in a mineralogical journal, and mineralogists would be discouraged from attempting to produce better data.

*Selected Powder Diffraction Data for Minerals* (1974), which was produced by the Joint Committee of Powder Diffraction Standards, contains X-ray diffraction powder data for about 1850 minerals. Future editions will include both additional and replacement data. The reasons for replacement data include (a) a larger  $2\theta$  range, (b) additional reflections with weak intensities, (c) greater accuracy in measurement of intensity and interplanar spacing, (d) better resolution, (e) improved indexing, and (f) additional mineralogical properties.

A standard for X-ray diffraction powder data has been recommended by Kennard *et al.* (1971) in the International Union of Crystallography commission report. Since their report is neither widely used nor very specific, the suggestions for adequate documentation of minerals are listed in Table 1.

### Discussion

Following the mineral's name and ideal formula (Table 1, 1a), cite its locality if it occurred naturally, then give its chemical analysis and the formula derived therefrom so as to indicate how far it deviates from its end-member composition. For synthetic specimens state the source of the constituents, method of preparation, and any subsequent treatment.

The Debye-Scherrer or Gandolfi camera is useful for routine mineral identification; however, it is better to use the Guinier camera or diffractometer to record data for publication, because the resolution is three to five times better. Poor data (*e.g.*, Debye-Scherrer with visually estimated intensities) may generally be used easily for identification against a good standard (*e.g.*, Guinier with densitometer measured intensities), but not vice versa. If insufficient quantity of the mineral is available and a Debye-Scherrer or Gandolfi camera is used (more than one Gandolfi pattern is measured, because Gandolfi may miss reflections of low multiplicity or give false intensities), then a minimum diameter of 114.6 mm is required to give adequate resolution.

For filtered radiation, only the target element and composition of the filter (*e.g.*, Cu radiation/Ni filter) are stated. For monochromatized radiation, the target element with spectral line and monochromator crystal with diffraction plane (*e.g.*,  $\text{CuK}\alpha$  radiation with graphite 002 monochromator) are stated.

In order that the data may be corrected if more precise constants become available, the *International Crystallographic Tables* (1974) recommend the continued publication of the wavelength value (*e.g.*,

TABLE 1. X-ray diffraction powder data suggestions

- 1.a. Mineral name and ideal formula.
- b. Locality, chemical analysis, and derived formula; or method of synthesis.
- 2.a. Type of instrument and diameter if camera.
- b. Radiation; and filter or monochromator.
- c. Wavelength value, or name of standard, plus its unit cell constant.
- d. Temperature °C.
- e.  $2\theta$  range greater than  $62^\circ$  ( $d = 1.5\text{\AA}$  for  $\text{CuK}\alpha$  radiation).
- f. Quantitative intensity measurement.
- g.  $I_i/I_c$ —intensity ratio of the strongest reflection of the mineral to the 113 of corundum.
3. List of  $d_{\text{obs}}$ ,  $d_{\text{calc}}$ ,  $I/I_i$ ,  $I_{\text{calc}}$  (if available), and  $hkl$ .
- 4.a. Space group(s) consistent with indexing.
- b. Unit cell constants with standard deviations.
- c.  $Z$ —the number of formula units per unit cell.
- d. Calculated density.
- e. Reasons for unindexed reflections.
- 5.a. Physical properties; color, hardness, density.
- b. Optical properties.
6. References.

1.5418Å) or the name of the standard with its unit cell constant (e.g., silicon 5.43088Å). The wavelength value with only the name of a standard is unacceptable. If a standard is used, it is the unit cell constant that is needed for correction rather than a wavelength value. A silicon standard is now commercially available from the U.S. National Bureau of Standards, and a standard to provide larger  $d$  values is being sought. Because the unit cell constants vary with temperature, an exact temperature is needed. A statement such as "room temperature" is unacceptably vague.

The three entries in the Hanawalt search manual of *Selected Powder Diffraction Data for Minerals* (1974) are based upon the three strongest reflections which occur before  $90^\circ 2\theta$  ( $d > 1.09\text{\AA}$  for  $\text{CuK}\alpha$  radiation). Only 30 percent of the data in the Powder Diffraction File is recorded to  $2\theta$  greater than  $90^\circ$ , whereas 70 percent is recorded to  $2\theta$  greater than  $62^\circ$  ( $d < 1.54\text{\AA}$  for  $\text{CuK}\alpha$  radiation). In order that published X-ray diffraction powder data may be used successfully in this search manual,  $d$  should be given for  $2\theta$  angles up to  $90^\circ 2\theta$ ; however, for many minerals little useful data is recorded with  $2\theta$  greater than  $62^\circ$ , which appears to be the minimum limit. Such statements as "plus 15 lines down to  $1.08\text{\AA}$ " are unacceptable because they are useless, as the number of reflections recorded depends on the ability of the method to detect weak reflections.

Intensity measurement may be made with counter methods, a densitometer, a photographic strip, or a visual estimate. For routine mineral identification, a

visual estimate of intensities from a film is sufficient. In order to record all weak reflections, the film is commonly overexposed. Therefore the intensities of the strong reflections are similar. Because many users record quantitative intensity data for routine mineral identification, this is the minimum publication standard. If equipment is not available to use either counter methods or a densitometer, a photographic strip as described by Klug and Alexander (1974) should be used. In the future, Kennard *et al.* (1971) expect that the observed intensities will be compared with calculated intensities to quote a discrepancy index  $R_I$ , where  $R_I = \Sigma(I - I_{\text{calc}})/\Sigma I$ .  $R_I$  is only good where the structure is accurately known.

The relative reflection intensity (peak height) method is used to obtain semiquantitative values of the minerals in a rock. In order to use this method, the intensity of the strongest reflection ( $I_i$ ) of all minerals must be known relative to the intensity of a standard ( $I_c$ ). The 113 reflection of corundum ( $\text{Al}_2\text{O}_3$ ) has been selected as this standard by the Joint Committee of Powder Diffraction Standards because of corundum's commercial availability as "Linde A" in approximately  $0.3\ \mu\text{m}$  size, its purity, its chemical stability, and its freedom from orientation due to particle shape, although one must check that it is well crystallized. If enough of the mineral is available, the ratio  $I_i/I_c$  should be determined from a 1:1 mixture with corundum.

The observed spacings ( $d_{\text{obs}}$ ) are listed only to the proper number of significant figures; this means that the number of significant figures will increase systematically as  $d$  decreases, according to the precision of the  $2\theta$  measurement. The calculated spacings ( $d_{\text{calc}}$ ) are all listed out to the maximum observed  $2\theta$  so that the indexing may be evaluated.

The reflection intensities ( $I$ ) are quoted relative to the strongest reflection ( $I_i$ ), which is taken arbitrarily as 100. The intensities are measured as peak intensities unless otherwise stated. To insure accurately measured intensities, special precautions are needed to avoid preferred orientation in minerals which have prominent cleavages. Intensity terms such as weak and strong are useful for routine mineral identification but are too vague for data publication. Although methods are described by Henry *et al.* (1961) for the indexing of powder X-ray diffraction data, the indexing obtained has been found incorrect in a number of cases. For instance the mineral ferritungstite is described as tetragonal ( $a = 10.28\text{\AA}$ ,  $c = 7.77\text{\AA}$ ), but recent single crystal X-ray diffraction indexing by Machin (personal communication) shows it to be

cubic ( $a = 10.28\text{\AA}$ ). Therefore it is desirable to use single crystal methods whenever possible.

If approximate unit cell constants—preferably by single crystal X-ray diffraction—have been recorded by the investigator or by previous investigators, the unit cell constants should be refined from the powder data by the least-squares method. Many such least-squares computer programs are available (*e.g.*, Appleman *et al.*, 1972). It is useful to state whether an absorption correction is applied or not, because the absence of an absorption correction may cause a large error in both intensity and  $d$  (*e.g.*, a sulfosalt mineral with Cu radiation in a Debye-Scherrer camera). The estimated standard deviation determined by a least-squares method is quoted in brackets to indicate the error in the last figure (*e.g.*,  $5.43088(4)\text{\AA}$ ). An estimated error should not be published because it is unreliable (Kennard *et al.*, 1971).

Calculated values such as density and  $Z$  (number of formula units per unit cell) are useful, since they provide a check. Other calculated values such as axial ratios and volume are useful but not essential. A discussion of unindexable reflections should indicate the probability that these reflections represent an impurity, a supercell, or an incorrect choice of unit cell.

All mineral species may be distinguished one from another with a chemical analysis and a unit cell determination. However, optical and physical properties are given as useful additional information. If these properties are taken from the literature, adequate references should be given.

## Conclusions

Because published X-ray diffraction powder data will be used as standards by other mineralogists, they should meet certain minimum requirements which are obtainable today in most laboratories. Such a procedure will eliminate the publication of an unnecessary series of minor improvements.

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