# MAXIMUM ERROR IN SOME MINERALOGIC COMPUTATIONS

# H. W. FAIRBAIRN AND C. W. SHEPPARD, Massachusetts Institute of Technology, Cambridge, Mass.

#### CONTENTS

Abstract	673
INTRODUCTION	674
DETERMINATION OF DENSITY.	675
Suspension method.	675
Hydrostatic method	676
Jolly balance.	675
Berman balance	676
Pycnometer method	678
X-radiation method.	680
Comparative accuracy.	682
DETERMINATION OF REFRACTIVE INDEX	683
MINIMUM DEVIATION METHOD	683
GRAZING INCIDENCE METHOD.	686
Universal stage extrapolation method	687
Optic angle method	689
Comparative accuracy.	691
DETERMINATION OF BIREFRINGENCE.	691
GENERAL COMPENSATOR METHOD (Berek)	691
Emmons extrapolation method	693
Optic angle-compensator method	693
Comparative accuracy.	694
DETERMINATION OF OPTIC ANGLE.	695
Compensator method	695
Refractive index method.	695
Extinction angle method	697
Optic plane horizontal.	697
Optic plane vertical	699
INTERFERENCE FIGURE METHODS.	700
Comparative accuracy.	701
SUMMARY	702
Acknowledgments	702

#### ABSTRACT

The notable lack of quantitative information regarding errors in many mineralogic computations has prompted the writers to construct a series of diagrams from which such information can be readily obtained. These include various determinative methods for density, refractive index, birefringence, and optic angle. Assuming a skilled operator, maximum values of the error in single observations are assigned to each procedure, so that the diagrams represent "worst" values of error, rather than a "probable" error as determined from a series of observations. Comparison of the various procedures is based on this "maximum expected" error.

## INTRODUCTION

It is a truism that all physical measurements are approximations which approach, in varying degree, an unattainable absolute value. As a result it is essential that the degree of approximation, or amount of fractional deviation, be adequately known. In the field of mineralogy everyone knows about this, but few have consistently done anything about it. For various reasons the subject as a whole has been treated in the manner of a poor relation, with much overstatement and some understatement of the fractional deviations obtained (Hey, 1933). The present paper is an attempt to improve this situation.

Deviations (also called uncertainties or errors) are classified as systematic (periodic) or random (accidental). Systematic errors are inherent in every experimental investigation (e.g. temperature variations in density and refractometric work) and can be controlled. This control is in some cases fine enough so that this type of error is negligible compared with the random error. Random deviations arise through reading of scales, adjustment of extinction positions, etc. For a single observation the uncertainty of the measurement depends in part on the skill of the observer, in part on the character of the apparatus. If repeated observations are made, the random error may be expressed quantitatively by calculating a "probable error." As there is a 50% probability of a measurement differing from the true value by more than this amount, the "probable error" of an observation may give a false impression of accuracy. In the present discussion "maximum expected error" is considered only-i.e., it represents the probable worst value which a skilled operator would obtain from a single measurement with a given apparatus. If it is known in advance how large this maximum expected error is likely to be and if this value, added to the known systematic error, gives a total uncertainty which can be tolerated for the work in hand, the labor of computing a standard "probable error" may be avoided. This maximum error is of course not a precise quantity, but the numerical values used in constructing the diagrams given here are believed to be large enough so that the curves give fractional deviations which would be exceeded only in rare instances.

The general method followed is (1) differentiation of the basic formula with respect to all pertinent variables, (2) assumption of maximum expected values for the differentials, (3) solution of the differential equation to determine the maximum expected random error, (4) calculation of the systematic error, (5) addition of random and systematic errors, (6) construction of a diagram.

It is assumed that the reader is familiar with the determinative methods under scrutiny and has acquired enough manipulative skill to avoid random errors appreciably greater than those shown in the diagrams. In cases where the observer believes that the uncertainty in any of his own measurements differs markedly from the values used here, an adjusted diagram can usually be made with little labor by referring to the proper differential equation.

## DETERMINATION OF DENSITY

Four commonly used methods of density determination are considered and their relative accuracies compared. The suspension, hydrostatic, and pycnometer procedures give relative density, or "specific gravity,"<sup>1</sup> whereas the *x*-radiation method measures density directly, without use of a reference fluid such as water or toluene.

SUSPENSION METHOD. Although this method does not involve any computation and is limited in its application, its potential accuracy is worthy of note, especially where Clerici's solution is used (Jahns, 1939). The random error in density inherent in Jahns' refractive index-density curve is given as .01. A second random error arises from reading the Abbé refractometer, and may be assumed to be .0005. Using the slope of this curve to obtain the ratio of density and index change (dD/dn), the uncertainty in density is found to be .00044, negligible in comparison with the first random error. The total random error of .0104 is converted to a fractional deviation dD/D, this value being plotted against D in Fig. 2 (inset, top left). It is assumed that the systematic error arising from temperature variations can be adequately controlled.

Extension of the density range through use of a glass float (of known weight and density) attached to the mineral fragment can be achieved, but with relative loss in accuracy. This case is not considered here (see Bannister and Hey, 1937).

HYDROSTATIC METHOD. A number of methods of this type have been described, of which two are discussed here.

Jolly Balance. The expression for density is

$$\mathsf{D} = \frac{\mathsf{W}_{\mathsf{A}}\mathsf{D}_{\mathsf{W}}}{\mathsf{W}_{\mathsf{A}} - \mathsf{W}_{\mathsf{W}}}$$

where  $W_A$  = weight of substance in air.

Ww=weight of substance in water.

 $D_w = density$  of water at room temperature relative to  $D_w = 1$ at 4°C.

<sup>1</sup> Although widely used, "specific gravity" is terminologically incorrect as a synonym for relative density, and is physically incorrect as a synonym for density determined by the x-radiation method. "Gravity" implies the weight of a body, i.e., the earth's attraction for it, which is not an intrinsic property, whereas by definition density is the mass of a body per unit volume, the mass being an intrinsic and invariable property.

The fractional deviation is given by

$$\frac{\mathrm{dD}}{\mathrm{D}} = \frac{\mathrm{W}_{\mathrm{A}}\mathrm{dW}_{\mathrm{W}} + \mathrm{W}_{\mathrm{W}}\mathrm{dW}_{\mathrm{A}}}{\mathrm{W}_{\mathrm{A}}(\mathrm{W}_{\mathrm{A}} - \mathrm{W}_{\mathrm{W}})} + \frac{\mathrm{dD}_{\mathrm{W}}}{\mathrm{D}_{\mathrm{W}}},$$

where  $dW_w$  and  $dW_A$  are the uncertainties in determination of  $W_A$  and  $W_w$ , respectively, and  $dD_w$  is the uncertainty in density of water at any temperature. As  $dW_A$  and  $dW_W$  are obviously equal they may be replaced by dW. Furthermore, the uncertainty in  $D_w$  is relatively negligible so that, finally,

$$\frac{\mathrm{dD}}{\mathrm{D}} = \frac{\mathrm{dW}(\mathrm{W}_{\mathrm{A}} + \mathrm{W}_{\mathrm{W}})}{\mathrm{W}_{\mathrm{A}}(\mathrm{W}_{\mathrm{A}} - \mathrm{W}_{\mathrm{W}})},$$

which represents the fractional deviation arising from the random errors of reading the scale. The obvious source of systematic error would be temperature variations which would affect the density of the water. However, it is found that, between 15° and 25°C. (room temperature range), this error may be neglected.

Figure 1 has been prepared from data obtained with the current apparatus offered by the Central Scientific Company. Two springs are provided to extend the range of the balance. The uncertainty of any individual reading of the scale should not exceed one-quarter of a division. In order to compare directly with errors found in the other weighing methods, the springs were calibrated in grams, giving dW = .005 gm. for the light spring, and dW = .025 gm. for the heavy spring.<sup>2</sup> This conversion is of course not ordinarily necessary. Per cent fractional deviation is plotted against density for each spring, using four values of WA known to be within the range of the scale. The sensitivity of each spring is considered constant within the range selected. It is seen from Fig. 1 that least accuracy (greatest fractional deviation) is obtained where W<sub>A</sub> is low and D is high, and, conversely, that maximum accuracy is to be expected from the combination of high W<sub>A</sub> and low D. Furthermore, the variation in dD/D with D is much less for high  $W_A$  than for low  $W_A$ . These observations hold also, in varying degree, for the other balance methods discussed (Figs. 2 and 3).

Berman Balance. As with the Jolly balance the fractional deviation is

$$\frac{\mathrm{d}\mathrm{D}}{\mathrm{D}} = \frac{\mathrm{d}\mathrm{W}(\mathrm{W}_\mathrm{A} + \mathrm{W}_\mathrm{W})}{\mathrm{W}_\mathrm{A}(\mathrm{W}_\mathrm{A} - \mathrm{W}_\mathrm{W})} + \frac{\mathrm{d}\mathrm{D}_\mathrm{T}}{\mathrm{D}_\mathrm{T}},$$

where dD<sub>T</sub> and D<sub>T</sub> refer to toluene instead of water. At any given tem-

<sup>2</sup> Figure 1 will probably require some adjustment for Jolly balances of different make.

perature there is an uncertainty  $dD_T = .0005$  in the density of toluene (Timmermans, 1912). The random error dW of a single scale reading on



FIG. 1. Jolly balance. Variation in accuracy for different densities. Random error computed for  $W_A$  values of 1, 2, 3, 4 gm. (using light spring) and 10, 20, 30, 40 gm. (using heavy spring). Based on an error of .25 division in reading the scale.



FIG. 2. Berman balance and (inset, top left) Clerici solution method (Jahns). Random error for Berman balance computed for  $W_A$  values of 5, 15, 20, 25, 50 mg. Based on dW = .01 mg. Full lines (15, 20, 25 mg.) cover the range of maximum sensitivity of the balance as specified by the manufacturer. Random error for Clerici solution method based on experimental data given by Jahns (1939).

the balance should not exceed .01 mg. The systematic error arising from determinations made at various temperatures is relatively negligible in the range  $15^{\circ}-25^{\circ}$ C. Surface tension deviation may also be neglected where the suspension wire diameter is a small fraction of millimeter. Figure 2 is therefore constructed directly from the equation given above. Optimum conditions of accuracy are realized only for W<sub>A</sub> values from 15 to 25 mg., as specified by the manufacturer.

Where a determination is made with several small fragments instead of with a larger, single piece, accuracy will probably be lowered because of less perfect wetting. Unlike the pycnometric method, this systematic error can not be eliminated.

PYCNOMETER METHOD. Density by the pycnometer procedure is given by

$$D = \frac{(W_2 - W_1)D_T}{W_2 - W_3 + D_T V}$$

where 
$$W_1$$
 = weight of pycnometer

W<sub>2</sub> = weight of pycnometer+powder W<sub>3</sub> = weight of pycnometer+powder+toluene D<sub>T</sub> = density of toluene

V = volume of pycnometer.

If a silica-glass pycnometer is used, the uncertainty in V may be reduced by careful calibration to a relatively negligible value (Ellsworth, 1928). In the following expression for fractional deviation V is therefore considered constant

$$\frac{\mathrm{dD}}{\mathrm{D}} = \frac{2\mathrm{dW}}{\mathrm{W}_2 - \mathrm{W}_1} + \frac{\mathrm{dD}_{\mathrm{T}}}{\mathrm{D}_{\mathrm{T}}} \left( \frac{\mathrm{W}_2 - \mathrm{W}_3}{\mathrm{W}_2 - \mathrm{W}_3 + \mathrm{D}_{\mathrm{T}} \mathrm{V}} \right).$$

The three uncertainties  $dW_1$ ,  $dW_2$ ,  $dW_3$  used in the first step of the differentiation are equal and have been replaced by dW in the final condensed expression above.<sup>3</sup> As the uncertainty in weighing on the ordinary

<sup>3</sup> As the writers have not succeeded in duplicating the expressions derived by one or two other authors for the pycnometric method, the derivation used here is given in detail.

$$D = \frac{(W_2 - W_1)D_T}{W_2 - W_3 + D_TV}.$$

Taking logarithms of each side,

$$\begin{split} \log \, D &= \log \, D_{\rm T} + \log \, (W_2 - W_1) - \log \, (W_2 - W_3 + D_{\rm T} V). \end{split}$$
 Differentiating,  $\frac{\mathrm{d} D}{\mathrm{d} D} &= \frac{\mathrm{d} D_{\rm T}}{\mathrm{d} W_2 - \mathrm{d} W_1} - \frac{\mathrm{d} W_2 - \mathrm{d} W_3 + \mathrm{V} \mathrm{d} D_{\rm T}}{\mathrm{d} W_2 - \mathrm{d} W_3 + \mathrm{V} \mathrm{d} D_{\rm T}}. \end{split}$ 

$$\overline{\mathbf{D}} = \overline{\mathbf{D}_{\mathrm{T}}} + \overline{\mathbf{W}_{2} - \mathbf{W}_{1}} - \overline{\mathbf{W}_{2} - \mathbf{W}_{3} + \mathbf{D}_{\mathrm{T}} \mathbf{V}}$$

chemical balance should not exceed .0001 gm., this value is assigned to dW in constructing Fig. 3.  $dD_T = .0005$  as in Fig. 2. Room temperature variations produce relatively negligible systematic errors. The 10 cc. bottle described by Ellsworth (1928) is used to show variations in accuracy for powder samples weighing 1, 2, 5, and 10 gm.; the 0.1 cc. bottle described by Winchell (1938) is used similarly for powder weights of 0.1, 0.2, and 0.5 gm.

Every precaution must be taken to wet the powder thoroughly, as failure to remove all the imprisoned air will lead to deviations much greater than the random error from weighing. Ksanda and Merwin (1939) have described an excellent technique of this kind.

Figure 3 shows that bottles of large capacity give smaller fractional deviations over the usual range of powder weights than do bottles of small volume, assuming equivalent conditions of weighing. This becomes obvious from inspection of the differential equation. Increase in V reduces the  $dD_T/D_T$  term, and increase in  $W_2-W_1$  (weight of powder in air) reduces the dW term. Offsetting this apparent superiority of the larger bottle, however, is the fact that its greater bulk of powder increases the

Collecting the dW1, dW2, dW3, and dDT terms separately,

$$\begin{split} \frac{\mathrm{d} \mathrm{D}}{\mathrm{D}} &= \mathrm{d} \mathrm{D}_{\mathrm{T}} \Big( \frac{1}{\mathrm{D}_{\mathrm{T}}} - \frac{\mathrm{V}}{\mathrm{W}_2 - \mathrm{W}_3 + \mathrm{D}_{\mathrm{T}} \mathrm{V}} \Big) - \mathrm{d} \mathrm{W}_1 \Big( \frac{1}{\mathrm{W}_2 - \mathrm{W}_1} \Big) \\ &+ \mathrm{d} \mathrm{W}_2 \Big( \frac{1}{\mathrm{W}_2 - \mathrm{W}_1} - \frac{1}{\mathrm{W}_2 - \mathrm{W}_3 + \mathrm{D}_{\mathrm{T}} \mathrm{V}} \Big) \\ &+ \mathrm{d} \mathrm{W}_3 \Big( \frac{1}{\mathrm{W}_2 - \mathrm{W}_3 + \mathrm{D}_{\mathrm{T}} \mathrm{V}} \Big). \end{split}$$

For determination of maximum error all the bracketed expressions must have the same sign. The dW<sub>1</sub> term is therefore made positive. (The minus signs within the dD<sub>T</sub> and dW<sub>2</sub> brackets must be left unchanged, as D<sub>T</sub> and W<sub>2</sub> occur in both numerator and denominator of the original density equation. Errors in their measurement would therefore be expected to compensate each other partially, as shown by the minus signs in the differential equation.) Furthermore, as  $dW_1 = dW_2 = dW_3$ , we replace each by dW. Thus

$$\begin{split} \frac{\mathrm{d}D}{\mathrm{D}} &= \mathrm{d}D_{\mathrm{T}} \bigg[ \frac{\mathrm{W}_{2} - \mathrm{W}_{3}}{\mathrm{D}_{\mathrm{T}}(\mathrm{W}_{2} - \mathrm{W}_{3} + \mathrm{D}_{\mathrm{T}}\mathrm{V})} \bigg] \\ &+ \mathrm{d}W \bigg[ \frac{(\mathrm{W}_{2} - \mathrm{W}_{3} + \mathrm{D}_{\mathrm{T}}\mathrm{V}) + (\mathrm{W}_{2} - \mathrm{W}_{3} + \mathrm{D}_{\mathrm{T}}\mathrm{V}) - (\mathrm{W}_{2} - \mathrm{W}_{1}) + (\mathrm{W}_{2} - \mathrm{W}_{1})}{(\mathrm{W}_{2} - \mathrm{W}_{1})(\mathrm{W}_{2} - \mathrm{W}_{3} + \mathrm{D}_{\mathrm{T}}\mathrm{V})} \bigg] \\ &= \mathrm{d}D_{\mathrm{T}} \bigg[ \frac{\mathrm{W}_{2} - \mathrm{W}_{3}}{\mathrm{D}_{\mathrm{T}}(\mathrm{W}_{2} - \mathrm{W}_{3} + \mathrm{D}_{\mathrm{T}}\mathrm{V})} \bigg] + \mathrm{d}W \bigg[ \frac{2}{\mathrm{W}_{2} - \mathrm{W}_{1}} \bigg]. \end{split}$$

If V is not considered constant the term  $\left[\frac{D_T dV}{W_2 - W_3 + D_T V}\right]$  must be added to the above.

difficulty of removing the last traces of trapped air. Homogeneity in composition of the sample is also more difficult to attain with a large sample. It is probable therefore that in practice the accuracy of the two bottles will be about the same.

In the micropycnometric procedure described by Bannister and Hey (1937) only 15 to 25 mg. of sample are required, with a reported accuracy of 0.5%. As part of this error stems from an uncertainty in the volume of liquid used, a greater error than that of Fig. 3 would be expected.



FIG. 3. Pycnometer method. Variation in accuracy for different densities. Random error for 10 cc. bottle (Ellsworth type) and .1 cc. bottle (Winchell type). Full lines refer to the 10 cc. bottle for mineral weights (in air) of 1, 2, 5, 10 gm.; broken lines refer to the .1 cc. bottle for mineral weights (in air) of .1, .2, .5 gm. Based on dW=.0001 gm. and  $dD_T$ =.0005.

However, uncertainties regarding the homogeneity and wetting of the powder may be better controlled in the Bannister-Hey method than in the others, and too much emphasis should not be placed therefore on the purely mathematical aspects of the case.

X-RADIATION METHOD. Density by this method is expressed by

$$D = \frac{MZ}{AV}$$

where M = molecular weight of the material

Z=number of formula-units in a unit cell

V = volume of unit cell

A = Avogadro's number  $(6.02 \times 10^{23})$ .

As V is the single variable,<sup>4</sup>

$$\frac{\Delta D}{D} = -\frac{\Delta V}{V}$$

In a cubic crystal,  $a_0 = d(h^2 + k^2 + l^2)^{1/2}$ where  $a_0 =$  length of side of unit cell,

d =interplanar spacing of planes with indices hkl.

Therefore  $\frac{\Delta a_0}{a_0} = \frac{\Delta d}{d}$ . But  $\frac{\Delta V}{V} = \frac{\Delta (a_0^3)}{a_0^3} = \frac{3(\Delta a_0)}{a_0} = \frac{3\Delta d}{d}$ .

From Bragg's equation  $d = \lambda/2 \sin \theta$ , where  $\lambda =$  wave length of x-radiation used,

 $\theta = diffraction angle.$ 

The fractional deviation of d is  $\Delta d/d = -\cot \theta \Delta \theta$ . Expressing the fractional deviation in density in terms of the diffraction angle,  $\Delta D/D = 3 \cot \theta \Delta \theta$  (for cubic crystals only).

Application of this equation is confined here to powder photography. The error in reading a millimeter scale placed on a line of the film should not exceed .25 mm. for any single measurement. Therefore the uncertainty in the distance between such a line and its mate on the other side of the line of zero diffraction is 0.5 mm. As this total distance in a camera of 57.3 mm. diameter is equivalent to  $4\theta$ , the error in  $\theta$  is .125°. That is,  $\Delta\theta = .125/57.3 = .00128$  radians. The curve R for random error in Fig. 4 is based on this value.

The four systematic errors inherent in x-ray crystal diffraction work —absorption of radiation by the specimen, eccentricity of the sample with respect to the camera, film shrinkage after development, and uncertainty in the camera radius—must each be considered on its merits. As details are given by Buerger (1942) for such corrections the matter is taken up only briefly here. Use of a two-hole film (Straumanis method) permits the camera radius and film shrinkage errors to be combined, and for a carefully constructed camera and film dried at room temperature, the error from this source is relatively negligible. It does not appear in Fig. 4.

The eccentricity error is small but appreciable. Its curve (E in Fig. 4) is based on a maximum expected displacement of the sample relative to the true center of the camera of .025 mm. The equation used is given by Buerger (1942, p. 413). The deviation may be positive or negative.

<sup>4</sup> To avoid confusion with the interplanar spacing symbol d,  $\Delta$  replaces here the customary differential symbol. The absorption error (Buerger, 1942, p. 414) is based on complete absorption, a specimen diameter of .25 mm., a pin-hole—specimen distance of 10.6 mm., and camera diameter 57.3 mm. Its curve (A in Fig. 4) shows an order of magnitude for  $\Delta D/D$  similar to the curve R, and of the same sign.

The total value of the maximum expected error is shown by curve T and has been drawn using positive values for the individual errors. As the random error may be opposite in sign to the absorption error, and is



FIG.4. X-ray method. Variation in accuracy for different diffraction angles. Random error (curve R) based on an uncertainty of .25 mm. in reading the position of a diffraction line. Absorption error (curve A) from data in Buerger (1942). Eccentricity error (curve E) likewise from data in Buerger (1942). Curve T shows total error where R, A, E are assumed to have the same sign.

of the same order of magnitude, the total error may, however, be very small. Curve T represents the worst possible case. The diagram does not include values smaller than 50°, as the accuracy decreases very rapidly in this range.

COMPARATIVE ACCURACY. Excluding the x-ray method, comparison of the remaining procedures shows that the pycnometer method has the greatest inherent accuracy, the Jolly balance method the least. Choice of method is dictated by the nature of the material and the degree of accuracy required. For most work the accuracy range of the Berman balance is adequate, provided that a single fragment of suitable weight can be obtained.

Direct comparison of these weighing methods with the x-radiation

method is not possible, as the latter gives the density of the unit cell whereas the former give values for aggregates of unit cells. The individual cells in these aggregates are rarely, if ever, packed together perfectly, with the result that lower density values are obtained than from the x-ray procedure. If it is desired to contrast the two density values for a given material, a weighing method should be selected which gives an accuracy comparable with that indicated by the  $\theta$  value chosen in Fig. 4. In general, the Berman balance would satisfy this requirement.

### DETERMINATION OF REFRACTIVE INDEX

As this paper is concerned with errors in computation only, the accuracy of direct-reading instruments will not be discussed. In the case of refractometers the accuracy of the widely used Abbé type has recently been reviewed by Tilton (1942) in an informative paper. It need only be stated here that the ordinary Abbé used in mineralogical laboratories reads correctly to  $\pm$ .0002 in its lower range, but is considerably less accurate in its upper range. Other direct-reading refractometers (Fisher, Nichols, etc.) are usually reliable to  $\pm$ .001.

MINIMUM DEVIATION METHOD. In the field of precise refractometry the minimum deviation method is preferable to any other. Where moderate precision is required, as in standardization of oils or melts for use in the immersion method of refractive index determination, it affords the only universal method for the entire range of indices. The accuracy of the method has been discussed by Tilton (1935) who lists 19 sources of error for determinations of the highest precision ( $\pm$ .000001). As mineralogists seldom require this accuracy for crystal measurement, and never for immersion oils or melts, only the random error of reading prism and minimum deviation angles need be considered here.

The index of refraction is given by

$$n = \frac{\sin \frac{\mathbf{A} + \mathbf{D}_{\mathrm{m}}}{2}}{\sin \frac{\mathbf{A}}{2}},$$

where A = angle of the prism.

 $D_m = minimum$  deviation angle.

Differentiating partially with respect to A,  $dn = -1/2 \sin D_m/2 \csc^2 A/2 d A$ , and partially with respect to  $D_m$ ,  $dn = 1/2 (\cos D_m/2 \cot A/2)$ 

 $-\sin D_m/2$  dD<sub>m</sub>. As it is probable<sup>5</sup> that dA = dD<sub>m</sub>, we replace each by dr, so that the total random error is

$$\Sigma(\mathrm{dn}) = \frac{1}{2} \left[ \operatorname{cosec} \frac{\mathrm{A}}{2} \cos \frac{\mathrm{A} + \mathrm{D_m}}{2} - \operatorname{cosec^2} \frac{\mathrm{A}}{2} \sin \frac{\mathrm{D_m}}{2} \right] \mathrm{dr}.$$

In constructing Fig. 5 the error in the prism and minimum deviation angles is assumed to be  $\pm 1'$ , so that dr = .000291 radians. The second term in the differential equation is considered positive in order to give



FIG. 5. Minimum deviation method. Variation of random error in n for a series of n values. Computations shown for prism angles of 25°, 30°, 40°, 50°, 60°, with the % accuracy given for each. Steep curve transecting the prism curves is the locus of limiting values of prism angles for determination of a given refractive index. Diagram based on an uncertainty of  $\pm 1'$  in determination of prism and minimum deviation angles.

dn its maximum expected value.<sup>6</sup> Most single determinations will have greater accuracy than that indicated by the graph. In working with crystal prisms the deviation is likely to be much less than 1', but with the ordinary hollow cell used for oil determinations this is unlikely, and for crude prisms composed of S-Se mixtures may be much greater than 1'.

Figure 5 shows the total maximum expected error for prisms of varying

<sup>5</sup> This may not be true if the prism angle is determined from readings of the table circle, and the minimum deviation angle from readings of the telescope circle. The table angles of small spectrometers and goniometers tend to be less accurate than telescope angles. However, if the prism angle is determined by the split-beam method, no table angle need be used, and except in high-precision work gives very satisfactory results (Guild, 1923).

<sup>6</sup> The small numerical range of the common refractive indices makes it unnecessary to plot the variation in fractional deviation for different values of n.

angle over a wide range of indices. For a given index greatest accuracy (least dn/n%) is attained where large prisms are used. Inspection of the formula

$$n = \sin \frac{A + D_m}{2} / \sin \frac{A}{2}$$

indicates a maximum value of n for any given prism angle. The boundary curve in Fig. 5 shows this graphically. For example, the limiting refractive index determinable with a 60° prism angle is 2.0. In practice, since the



FIG. 6. Minimum deviation method where prism angle is  $60^{\circ}$ . Curve P shows random error arising from prism angle uncertainty of 1'. Curve D<sub>M</sub> shows random error arising from minimum deviation uncertainty of 1'. Upper curve shows the total error where P and D<sub>M</sub> are assumed to have the same sign.

proportion of transmitted light at grazing incidence is greatly reduced relative to the reflected portion, it is never possible to proceed to the limit shown in the diagram.

Figure 6 gives greater detail for a  $60^{\circ}$  prism. Curve P shows the variation in prism angle error for various indices;  $D_m$  shows dn for different indices arising from measurement of the minimum deviation angle. At the limiting index of 2.0 the prism angle error reaches its maximum whereas the minimum deviation error becomes zero. The upper, straight line represents the total maximum expected error. If the Gifford method<sup>7</sup>

<sup>7</sup> This method (Gifford, 1902) makes use of a closed prism whose angles approximate 60°. Minimum deviation angles are measured across each prism and an average computed. Angle A may then be assumed equal to 60° without any accurate measurement of the individual prisms. An uncertainty in A of the order of magnitude of 1° causes an uncertainty of only  $\pm$ .0001 in *n*. As there need be no difficulty in maintaining the prism deviations at much less than 1°, the resultant prism angle error using this method becomes negligible.

is used, the error in prism angle becomes negligible and the total uncertainty is shown by  $D_m$ . In all cases where the demands of this method can be met, increased accuracy will result, particularly for refractive indices approaching 2.0 in magnitude.

Where the goal of accuracy is in the neighborhood of  $\pm$ .0001, systematic errors become significant only for determinations made on liquids. Temperature corrections are necessary, particularly for methylene iodide



FIG. 7. Grazing incidence method (Pulfrich refractometer). Variation in dn with n shown for two prisms of refractive index as marked. Approximate % accuracy at curve maxima is also given. Based on an uncertainty of  $\pm 1'$  in reading the scale.

and mixtures containing it, and require control to at least 0.1°C. if the index error limit of .0001 is to be maintained. In addition the hollow cell must be constructed of optically flat glass. Suitable material may be selected according to the method suggested by Larsen and Berman (1934). In Figs. 5 and 6 it is assumed that these systematic errors can be reduced to negligible proportions and that only random errors remain.

GRAZING INCIDENCE METHOD. This method is incorporated in the widely used Pulfrich refractometer. Although less used by mineralogists than by chemists (Gibb, 1942, p. 333), and inherently less accurate than instruments used for precise minimum deviation work, a brief comparison is not out of place. Refractive index is given by

$$n = (n_p^2 - \sin^2 r)^{1/2}$$

where  $n_p = refractive$  index of prism,

r = angle read on divided circle. Differentiation gives

$${\rm dn}\,=\,-\,\left[\frac{\sin\,2r}{2(n_{\rm p}{}^2\,-\,\sin^2\,r)^{1/2}}\right]\!{\rm d}r.$$

The error in a single reading in the middle range of r values is not likely to exceed 1', so that dr = .000291 radians. Figure 7 shows a graphical solution of the differential equation for two prisms of n=1.620 and n= 1.752. For each prism there is an r value which gives maximum fractional deviation (.07% and .06% as indicated). Thus for material of n=1.6 the maximum expected error would be only about one-half as great where the lower index prism is used as where the higher one is used. For high and low r values, however, dr may easily exceed the value used in the diagram, so that the accuracy indicated in the lower part (dn < .00004) may not be realized. However, even the worst values at the noses of the curves are as good, or better, than the accuracy to be expected from ordinary four-figure minimum deviation measurements.

UNIVERSAL STAGE EXTRAPOLATION METHOD. In cases where one critical index alone can be determined in a given oriented optic symmetry plane, measurement of an intermediate index at a known angle in this plane makes possible the computation of the other critical index. This method, first used by Pauly (Johannsen, 1918, p. 266), and later developed by Emmons (1943, pl. 10) depends on the following equation

$$n_{\rm x} = \frac{n_2 (n_1^2 \sin^2 \phi + n_{\rm x}^2 \cos^2 \phi)^{1/2}}{n_1},$$

where  $n_x = unknown$  critical index,

 $n_1 = known$  critical index,

 $n_2 = intermediate index,$ 

 $\phi$  = rotation angle used in obtaining n<sub>2</sub>.

Assuming that the uncertainties in  $n_1$  and  $n_2$  are the same, and using dn to represent both, the differential equation is:

$$\frac{\mathrm{dn}_{\mathbf{x}}}{n_{\mathbf{x}}} = \left[\frac{1}{n_2} + \frac{n_{\mathbf{x}}^2 \cot^2 \phi}{n_2^2} \left(\frac{1}{n_2} - \frac{1}{n_1}\right)\right] \mathrm{dn} + \left(1 - \frac{n_{\mathbf{x}}^2}{n_1^2}\right) \cot \phi \mathrm{d}\phi.$$

If dn = .001 and the uncertainty<sup>8</sup> in  $\phi$  is 1° ( $d\phi = .0174$  radians), the equation appears graphically as in Fig. 8. It is assumed that  $n_1 > n_x$ . In Fig. 8  $dn_x$  is plotted against  $(n_1 \cdot n_x)$  for different values of  $\phi$  using the computations made for  $n_1 = 1.6$ . For other values of  $n_1$  no appreciable difference in the deviations is obtained. For  $\phi = 90^\circ$  inspection of the differential equation shows that  $dn_x = (n_x/n_2) \cdot dn$  and since  $n_2$  now equals  $n_x$ , then  $dn_x = dn = .001$  as shown in Fig. 8. The total dn term remains fairly constant at .001+, most of the variation being shown by

<sup>8</sup> The uncertainty in  $\phi$  stems from the initial random error in orienting the optic symmetry plane rather than from any inherent defect in the OEW axis of the stage.

the  $d\phi$  term. In general,  $dn_x$  is least where large angles are combined with low partial birefringence. Except for angles of less than 20°, however,  $dn_x$  changes little where partial birefringence is low.



FIG. 8. Extrapolation method. Variation in  $dn_x$  for different partial birefringence  $(n_1 - n_x)$ . Shown for three values of  $\phi$ , where  $n_1 = 1.6$ . Based on dn = .001 and an uncertainty in  $\phi$  of 1°.



FIG. 9. Optic angle method. Variation in  $d\gamma$  (or  $d\alpha$ ) for different values of  $\gamma - \beta$  (or  $\alpha - \beta$ ). Four selected values of the optic angle are used. Diagram based on  $\beta = 1.50$  and an optically positive crystal. Full lines refer to  $d\alpha$  only; broken lines to  $d\gamma$ . The uncertainty in determination of the known refractive indices is .001 and in the optic angle 1°. If  $n_1 < n_x$ ,  $dn_x$  increases by a few per cent for high  $n_x$  and birefringence values; for low values the change is inappreciable. No diagrams for this case have been constructed.

OPTIC ANGLE METHOD. Mertie's nomogram (Mertie, 1942) showing the relations between  $\alpha$ ,  $\beta$ ,  $\gamma$ , and V, based on ellipsoid geometry, is a necessary prerequisite to the deviation diagrams of this paper. As differentiation of the full equation gives a long, involved expression, the approximate equations

$$\sin^2 V = \frac{\beta - \alpha}{\gamma - \alpha}$$
 for optically positive substances,  
$$\sin^2 V = \frac{\gamma - \beta}{\gamma - \alpha}$$
 for optically negative substances,

are used here. Differentiation of these with respect to  $\alpha$ ,  $\beta$ ,  $\gamma$  in turn, gives

$$d\alpha = dn + \frac{(\beta - \gamma) \sin 2V dV}{\cos^4 V}$$
  

$$d\gamma = dn + \frac{(\beta - \alpha) \sin 2V dV}{\sin^4 V}$$
  

$$d\alpha = dn + \frac{(\beta - \gamma) \sin 2V dV}{\sin^4 V}$$
  

$$d\alpha = dn + \frac{(\beta - \alpha) \sin 2V dV}{\sin^4 V}$$
  

$$d\gamma = dn + \frac{(\beta - \alpha) \sin 2V dV}{\cos^4 V}$$
  
for optically negative substances.

 $d\beta = dn + (\gamma - \alpha) \sin 2V dV$  for either positive or negative substances,

where dn substitutes for  $d\beta$  and  $d\gamma$ ,  $d\beta$  and  $d\alpha$ ,  $d\alpha$  and  $d\gamma$ , respectively, and is assumed equal to .001. The uncertainty in direct measurement of 2V need not exceed  $\pm 1^{\circ}$  if both optic axes are found. If only one axis can be oriented the uncertainty will be  $\pm 2^{\circ}$ . For low to moderate refringence and birefringence

$$d\alpha(+) = d\gamma(-)$$
 and  $d\gamma(+) = d\alpha(-)$ .

Figure 9 is based on a constant value of  $\beta = 1.50$ , an optically positive substance and dV = .0174 radians (uncertainty in V of  $\pm 1^{\circ}$ ). It shows the variation in  $d\alpha$  with change in  $\alpha$ - $\beta$ , and the variation in  $d\gamma$  with change in  $\gamma$ - $\beta$ , for selected values of V. As would be expected, the closer  $\alpha$  (or  $\gamma$ ) approaches  $\beta$  the smaller is  $d\alpha$  (or  $d\gamma$ ). The rate of increase in  $d\alpha$  (or  $d\gamma$ ) is greater for small V values than for large. The percent fractional deviation (accuracy) follows the same trend. Figure 10 is similar to 9, but is based on  $\beta = 1.90$ . The same type of variation persists, but  $d\alpha$  and  $d\gamma$  are on the whole several times larger. For  $\beta$  values other than 1.50 and 1.90 interpolation or extrapolation will give a reasonably good result.



FIG. 10. Optic angle method. Same as Figure 9, but based on  $\beta = 1.90$ .



FIG. 11. Optic angle method. Variation in  $d\beta$  for different values of total birefringence  $(\gamma - \alpha)$ . Four selected values of the optic angle are used. Based on uncertainties of .001 in determination of the known refractive indices, and of 1° in the optic angle.

Figure 11 is of similar form, but the variation is simpler in character. The curves are valid for any value of  $\beta$ , and for both positive and negative substances. In contrast with Figs. 9 and 10, d $\beta$  is smaller for small V

values than for large. The overall range of d $\beta$  is also considerably less than for d $\alpha$  and d $\gamma$ .

If the refractive indices are determined by precision methods, dn will be much less than .001. However, as the immersion method is rapid and widely used, the diagrams have been constructed for dn = .001.

COMPARATIVE ACCURACY. It has already been pointed out that the minimum deviation method is capable of greater precision than any other. However, the small spectrometers used for this method in most laboratories give results which are usually less accurate than those obtained with the Pulfrich refractometer, although adequate for practically all mineralogic work.

In contrast, the extrapolation and optic angle methods, insofar as they depend on immersion in oils, are much less accurate, giving third decimal place accuracy only.

# DETERMINATION OF BIREFRINGENCE

GENERAL COMPENSATOR METHOD (*Berek*). Determination of refractive indices to  $\pm$ .001 (immersion method) yields birefringence values accurate to  $\pm$ .002. This direct method may be compared with an indirect method which makes use of the Berek compensator. Birefringence is determined by:

$$B = \frac{\Gamma'}{t/\cos\theta'}$$

where  $\Gamma' = \text{retardation}$  in the unknown for a particular orientation.

t = thickness of thin section.

 $\theta'$  = angle between path of light and normal to the thin section. By differentiation,  $dB/B = d\Gamma'/\Gamma' - \tan\theta' d \ \theta' - dt/t$ . The thickness t is found from a reference mineral of constant B (e.g. quartz), and  $t = \Gamma'' \cos \theta''/B$ , where  $\Gamma''$  and  $\theta''$  are analogous to  $\Gamma'$  and  $\theta'$ . Differentiating,  $dt/t = d\Gamma''/\Gamma'' - \tan \theta'' d \theta''$ . By substitution in the original dB/B equation, and assuming positive values for each term (to give the maximum deviation)

$$\frac{\mathrm{dB}}{\mathrm{B}} = \frac{\mathrm{d}\Gamma'}{\Gamma'} + \tan\,\theta'\mathrm{d}\,\theta' + \frac{\mathrm{d}\Gamma''}{\Gamma''} + \tan\,\theta''\mathrm{d}\,\theta''.$$

A general expression for  $d\Gamma'/\Gamma'$  and  $d\Gamma''/\Gamma''$  may be obtained from the basic compensator formula,  $\log \Gamma = \log C + \log f$  (i) where C = constant of the compensator;  ${}^{9}f(i) = \text{function of angle of rotation i of compensator}$  drum. As  $f(i) = \sin^{2}i + .204 \sin^{4}i + \cdots$  for a calcite compensator (Berek, 1913), differentiation of the compensator formula gives:

<sup>9</sup> This constant must be determined for each instrument.

### H. W. FAIRBAIRN AND C. W. SHEPPARD

$$\frac{\mathrm{d}\Gamma}{\Gamma} = \frac{\sin 2i(1 + .408 \sin^2 i)\mathrm{d}i}{\sin^2 i + .204 \sin^4 i}$$

The maximum expected uncertainty of a single reading of the compensator drum is assumed to be 0.2°. The uncertainty in 2i would then be 0.4° and for i would be 0.2°. Then di = 0.2/57.3 = .00349 radians. Curve d $\Gamma/\Gamma$  in Fig. 12 shows the per cent variation in fractional deviation with change in  $\Gamma$ .<sup>10</sup> It is seen that accuracy is much increased where  $\Gamma$  is not too small.



FIG. 12. Berek compensator. Variation in d $\Gamma$ , and % accuracy of  $\Gamma$ , for different values of  $\Gamma$ . Based on an uncertainty of  $\pm .2^{\circ}$  in reading the compensator drum.

The uncertainties in  $\theta'$  and  $\theta''$  may be assumed equivalent. Their magnitude depends on (1) error made in orienting the sections, (2) error in obtaining  $\theta'$  and  $\theta''$  on the stereographic net, (3) error in the final hemisphere correction. Error 3 applies only to the unknown, as the refractive indices of the reference mineral are known. For the worst case, therefore, a maximum uncertainty of  $\pm 2^{\circ}$  is not improbable. Where  $\theta'$  and  $\theta''$  are both small, however, errors 2 and 3 will be negligible and the uncertainty should not exceed  $\pm 1^{\circ}$ . The general importance of small  $\theta$  values is indicated clearly in Fig. 13.

No simple diagram will show the variation in accuracy of B, but the total fractional deviation in any given case can be found by adding the values of the four terms in the equation for dB/B.

<sup>10</sup> The values in Fig. 10 are about double those given by Berek (1924, Fig. 22, p. 46). His calculation, however, is of a "mean" error, not a maximum expected deviation.

The preceding discussion implies strict uniformity in thin section thickness. As this condition is seldom realized, and, as it is physically impossible for the reference mineral and the unknown to occupy the same area of the section, a systematic error is thereby introduced which has not yet been considered. In the case of a strongly wedge-shaped section, detection by means of interference colors is easy, and the mount discarded if necessary. The thickness of apparently uniform sections can be rapidly checked by orienting three or four widely separated reference grains and noting the discrepancy in thickness obtained. Where this is small, e.g., .002 mm. across the whole section, it can be shown that, if unknown and reference mineral lie reasonably near to each other, a negligible error in B will result. In the case of mineral fragment mounts a reference mineral can always be added, so that close spatial association with the unknown is realized without difficulty.

In summary the accuracy of the indirect method increases where (1) thick rather than thin sections are used, (2) measurements are made on grains requiring the least angular rotation for their orientation, (3) the reference grain is as close as possible to the unknown.

EMMONS EXTRAPOLATION METHOD. A new procedure described by Emmons (1943, plate 13), based on the Biot-Neumann equation, permits determination of total birefringence in any crystal where the optic plane is vertical. The compensator used may be of fixed retardation (standard gypsum or mica plate) or variable (Berek, graduated wedge, etc.). As the analytical work on which Emmons' plate 13 is based has not been published, no diagram of maximum error appears in this paper. Comment on the probable accuracy of the method will be found in the following section.

OPTIC ANGLE-COMPENSATOR METHOD. The approximate relation

$$B_{T} = \frac{B_{P}}{\sin \theta \sin \theta'}$$

developed by Biot and Neumann (Johannsen 1918, p. 351), where  $B_T = \text{total}$  birefringence of the crystal,  $B_P = \text{partial}$  birefringence (as measured on a randomly oriented crystal section),  $\theta$  and  $\theta'$  are the angles subtended by each optic axis with the normal to the crystal section, becomes  $B_T = (B_P/\sin^2 V)$  where the optic plane is parallel to the microscope axis, with X or Z vertical, thus making  $\theta = V = \theta'$ . A graphical solution of this equation is given by Emmons (1943, plate 11). Where  $B_T > 0.1$  there will be an appreciable correction to apply to V (see Larsen and Berman, 1934, Fig. 1, or Emmons, 1943, plate 13). By differentiation,

$$\frac{\mathrm{dB_T}}{\mathrm{B_T}} = \frac{\mathrm{dB_P}}{\mathrm{B_P}} - 2 \text{ cot VdV.}$$

 $dB_P/B_P$  consists of four terms as described for the general compensator method (Figs. 12 and 13). The additional term 2cotVdV is shown graphically in Fig. 13 for two values of dV. The uncertainty in measuring an optic axis position need not exceed  $\pm 1^\circ$ ; therefore if both axes can be measured directly, the error in 2V is  $\pm 2^\circ$  and in V is  $\pm 1^\circ$ . If, however, only one axis position can be measured, the uncertainty in V is  $\pm 2^\circ$ . Both these cases are included in Fig. 13. It is obvious that 2cotVdV is least where V is large and that the method fails badly for small V values.



FIG. 13. Trigonometric terms used in the compensator methods. Tan  $\theta d\theta$  curve (general compensator method) based on an error of  $\pm 2^{\circ}$  in  $\theta$ . 2 cot VdV curves (optic angle-compensator method) based on an uncertainty in V of  $\pm 1^{\circ}$  in curve (a) and of  $\pm 2^{\circ}$  in curve (b).

COMPARATIVE ACCURACY. Inspection of the differential equations derived for the first two birefringence procedures indicates that the general method is potentially superior to the optic angle method. Presence of the 2cotVdV term in the latter decreases the relative accuracy markedly. Total birefringence may be more accurately determined therefore on an optic normal section using the general method.

It is probable that the fractional deviations in the Emmons extrapolation method are of the same order of magnitude as those in the optic angle method, i.e., somewhat less accuracy is to be expected than in the general method.

Comparison of the general method (indirect) with direct determina-

tions of B may be made in an approximate way as follows. Where refractive indices are determined to  $\pm .001$  (immersion method) the uncertainty in birefringence would be  $\pm .002$ . For B = .01 the fractional deviation is then 20%; for B = .10 it is 2%. Inspection of the range of values in Figs. 12 and 13 for the indirect general method indicates that a total fractional deviation in birefringence of 15% might commonly occur. By using thick sections and selecting grains which do not require appreciable rotation for their orientation, the above value might easily be reduced to 5% as a maximum expected error. Comparison of the two methods depends therefore on auxiliary data, particularly on the magnitude of B and  $\theta$ . For low birefringence the indirect general method may, in many cases, be preferable; for high birefringence the direct method is superior. Values of B obtained from precise prism determination of refractive indices would, of course, be superior in all cases to the indirect method.

## DETERMINATION OF OPTIC ANGLE

Accurate information regarding the size of the optic angle in biaxial crystals is less important than accurate determination of refractive indices. However, as a number of procedures for optic angle determination are in common use, it is advisable to consider their relative merits.

COMPENSATOR METHOD. The approximate relation between optic angle and birefringence,  $\sin^2 V = B_P/B_T$  is equivalent to  $\sin^2 V = \Gamma_P/\Gamma_T$ , where retardations are computed for a common thickness of section,  $\Gamma_P$  is the retardation in a section normal to X or Z, and  $\Gamma_T$  is the retardation in a section normal to Y. Wright's graphical solution of this equation is given by Emmons (1943, plate 11). Differentiating,<sup>11</sup>

$$\mathrm{dV} = \frac{\Gamma_{\mathrm{T}} \mathrm{d}\Gamma_{\mathrm{P}} - \Gamma_{\mathrm{P}} \mathrm{d}\Gamma_{\mathrm{T}}}{\Gamma^{2}_{\mathrm{T}} \sin 2\mathrm{V}}$$

Using the Berek compensator,  $d\Gamma_P$  and  $d\Gamma_T$  are obtained from Fig. 12. In Fig. 14 dV/V (%) is plotted against  $\Gamma_T$  for several selected values of V. In general, accuracy is seen to be greatest for large retardations; in particular, where V is large as well.

As the basic formula above is an approximation, an appreciable correction to V must be applied where B>0.1 (Larsen and Berman, 1934, Fig. 1). This correction, however, would result in negligible change in Fig. 14.

REFRACTIVE INDEX METHOD. The approximate equations  $\cos^2 V_{\alpha} = (\beta - \alpha)/(\gamma - \alpha) = \sin^2 V_{\gamma}$ , and  $\sin^2 V_{\alpha} = (\gamma - \beta)/(\gamma - \alpha) = \cos^2 V_{\gamma}$  may be used

<sup>11</sup> The negative sign in the expression is changed to positive for computation of maximum error.

to determine V if all three indices are known. The subscript  $\alpha$  refers to a negative,  $\gamma$  to a positive mineral. Differentiating  $\cos^2 V_{\alpha}$ ,



 $F_{IG}. \ 14. \ Compensator \ method. \ Variation \ in \ accuracy \ of \ V \ for \ different \ values \ of \ total \ retardation \ (\Gamma_T). \ Diagram \ shows \ curves \ for \ four \ values \ of \ V.$ 

As  $\alpha < \beta < \gamma$ , dV will have its maximum value where d $\beta$  is positive, d $\alpha$  and d $\gamma$  are negative. The equation is then rewritten

$$dV = \frac{(\gamma - \alpha)d\beta - (\beta - \gamma)d\alpha - (\alpha - \beta)d\gamma}{(\gamma - \alpha)^2 \sin 2V}$$

Furthermore,  $d\alpha = d\beta = d\gamma$ , permitting the substitution of dn, so that

dV (radians) = 
$$\frac{2 dn}{(\gamma - \alpha)^2 \sin 2V}$$
 or dV (degrees) =  $\frac{57.3 \times 2 dn}{(\gamma - \alpha)^2 \sin 2V}$ .

The uncertainty in n for the immersion method need not exceed  $\pm$ .001, and for precise prism work  $\pm$ .0001. Figure 15 is constructed for these values of dn, the curves representing various values of V as marked. In general, accuracy is greatest for high birefringence; in particular for high V values. It is obvious that an optic angle computation where dn = .001 is useful for relatively few substances (see Mertie, 1942), and that prism refractometry is required if any precision in V is expected by this method. Even with precision methods the accuracy is low if V is small.

## MAXIMUM ERROR IN MINERALOGIC COMPUTATIONS

EXTINCTION ANGLE METHOD. This method, first made practical by Berek (1924) and later amplified by Dodge (1934), provides a means of determining the optic angle independently of either refractive indices or retardation. It is discussed in two parts as outlined below.

Optic plane horizontal. This is the most useful case. The geometrical relations are as follows (Dodge, 1934):

$$\phi = \frac{\mathbf{K} + \mathbf{K}'}{2}, \ \tan \mathbf{K} = \tan \left(\bar{\phi} + \mathbf{V}\right) \cos x, \ \tan \mathbf{K}' = \tan \left(\bar{\phi} - \mathbf{V}\right) \cos x,$$



FIG. 15. Refractive index method. Variation in accuracy of V for different values of total birefringence  $(\gamma - \alpha)$ . Curves shown for optic angle values of 10°, 20°, 30°, 45°. Based on refractive index uncertainties of .001 and .0001.

where the following rotations are made, in the order listed-

 $\overline{\phi}$  is a fixed angle of rotation on the outer vertical axis of the stage;

x is a fixed angle of rotation on the outer east-west axis of the stage;

 $\phi$  is an angle of rotation to extinction made on the microscope axis. The graphical solution of these equations will be found in Dodge (1934) and also in Emmons (1943).

For the so-called "normal" case, where  $\bar{\phi} = 45^{\circ}$ , and x is set equal to some given angle, we assume V and  $\phi$  to be the only variables<sup>12</sup> in the above relation. Differentiating,

$$\mathrm{dV} = \frac{2\mathrm{d}\phi}{\sin\,4\phi\,\tan\,2\mathrm{V}}$$

<sup>12</sup> The uncertainty in x arising from incorrect orientation of the optic symmetry plane is lessened very considerably here by the large  $\bar{\phi}$  value used, and is neglected in the differential equation. Where  $\bar{\phi}$  is small x cannot be considered constant.

#### H. W. FAIRBAIRN AND C. W. SHEPPARD

Fig. 16, showing dV/V plotted against V, contains two curves (full lines) derived from this equation, for values of  $x = 54.7^{\circ}$  and 70°. The uncertainty in  $\phi$  need not exceed  $\pm 1^{\circ}$  if the optic axes are more nearly horizontal than vertical for the orientation in which  $\phi$  is determined. If, however, the opposite condition holds, as it will in many cases, the uncertainty in  $\phi$  is likely to be more nearly  $\pm 2^{\circ}$ . As Fig. 16 is based on this larger value, dV/V may be halved if the optic axes approximate a horizontal position under the conditions just stated. It is seen that high V and high x increase the potential accuracy of the measurement. Two incom-



FIG. 16. Extinction angle method (optic plane horizontal). Variation in accuracy of V for different values of V. Full lines for  $\bar{\phi}=45^{\circ}$  and x=54.7 and 70° as marked. Broken lines for  $x=70^{\circ}$  and  $\bar{\phi}=15^{\circ}$  and 30°. These four curves based on an uncertainty in  $\phi$  of  $\pm 2^{\circ}$ . Curves D<sub>1</sub> and D<sub>2</sub>, for direct readings of optic angle, are based on uncertainties in the optic angle of 1° and 2°, respectively.

plete curves for  $\overline{\phi} = 15^{\circ}$  and  $30^{\circ}$  (both for  $x = 70^{\circ}$ ) have also been plotted, using the slopes of the proper curves given by Dodge (1934, plates I and II). Although these curves indicate higher accuracy than where  $\overline{\phi} = 45^{\circ}$ , it must be recalled that x is not constant for such small values of  $\overline{\phi}$  (see footnote to previous paragraph). As the differential equation for  $\overline{\phi} < 45^{\circ}$ and x variable is extremely cumbersome, no computations have been made. However, the discrepancy in fractional deviation between curves based on  $\overline{\phi} = 45^{\circ}$  and  $\overline{\phi} = 15^{\circ}$  is less than Fig. 16 indicates.

Figure 16 includes also two curves, marked  $D_1$  and  $D_2$ , which show the variation in accuracy where V is measured directly.  $D_1$  is based on the case where both optic axes are measured and the uncertainty may attain

a value of  $\pm 1^{\circ}$ ; D<sub>2</sub> is for the case of one measured axis and an uncertainty of  $\pm 2^{\circ}$ . Assuming an uncertainty of  $2^{\circ}$  in  $\phi$ , and  $\phi = 45^{\circ}$ , it is seen that the computed values of V approximate the accuracy of the direct method only for the highest values of V; for small optic angles a small value of  $\phi$ is required to attain comparable accuracy.

Optic Plane Vertical. This orientation is considered here only for the case of a horizontal acute bisectrix. Where the acute bisectrix is vertical



FIG. 17. Extinction angle method (optic plane vertical). Similar to Fig. 16.

it is usually possible to measure both axes directly and thus avoid indirect methods. The basic equation (Dodge, 1934) is:

$$\sec \mathbf{V} = \left(\sin^2 \bar{\phi} + \frac{\cos 2\bar{\phi}}{\sin^2 x} - \frac{\cos x}{\sin^2 x} \sin 2\bar{\phi} \cot 2\phi\right)^{1/2}$$

where  $\bar{\phi}$ , x, and  $\phi$  are the same quantities used in the previous section and rotations are made in the same order. As before,  $\phi$  and V are assumed to be the only variables, although this is true only where x is not appreciably affected by incorrect setting of the optic symmetry plane. Differentiating,

$$dV = -\frac{\cos x \sin 2\phi \cos V d\phi}{\sin^2 x \sin^2 2\phi \tan V \left(\sin^2 \phi + \frac{\cos 2\phi}{\sin^2 x} - \frac{\cos x}{\sin^2 x} \sin 2\phi \cot 2\phi\right)^{1/2}}$$

For selected values of  $\phi$  and x this expression becomes much less formidable in appearance. The uncertainty in  $\phi$  is taken as  $\pm 2^{\circ}$ , but with the

same reservation as discussed in the previous section. Figure 17 shows the variation in dV/V (%) with change in V for two typical curves taken from Dodge (1934, plates IV and V). In addition, a portion of the fractional deviation curve for the "normal" case is included (upper right of Fig. 17). Where the uncertainties in  $\phi$  are the same it is seen that greater accuracy can be obtained in the computation of V with small  $\bar{\phi}$  than is otherwise the case.<sup>13</sup> The curves D<sub>1</sub> and D<sub>2</sub> described in Fig. 16 are replotted in Fig. 17 for comparison of direct and computed values of V. As they cover about the same field in the diagram as the two curves  $\bar{\phi} = 10^{\circ}$  and  $\bar{\phi} = 15^{\circ}$ , it is seen that there is little to choose between the two methods under these conditions. If, however, the orientation conditions indicate a lower value of d $\phi$  than that on which Fig. 17 is based, the computed value may be more accurate than that obtained by direct measurement. In all cases, direct measurement is preferable to the computed value based on  $\bar{\phi} = 45^{\circ}$ .

INTERFERENCE FIGURE METHODS. A number of methods based on interference figures are known (Johannsen 1918), but few are in widespread use at present. Where  $2V < 60^{\circ}$  and a centered acute bisectrix figure is obtainable, Mallard's method is convenient to use. The basic relation is  $\sin V = D/K\beta$ , where D =one-half the distance between the points of emergence of the optic axes of the crystal plate, K = a constant of the optical system (previously determined using minerals of known optic angle),  $\beta =$ intermediate refractive index of the crystal under examination.

Assuming any random error in K to be negligible relative to the uncertainty in measuring 2D, differentiation of the above equation gives

dV (radians) = tan V 
$$\left(\frac{dD}{D} - \frac{d\beta}{\beta}\right)$$
.

If K = 30 for the given optical system the uncertainty in 2D need not exceed 0.5 scale divisions, so that dD = .25. If  $d\beta$  is known to  $\pm .001$ , it is easily shown that  $d\beta/\beta$  is negligible relative to dD/D, so that, finally, dV (degrees) = 57.3dD/D tan V. Curve M in Fig. 18 is based on this equation. It is seen that the accuracy of the method is low for small optic angles.

Curve C shows the variation of dV/V with V where the optic angle is estimated from curvature of a single isogyre. With practice the uncertainty in estimating 2V by this method<sup>14</sup> need not exceed 6°, so that  $dV=3^{\circ}$ . Curve C is based on this value.

 $^{13}$  The same comment made in the previous section regarding uncertainty in x for low  $\bar{\phi}$  values applies here.

<sup>14</sup> E. S. Larsen, personal communication.

For comparison, curve  $D_1$  (showing the fractional deviation in the direct method for  $dV = 1^\circ$ ) is included in Fig. 18.

COMPARATIVE ACCURACY. Inspection of the diagrams (Figs. 14-18) makes apparent the difficulty of general comparison of optic angle methods. Except where V and B are small, the refractive index method is



FIG. 18. Interference figure methods. Variation in accuracy of V for Mallard's method (curve M), where K = 30 and dD = .25. Curve C represents the estimation method where  $dV=3^{\circ}$ . Curve D<sub>1</sub> is for the direct method where  $dV=1^{\circ}$ .

undoubtedly the most accurate if the indices are determined by the minimum deviation prism method. However, where the indices are determined by matching with an oil to  $\pm$ .001, the method yields results which are not much better on the average than results obtained from estimating the curvature of an isogyre.

Where favorable conditions for rotation exist, and with the uncertainty in  $\phi$  not in excess of 1°, the extinction angle method will give values of V almost as free from error as the refractive index method (for dn=.0001 and B>.02). Where the uncertainty is  $\pm 2^{\circ}$ , however, the accuracy is approximately the same as the refractive index method with dn=.001.

Comparison of the compensator method with other methods requires the assumption of a definite thickness for the section. Thus for t=.02mm. the dV/V compensator values are about intermediate between those obtained from the extinction angle and refractive index methods. Although of restricted application, Mallard's interference figure method is more accurate than direct measurement of optic angle with the universal stage, if the maximum values for dD and dV used in the diagrams are accepted as probable.

Comparison of the three indirect universal stage methods with the direct method shows in most cases that the latter is at least equal, or definitely superior, in accuracy to the former. Exceptions occur with the refractive index method where dn = .0001 and B and V are moderate to large, and with the extinction angle method where  $\phi$  is small and x large.

For all methods less accuracy is possible for low values of optic angle than for high values.

### SUMMARY

The usefulness of the diagrams presented in this paper depends on good judgment in selecting a reasonable maximum value of the uncertainty in any given measurement. In choosing the values on which the preceding figures are based the authors have assumed a skilled operator who has at his disposal good material and equipment. Where a series of readings of the same measurement is taken and a "probable error" computed, greater accuracy should be attained than shown here. Where the working material is poor less accuracy is to be expected. In general, where the uncertainties in measurement are believed to differ from those used in the diagrams, it is necessary only to substitute in the differential equation the revised value for the original and to construct a new graph.

A set of these graphs readily available in the laboratory should prove highly useful by providing instant information regarding the order of magnitude of the maximum error to be expected in a given procedure. It is the authors' hope that in time a more realistic attitude will be developed toward mineralogic measurements than is now apparent from much of the published quantitative data.

## ACKNOWLEDGMENTS

The writers are indebted to Dr. E. S. Larsen of Harvard University for critical examination of the manuscript and for several helpful suggestions.

#### References

BANNISTER, F. A., AND HEY, M. H. (1937), A new micro-pyknometric method etc.: Mineral. Mag., 25, 30-37.

BEREK, M. (1913), Zur Messung der Doppelbrechung etc.: Central. Miner., 388-396.

BEREK, M. (1924), Mikroskopische Mineralbestimmung etc.: Gebrüder Borntraeger, Berlin. BERMAN, HARRY (1939), A torsion microbalance for the determination of specific gravities of minerals: Am. Mineral., 24, 434-440.

BUERGER, M. J. (1942), X-ray Crystallography: John Wiley and Sons, Inc., New York.

- DODGE, T. A. (1934), The determination of optic angle etc.: Am. Mineral., 19, 62-75.
- ELLSWORTH, H. V. (1928), A simple and accurate constant-volume pyknometer for specific gravity determinations: *Mineral. Mag.*, 21, 431-435.
- EMMONS, R. C. (1943), The Universal Stage: Geol. Soc. Am., Memoir 8.
- GIBB, T. R. P. (1942), Optical Methods of Chemical Analysis: McGraw-Hill Book Co. Inc., New York.
- GIFFORD, J. W. (1902), Refractive indices of fluorite, etc.: *Proc. Roy. Soc.* (Lond.), **70**, 329–332.
- GUILD, J. (1923), Goniometry: Dict. App. Physics, 4, 112, MacMillan & Company, Ltd., London.
- HEY, M. H. (1933), On the accuracy of mineralogic measurements: *Mineral. Mag.*, 23, 495–500.
- JAHNS, R. H. (1939), Clerici solution for specific gravity determination etc.: Am. Mineral. 24, 116–122.
- JOHANNSEN, A. (1918), Manual of Petrographic Methods: McGraw-Hill Book Co., Inc., New York.
- KSANDA, C. J., AND MERWIN, H. E. (1939), Improved technique in micropycnometric density determination: Am. Mineral., 24, 482-484.
- LARSEN, E. S., AND BERMAN, HARRY (1934), The Microscopic Determination of the Nonopaque Minerals: U. S. Geol. Surv., Bull. 848.
- MERTIE, J. B. (1942), Nomograms of optic angle formulae: Am. Mineral., 27, 538-551.
- TILTON, L. W. (1935), Standard conditions for precise prism refractometry: Jour. Res. Nat. Bur. Standards, 14, 393-418.
- TILTON, L. W. (1942), Testing of Abbé refractometers: Jour. Opt. Soc. Am., 32, 371-381.
- TIMMERMANS, JEAN (1912), Recherches experimentales sur la densité des liquides etc.: Sci. Proc. Royal Dublin Soc., 13 (n.s.), 310-374.
- WINCHELL, HORACE (1938), A new micropycnometer for the determination of densities of heavy solids: Am. Mineral., 23, 805-810.