

On the accuracy of mineralogical measurements.

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ALMOST any scientific periodical devoted to mineralogy will afford examples of the failure on the part of some workers to realize the limitations of the accuracy of their measurements. Often results are calculated to far more places of decimals than the measurements can possibly warrant. In other instances measurements which show differences quite outside the limits of probable error are regarded as being in good agreement; this last failing applies especially to chemical analyses, which occasionally provide decided evidence against the formula they are supposed to support.

The accuracy of goniometric measurements is, of course, very variable, but only in rare cases does it reach 1', and even the most perfect crystals probably could not be relied on beyond $\frac{1}{4}'$; in the great majority of cases, diffuse reflections and vicinal growth lower the accuracy, and 5–10' is the probable accuracy of most goniometric measurements. A glance at a table of natural tangents will show that in the most favourable case, where the measurement is of an angle of the type $c(001):r(101)$ in the orthorhombic or a more symmetrical system, the probable error in the axial ratio for values of the measured angle between 45° and 60° is of the order of ± 0.0005 per 1' error in the measurement; with increase in the measured angle, the error in the axial ratio falls, to about ± 0.0003 per 1' with an angle of 80° ; on the other hand, an angle of 30° implies an error of ± 0.0011 per 1' error in the measurement. In the monoclinic and anorthic systems the probable accuracy of the axial ratio is somewhat less since several angles, all liable to error, are needed to compute the ratio. On the other hand, if several extra measured angles are taken into account by a suitable method of adjustment, the probable accuracy of the axial ratios is somewhat

enhanced. T. V. Barker¹ strongly advised such a procedure wherever it can be carried out without much additional labour, and by its application to first-class material, the accuracy of the axial ratios could probably be made about ± 0.0001 . Crystals as perfect as some of those grown by A. E. H. Tutton might occasionally justify the computation of an axial ratio to the fifth decimal place, with a probable error of say ± 0.00003 , but the accuracy of the average crystallographic measurement cannot possibly justify the publication of axial ratios to six or seven places of decimals, as has been done from time to time. Indeed, the accuracy of the axial ratios deduced from most goniometric work is probably of the order of ± 0.002 – 0.005 , and really only justifies three places of decimals in the axial ratios. While the writer would not suggest that the time-honoured practice of computing axial ratios to four places of decimals be dropped, it is important that it should be more generally recognized that the fourth place is, as a rule, superfluous.

Refractive index determinations by the immersion method are frequently accompanied by a statement of the probable maximum error, but there is often a tendency to over-estimate the accuracy of determinations by the prism method. Assuming that a good well-polished prism is cut, the angle of the prism can generally be obtained accurate to $\frac{1}{2}'$, but only rarely can the angle of minimum deviation of the refracted light be obtained closer than $1'$, and often the accuracy is less.

It is a simple matter to determine the error in the refractive index, n , consequent on given errors in the measurement of the prism angle, A , and the angle of minimum deviation, D . From the well-known equation $n = \sin(A + D)/2/\sin(A/2)$ we have by differentiation with respect to A and to D : $dn/dA = -\frac{1}{2}\sin\frac{D}{2}\operatorname{cosec}^2\frac{A}{2}$, and $dn/dD = \frac{1}{2}\left(\cos\frac{D}{2}\cot\frac{A}{2} - \sin\frac{D}{2}\right)$, A and D being measured in radians.

These equations show that the error in n consequent on a given error in A increases with increase of n and, very rapidly, with decrease of A , while the error consequent on a given error in D decreases with increase of n , but increases considerably with decrease of A .

A few probable errors calculated from the above equations are collected in table I. From this table it will be seen that, taking

¹ T. V. Barker, Graphical and tabular methods in crystallography. London, 1922, p. 100.

both sources of error into account, a refractive index determination by the prism method is subject to errors which depend only very slightly on the magnitude of the refractive index, but markedly on the angle of the prism used, increasing very rapidly as the prism angle decreases. Only with a good prism of reasonably large angle is a fourth place justified in a refractive index measured by the prism method. Where duplicate measurements differ by $5'$ (which often happens), or where a prism of as small an angle as 20° has to be used for any reason, three places of decimals only can justly be given. Very rarely can a fifth place of decimals be taken seriously, and since an error of $1''$ in each of the two measurements means 0.000006 in the refractive index a sixth decimal place is invariably worthless except in very highly specialized investigations.

TABLE I. The errors in a refractive index determination by the prism method consequent on an error of $\pm \frac{1}{2}'$ in the determination of the prism angle, A , on an error of $\pm 1'$ in the angle of minimum deviation, D , and on both errors jointly, calculated for various values of A and of the refractive index, n .

A .	n .	δn for $\delta A = \frac{1}{2}'$.	δn for $\delta D = 1'$.	δn for $\delta A = \frac{1}{2}'$ and $\delta D = 1'$.
60°	1.4	0.00007	0.00021	0.0003
	1.5	0.00009	0.00019	0.0003
	1.75	0.00015	0.00015	0.0003
30°	1.5	0.00035	0.00038	0.0007
20°	1.5	0.00079	0.00076	0.0015

The decrease in accuracy of a refractive index determination when small-angled prisms are used is clearly shown by the experiments of M. Kołaczowska,¹ which agree closely with the above figures. The advantages of a large-angled prism are somewhat discounted by the decrease in the amount of light falling on the prism, as pointed out by Kołaczowska, and also by the increased reflection at the prism faces, and the increased effect of imperfections in the refracting faces, so that the most accurate results will in general be obtained with prisms of angle considerably smaller than the largest-angled prism which will pass light in the 'minimum deviation' position.

The accuracy of the total-reflection method for refractive indices has been discussed in detail by F. Schwiétring,² who states that an

¹ M. Kołaczowska, Arch. Prac. Min. Tow. Nauk. Warszawa, 1926, vol. 1, p. 9. [Min. Abstr., vol. 3, p. 321.]

² F. Schwiétring, Zeits. Krist., 1930, vol. 75, p. 449 and vol. 76, p. 87, [M.A. 4 447]. W. Geffcken and H. Kohner (Zeits. Physikal. Chem., 1928, Abt. B,

accuracy of ± 0.0002 can be obtained, but it does not seem likely that many determinations will approach this figure.

Birefringence measurements always involve a determination of thickness of the plate used, and since there is no difficulty in accurately determining the path-difference, it is the accuracy of the thickness measurements that decides the accuracy of the result. Rarely can this exceed 1%, and in most determinations under the microscope 5% or even more is the probable error. Yet birefringences, measured apparently under the microscope, are regularly published to three or even four significant figures by some authors without comment, and used for the computation of optic axial angles.

The error in a directly measured optic axial angle can only be found by comparison of successive readings, and may be anything from 1' or 2' to several degrees. But since computed optic axial angles are often published to minutes or even half-minutes of arc, it is of some interest to see how far this is justifiable. As above mentioned, direct birefringence measurements will rarely exceed 1% in accuracy, and if we assume this accuracy in both $\gamma - \alpha$ and $\beta - \alpha$, the accuracy in $\sin V$ will also be about 1%, which means an accuracy of $2V$ round about 2% for large angles, improving for small ones; but for small ones, the accuracy in the smaller birefringence is very unlikely to reach 1%, so that on the whole we may say that the accuracy of an optic axial angle computed from birefringence measurements is never likely to exceed 2%, and will more often be of the order of 5–10%. This would justify, in favourable cases, a citation to $\frac{1}{2}^\circ$, but never to minutes of arc. The accuracy of an optic axial angle calculated from refractive index measurements can only be determined for specific instances, since the accuracy of the birefringence data needed will be very variable. But since the refractive indices are not likely to exceed ± 0.0003 in accuracy, we can say in general that the accuracy of $2V$ is likely to be about $0.06/B\%$, where B is the smallest birefringence.

Extinction-angles are very difficult to determine accurately and few authors quote them to a nearer approximation than 1° . By taking all the precautions mentioned in the text-books, a further accuracy, up to say 10', may be attained, perhaps even more in

vol. 1, p. 456, [M.A. 4-449]) were only concerned with liquids, and the high accuracy they claim could not possibly be extended to measurements on crystals without extraordinary precautions.

favourable cases. One possible source of error which is often neglected, the departure of a section plate from the intended direction by a degree or so, the author has recently discussed in some detail.¹

While the general tendency seems to be to over-estimate the accuracy of physical measurements on crystals, chemical analyses are often far too lightly valued—perhaps, often, because the mineralogist is not an analyst. Sometimes important analyses are entrusted to inexperienced students, with deplorable results, and the mineralogist bases his conclusions on an analysis which is quite unfit for publication. Both these tendencies are really different aspects of the same thing—a tendency in some quarters to treat the chemistry of a mineral too lightly. The probable accuracy to be expected in a careful analysis of good material by a skilled analyst is discussed in detail by Hillebrand and Lundell.² As they point out, the probable accuracy of an analysis varies greatly with the elements to be determined apart from all other factors, but in general terms we may say that with few exceptions³ the error in the determination of a substance present in amount exceeding 10 % should not greatly exceed 1 % of the amount there. Yet analyses showing silica varying from 37 to 42 % were until recently accepted as in fair agreement with a fixed formula for thomsonite. Silica in analcime ranges, according to the published analyses, from 52 to 56 %, but rarely is any suggestion made that the formula $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$ is inadequate. The formula of pyrite is always given as FeS_2 , and few writers mention that an excess or deficit of sulphur well outside the experimental error has been repeatedly shown by analyses. Where the atomic ratios calculated from an analysis depart from the suggested formula by more than about 1–2 %, some explanation is certainly called for.

A similar tendency is found in much X-ray work. With care, the unit cell size should be determined with an accuracy of at least 2–3 %, and a density determination should be more accurate than $\frac{1}{2}$ % as a rule, so that a departure of the molecular cell content from the ideal figure by more than about 3 % should be suspect—indeed $1\frac{1}{2}$ % can usually be attained. Yet there have been instances where 5 % (2.1 for 2) or even greater departures have been accepted without com-

¹ M. H. Hey, *Min. Mag.*, 1933, vol. 23, p. 367.

² W. F. Hillebrand and G. E. F. Lundell, *Applied inorganic analysis*. New York, 1929, pp. 3–6, 874 ff.

³ Mainly substances determined indirectly, as alumina or ferric iron in rock analyses. Here errors in several major constituents may, in an unfavourable case, fall on one minor constituent.

ment. At best, computation of the number of multiples of a selected ideal formula per unit cell is by no means an ideal practice. It is far better to compute, from an actual analysis of the material, the number of atoms of each kind in the unit cell. Dependence on an ideal formula which may be incorrect is thereby avoided, and the true accuracy of the work revealed. For if the material used does not exactly correspond to the ideal formula taken, by reason of isomorphous replacement or of inaccuracy of the formula, a quite incorrect idea of the accuracy or inaccuracy of the X-ray work may be given.

The statement of specific gravities is often made in an incomplete manner, thereby reducing the available accuracy. Thus 'sp. gr. 3.368 at 20° C.' does not state clearly whether the standard of comparison is water at 20° C. or at 4° C., and as the difference between the two interpretations amounts to 0.0087, it is of some importance. Probably the best method of statement is ' $D_4^{20} = 3.368$ (or $D_{20}^{20} = 3.377$), corrected to vacuum'. The vacuum correction (amounting in the above case to 0.003) is not needed where the measurements only justify a statement of the specific gravity to three significant figures.¹

One curious tendency which can sometimes give a quite misleading idea of the accuracy of measurements of all kinds is the misuse of decimal notation. Thus when a specific gravity is cited as 4.25, one is never sure whether the probable error is ± 0.01 , ± 0.05 , or even $\pm \frac{1}{4}$. Where the probable error is greater than ± 0.2 , to publish such a figure as 4.25 is most misleading; it should be cited as $4\frac{1}{4}$, which implies a probable error of $\frac{1}{4}$. A statement of hardness as 3.5 or 3.75 merely implies a value approximately midway between 3 and 4 or nearer 4 than 3. Such values should be given as $3\frac{1}{2}$ or $3\frac{3}{4}$.

¹ A. Hutchinson, *Min. Mag.*, 1924, vol. 20, p. 198.