An experimental investigation of extrapolation methods in the derivation of accurate unit-cell dimensions of crystals

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AN EXPERIMENTAL INVESTIGATION OF EXTRAPOLATION METHODS IN THE DERIVATION OF ACCURATE UNIT-CELL DIMENSIONS OF CRYSTALS

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ABSTRACT. Measurements on x-ray photographs of cylindrical specimens of different absorption and thickness taken in a camera without eccentricity show that the absorption error in the apparent unit-cell dimension a is proportional to

$$\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}.$$

The plot of a against $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$ is linear down to $\theta=30°$ for all four specimens used. The extrapolated values for a are in good agreement, and this extrapolation function is accordingly recommended in the case of data from well constructed cameras. Other extrapolation functions are also considered, and the effect of various sources of error discussed. A table of $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$ is given.

§ 1. INTRODUCTION

In the determination of accurate unit-cell dimensions from powder photographs, three sources of systematic error are usually considered, due to

(*a*) absorption of the x-ray beam in the specimen ;

(*b*) the displacement of the rotation axis of the specimen relative to the geometric centre of the cylindrical film, usually called the *eccentricity error* ;

(*c*) inaccurate determination of the camera constants.

It may be shown that errors due to these three causes vanish at $\theta=90°$, which corresponds to extreme back-reflection along the path of the incident beam. The procedure usually adopted, therefore, is to derive apparent cell dimensions a from a number of lines on the photograph, to plot these values against some function of the Bragg angle θ, and to extrapolate to a value corresponding to $\theta=90°$.

Some uncertainty exists as to the best function of θ to use in order to obtain a linear extrapolation. Current practice is to plot a against $\cos^2\theta$ for high-angle lines only (i.e. those with clearly resolved α-doublets) and to extrapolate linearly to $\cos^2\theta=0$. It appears that this function has been chosen because the eccentricity error $\left(\frac{\delta a}{a}\right)_{ecc}$ is easily shown to be proportional to $\cos^2\theta$. The absorption error $\left(\frac{\delta a}{a}\right)_{\text{abs}}$, however, is not proportional to $\cos^2\theta$. Various workers, on theoretical grounds, have derived different functions relating $\left(\frac{\delta a}{a}\right)_{\text{abs}}$ and θ. Thus

1. $\left(\frac{\delta a}{a}\right)_{\text{abs}} \propto \frac{\cos^2\theta}{\theta}$ Bradley and Jay (1932).

2. $\left(\frac{\delta a}{a}\right)_{\text{abs}} \propto \frac{\cos^2\theta}{\sin\theta}$ Jay (1944).

3. $\left(\frac{\delta a}{a}\right)_{\text{abs}} \propto \cot\theta\cos^2\theta$ Buerger (1942).

4 $\left(\frac{\delta a}{a}\right)_{\text{abs}} \propto \left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)$ Taylor and Sinclair (1944).*

The use of a $\cos^2\theta$ plot assumes that, whatever the nature of the absorption error function, it can be approximately represented by $\cos^2\theta$ at high angles. It is not always possible, however, to obtain a sufficient number of lines at angles high enough for this to be true, and we have carried out the work described here in order to obtain experimental evidence concerning the best extrapolation function for general use.

§ 2. EXPERIMENTAL

The camera used was the 19-cm. diameter high-temperature camera designed and described by Wilson (1941), the film being in two halves. The design minimizes the possibility of eccentricity, and after consultation with Mr. C. E. Chapman, who made the instrument, we satisfied ourselves that effectively no eccentricity could be present. The camera angle, θ_k, has been very carefully measured by Wilson and Lipson (1941), who discussed possible errors in this connection. In effect, then, we have used an excellently constructed and calibrated camera to investigate the *absorption error*, eccentricity and calibration errors being absent. The method of film measurement described by Lipson and Wilson (1941) avoids errors due to uniform film shrinkage, but requires an accurate value for the camera angle. We therefore thought it instructive to do some calculations using camera angles in error by a known amount.

For simplicity, the substance photographed should be cubic and give a large number of reasonably strong and sharp lines over a wide range of θ values. We chose the γ-structure Cu_9Al_4, which, with Cu radiation, gives a well resolved and intense α-doublet ($h^2+k^2+l^2=126$) at $\theta_{\alpha_1}=83°\cdot4$: $\theta_{\alpha_2}=84°\cdot8$, together with a large number of lines going down to the lowest order line measurable ($h^2+k^2+l^2=6$) with $\theta=12°\cdot7$. Table 1 gives a list of the lines measured, which will be seen to be distributed fairly evenly over the photograph. The Cu radiation was filtered to avoid the confusion inevitable with β-lines in a pattern of this complexity. The specimens were accurately centred and rotated during the exposure. The temperature for each exposure was kept constant by circulating water through the cooling jacket of the camera. Care was taken to ensure that the electron beam in the Metropolitan-Vickers x-ray tube was homogeneously

* Subsequently to our work.

Table 1

X-ray reflections from Cu_9Al_4; $CuK\alpha$ radiation
(Approximate θ values from thick diluted specimen)

$h^2+k^2+l^2$	θ	$h^2+k^2+l^2$	θ	$h^2+k^2+l^2$	θ
6	12·8	$66\alpha_1$	46·2	$102\alpha_2$	63·8
9	15·7	$66\alpha_2$	46·3	$108\alpha_1$	67·0
12	18·2	$72\alpha_1$	48·9	$108\alpha_2$	67·3
14	19·7	$72\alpha_2$	49·0	$114\alpha_1$	71·0
18	22·4	$76\alpha_1$	50·7	$114\alpha_2$	71·4
22	24·8	$78\alpha_1$	51·6	$118\alpha_1$	74·1
24	26·0	$90\alpha_1$	57·3	$120\alpha_1$	75·9
$36\alpha_1$	32·3	$90\alpha_2$	57·5	$120\alpha_2$	76·4
$48\alpha_1$	38·1	$98\alpha_1$	61·3	$122\alpha_1$	77·9
$54\alpha_1$	40·8	$98\alpha_2$	61·6	$126\alpha_1$	83·4
$54\alpha_2$	40·9	$102\alpha_1$	63·5	$126\alpha_2$	84·8

distributed over the target, i.e. no "hot-spots" were present. The camera was adjusted so that its slit-system made a small angle with the face of the target, thus securing a "foreshortened" circular focal spot, and this arrangement was accurately reproduced for each exposure.

§ 3. SPECIMENS USED

Filings of Cu_9Al_4 were annealed at 650° for ½ hour and sieved through a 350 B.S.S. mesh. This sample was used to prepare specimens (*a*) and (*b*) described below. Specimens (*c*) and (*d*) were prepared from the same filings annealed at a slightly higher temperature, 700°, for ½ hour.

Four specimens were prepared :

(*a*) A rod 0·59 mm. diameter made by rolling with gum tragacanth.

(*b*) As above, 1·46 mm. diameter.

(*c*) A silica tube, bore 0·45 mm., uniform wall thickness 0·025 mm., filled with Cu_9Al_4 powder packed as densely as possible.

(*d*) A Lindemann-glass tube, bore 1·35 mm., uniform wall thickness 0·016 mm., filled as above.

The use of gum tragacanth may be unfamiliar and will be described. The specimens are made by mixing the specimen powder with gum tragacanth powder, moistening, and rolling the resulting dough into a uniform rod. When dry, this rod is quite rigid. Specimen (*a*) was the thinnest one it was convenient to make with this technique, and was prepared with enough gum tragacanth roughly to satisfy the generally accepted condition for ensuring good photographs, namely, that $\mu r=1$, where μ = linear absorption coefficient of the specimen mixture, r = radius of specimen, the gum tragacanth acting as a diluent. Specimen (*b*) was prepared from the same mixture but was deliberately made very thick; the condition $\mu r=1$, of course, no longer applied. Specimens (*c*) and (*d*) approximated in density and absorption to a wire specimen. Here again one specimen was made as thin as possible and the other very thick. It should be pointed out that each of our specimens was a homogeneous solid cylinder. The method of preparing specimens by causing the powdered sample to adhere to the surface of a hair or a thin glass fibre gives a hollow cylinder.

§ 4. EXTRAPOLATIONS

The results for specimen (*b*) (the thick gum tragacanth specimen) were considered in some detail. The apparent a values were plotted against the following functions of θ :

$$\theta^\circ,\ \cot\theta,\ \cos^2\theta,\ \cot\theta\,.\cos^2\theta,\ \cot\theta\left(\frac{1+\cos^2\theta}{2}\right),$$

$$\frac{\cos^2\theta}{\sin\theta},\qquad \frac{\cos^2\theta}{\theta},\qquad \frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right).$$

These plots are shown in figure 1, and display several interesting features.

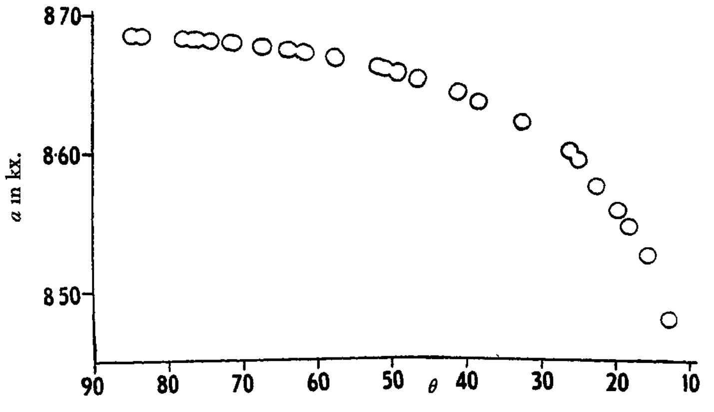


Figure 1 *a*.

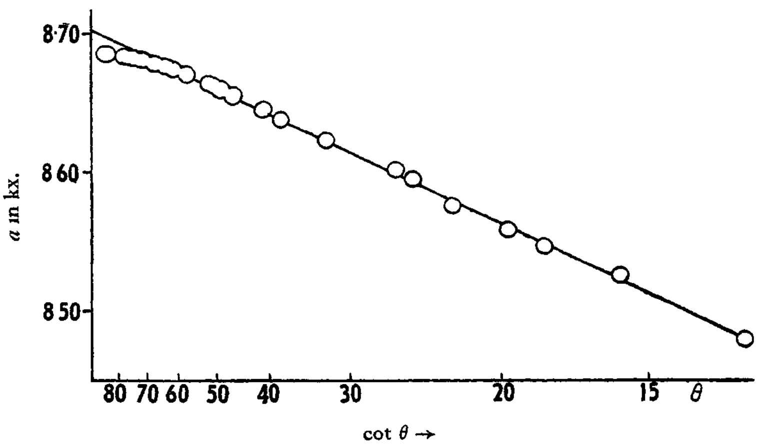


Figure 1 *b*.

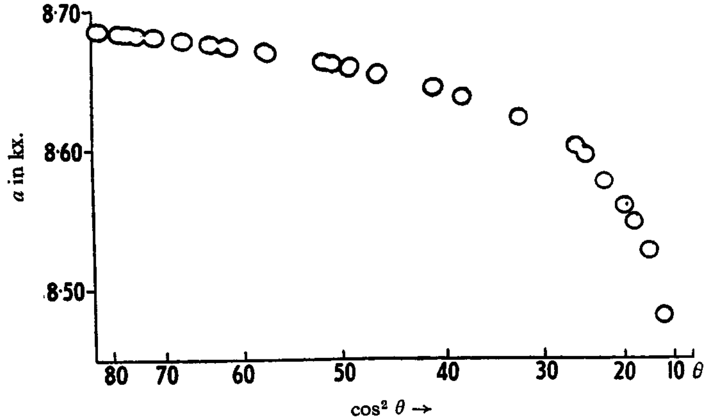


Figure 1 c.

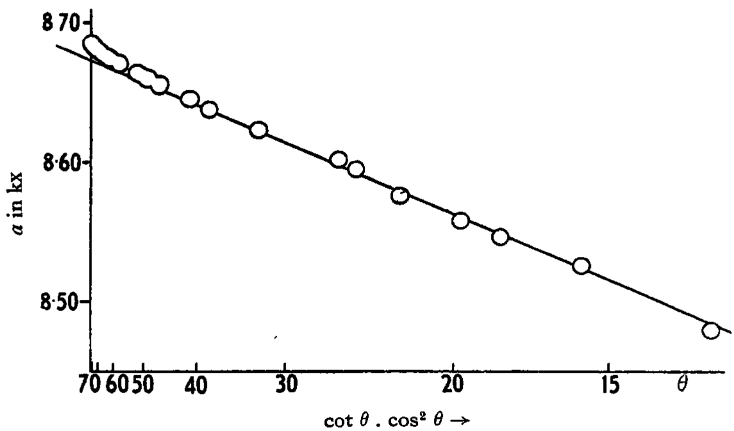


Figure 1 d.

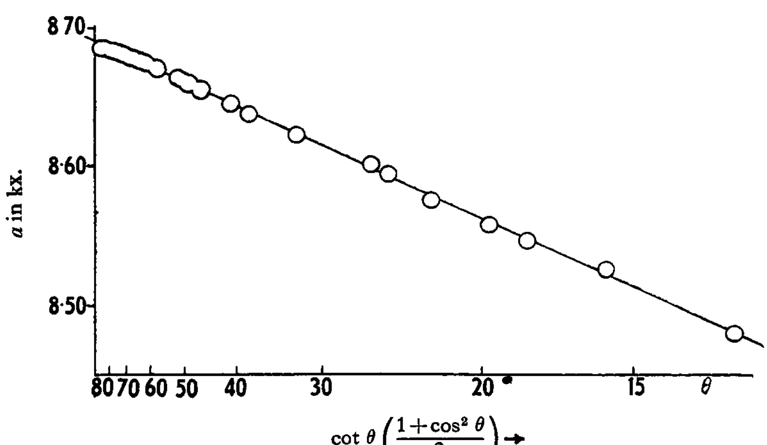
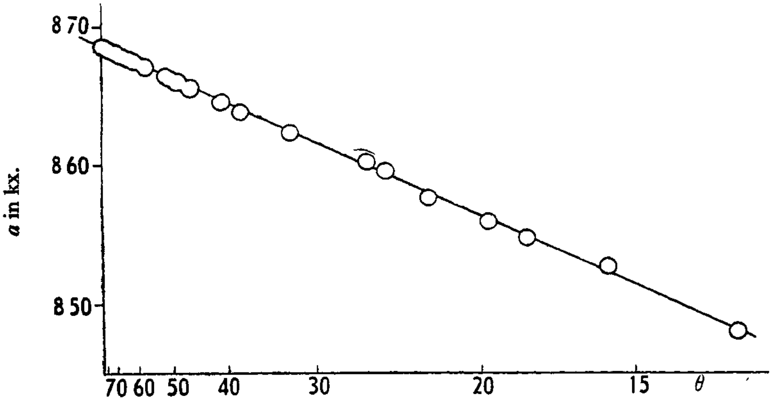
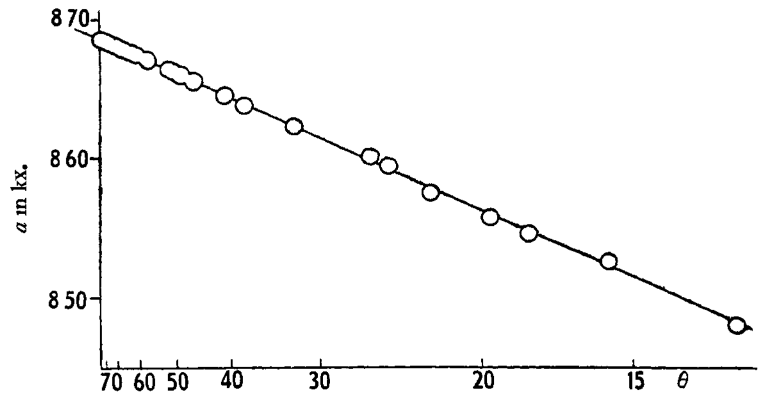


Figure 1 e,



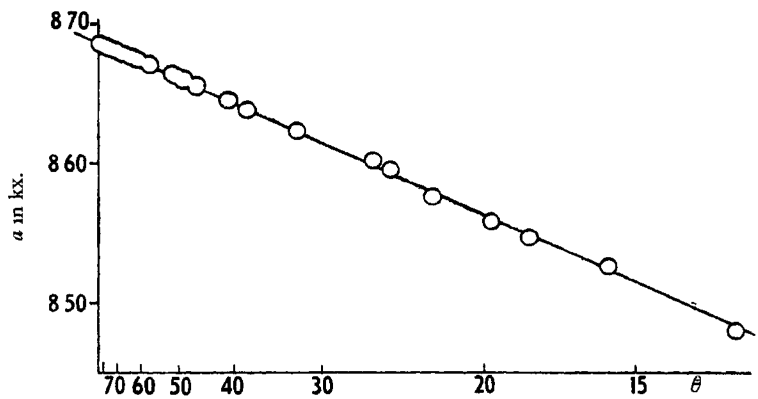
$\frac{\cos^2\theta}{\sin\theta} \rightarrow$

Figure 1 *f*.



$\frac{\cos^2\theta}{\theta} \rightarrow$

Figure 1 *g*.



$\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right) \rightarrow$

Figure 1 *h*.

Figure 1. Thick diluted specimen.
Plots of a against various functions of θ.

Firstly, the $\cos^2\theta$ plot is nearly linear only over a very small range, and its main advantage over the straightforward plot against θ is the way in which it compresses the high angle values towards $\cos^2\theta = 0$. Secondly, it is clear that the plot must be against $\cot\theta$, or against a very similar function, if linearity over the whole range is to be achieved. The plot against $\cot\theta$ itself shows a falling off from linearity at high angles, while the use of $\cot\theta\cos^2\theta$ (Buerger's absorption-error plot) gives the opposite deviation. A plot against the arithmetic mean of these two functions, $\cot\theta\,\dfrac{1+\cos^2\theta}{2}$, shows a marked improvement but still falls off at high angles. The plot against $\dfrac{\cos^2\theta}{\sin\theta}$ (or $\cot\theta\cos\theta$, the geometric mean) is apparently linear, as is the plot against the very similar function $\dfrac{\cos^2\theta}{\theta}$. A close examination of the two extrapolations, however, shows that in the case of the $\dfrac{\cos^2\theta}{\sin\theta}$

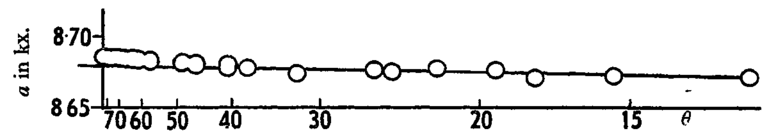


Figure 2 *a*.

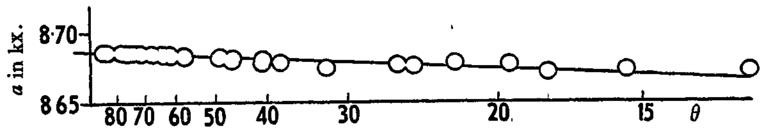


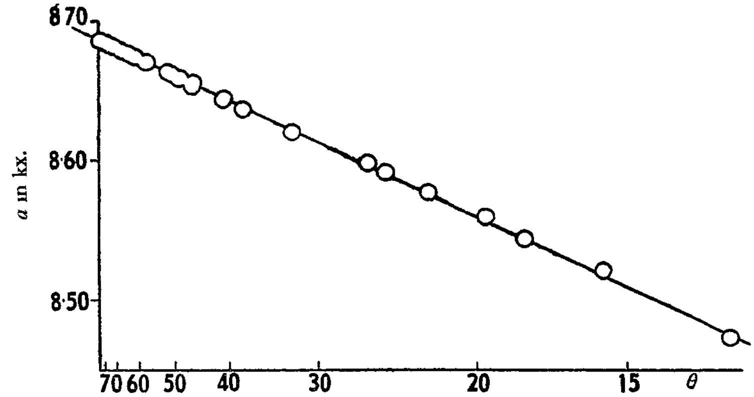
Figure 2 *b*.

Figure 2. Medium thickness diluted specimen.

plot the best straight line drawn through the high-angle points only has a slightly smaller slope than the best straight line drawn through all the points, whereas the reverse is true for the $\dfrac{\cos^2\theta}{\theta}$ plot. In conformity with these observations, a remarkably good linear plot is obtained against the arithmetic mean of these functions, $\dfrac{1}{2}\left(\dfrac{\cos^2\theta}{\sin\theta}+\dfrac{\cos^2\theta}{\theta}\right)$. In this case the best overall extrapolation coincides exactly with the best high-angle extrapolation, as is shown more clearly in the larger scale drawing in figure 5 *a* (lower plot).

The results for specimen (*a*), the gum tragacanth specimen of medium thickness, are not in agreement with these findings. The plot against $\dfrac{1}{2}\left(\dfrac{\cos^2\theta}{\sin\theta}+\dfrac{\cos^2\theta}{\theta}\right)$ is not linear over the whole range (figure 2 *a*). The high-angle points fall closely on a straight line, but the slope of this line is markedly greater than that of the line drawn through the low-angle points. The latter extrapolation, it is interesting to note, is almost horizontal. The plot against $\cot\theta$, on the other hand, is linear over the whole range (figure 2*b*).

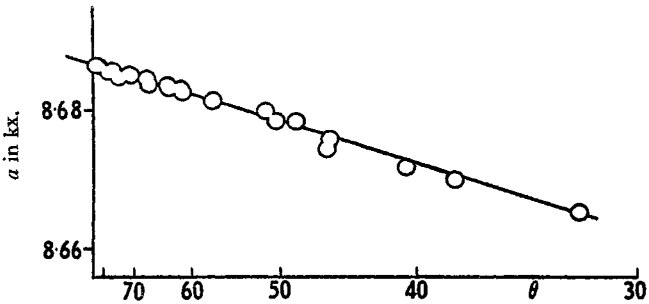
The thick undiluted specimen (*d*) gives similar results to those obtained with specimen (*b*). Plotting against $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$ gives a remarkably good straight line over the whole range (figure 3).



$\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)\rightarrow$

Figure 3 Thick undiluted specimen.

The undiluted specimen of medium thickness, specimen (*c*), behaves similarly to specimen (*a*). The plot against $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$ is not linear over the whole range, although a good straight-line extrapolation can be obtained with the high-angle points (figure 4 *a*). The linearity of the plot against $\cot\theta$ (figure 4 *b*) is not as good as with specimen (*a*), as there is a slight downwards bend at high angles. A plot against the arithmetic mean of the two functions is nearly linear over the whole range, but is unsuitable for extrapolation.



$\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)\rightarrow$

Figure 4 *a*.

Large scale plot of *a* against $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$ for lines with $\theta>30°$.

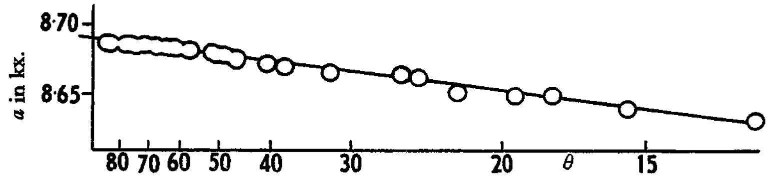


Figure 4 b.

Figure 4. Medium thickness undiluted specimen.

These results are summarized in the following table:

Specimen	Best overall plot for linearity	Best high-angle plot for accuracy	Low-angle limit of linearity for high-angle plot (θ)
(a) Medium thickness diluted	$\cot\theta$	$\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$	30°
(b) Very thick diluted	$\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$	,,	(13°)*
(c) Medium thickness undiluted	$\frac{1}{2}\left[\cot\theta+\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)\right]$	,,	30°
(d) Very thick undiluted	$\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$	,,	(13°)*

* For line 6, the lowest line measured. The true limit may be lower than this.

We interpret these results in the following way. Two factors are contributing to the errors in the apparent a values, (a) the absorption, and (b) systematic observational errors.

(a) The absorption error

$$\left(\frac{\delta a}{a}\right)_{\text{abs}} \propto \frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}.$$

This is in agreement with the theoretical finding of Taylor and Sinclair for the case of an "exponential" focus, although we had established the relation experimentally before they had reached this conclusion.

(b) Errors in a due to systematic observational errors in measuring θ are proportional to $\cot\theta$. This is easily confirmed by differentiating the Bragg equation :

$$a=\frac{\lambda}{2}\sqrt{h^2+k^2+l^2}\ \operatorname{cosec}\theta \quad \text{(for a cubic crystal);}$$

therefore $$\delta a=-\frac{\lambda}{2}\sqrt{h^2+k^2+l^2}\operatorname{cosec}\theta\cot\theta\,\delta\theta$$

and $$\frac{\delta a}{a}=-\cot\theta\,\delta\theta.$$

Systematic observational errors may arise in measuring the positions of lines on a film using the usual type of measuring instrument. An observer may systematically place the cross-hairs slightly to one side of the position of maximum line density, particularly if the background blackening has a marked slope. We have noticed that there is often a slight systematic discrepancy between readings made independently by the two of us.

In the thick specimens, absorption is the over-riding source of error, while in the specimen of "optimum" absorption and medium thickness, the effect of absorption is very slight. Hence the thick specimens give a linear plot against the absorption error function. When, however, the effect of absorption is negligible, the plot is no longer linear against this function; the only remaining source of error is observational and the plot becomes instead linear against $\cot\theta$. An intermediate case exists for the undiluted specimen of medium thickness. Here the plot is not strictly linear against either the absorption error function or against $\cot\theta$. The effect of observational errors being comparable with the absorption error, the plot is nearly linear against a mean of $\cot\theta$ and $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$.

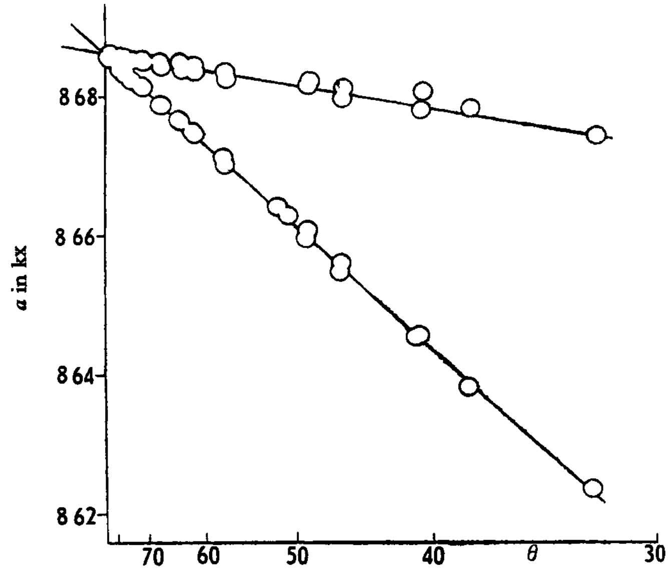
Having considered the question of the overall linearity of the plots, it is necessary to investigate the consistency with which any given type of plot will lead to a single value for a. Large-scale plots of apparent a vs. $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$ for the high-angle lines ($\theta > 30°$) are shown in figures 5 *a* and 5 *b*.

In both cases, the extrapolations for the medium and thick specimens converge very nearly to a point in spite of the considerable difference in slope. The following table gives a list of the extrapolated a values obtained, the maximum extrapolation deviation in each case being ± 0.0001 kx.

Specimen	a from $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$ extrapolation		Temp.
(*a*) Medium diluted	8·6863 kx.	difference = 0·0002 kx.	15°·8
(*b*) Thick diluted	8·6861 kx.		15°·4
(*c*) Medium undiluted	8·6866 kx.	" " "	16°·2
(*d*) Thick undiluted	8·6864 kx.		16°·4

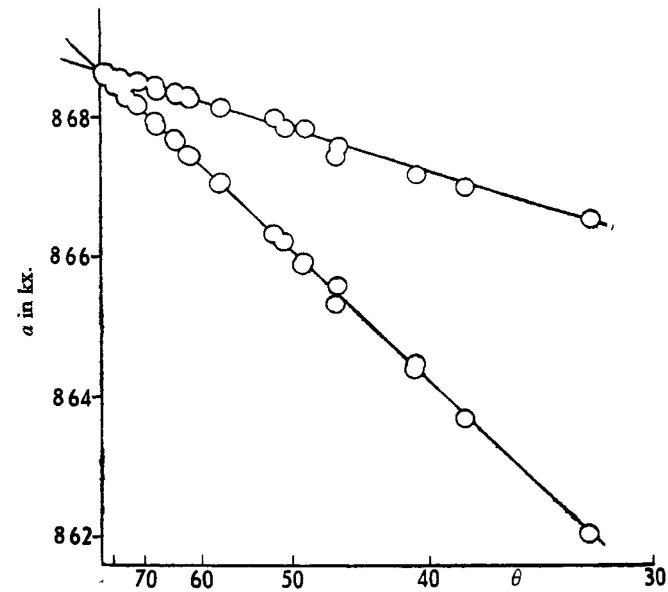
Mean value for $a = 8{\cdot}6864 \pm 0{\cdot}0003$ kx.

It will be noticed that the medium specimens in each case give a slightly larger value for a than the thick, and that the undiluted specimens give slightly higher values than the diluted. The slightly higher temperatures at which the undiluted specimens were photographed would tend to give slightly higher values for a. It is unlikely that the small difference of annealing temperature would have any measurable effect. Even so, the maximum error in the mean value of a from the four results is only about one part in 30,000. It is of interest that the value of a derived from the medium diluted specimen of "optimum" absorption is very close to the mean value.



$$\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)\rightarrow$$

Figure 5 *a*. Medium thickness diluted specimen (upper plot). Thick diluted specimen (lower plot).



$$\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)\rightarrow$$

Figure 5 *b*. Medium thickness undiluted specimen (upper plot). Thick undiluted specimen (lower plot).

Figure 5. Large-scale plots of a against $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$ for lines with $\theta > 30°$.

A similar large-scale plot was made for specimen (*a*) (diluted, medium thickness) against the function which gave the best overall linearity, namely, $\cot\theta$. This is shown in figure 6.

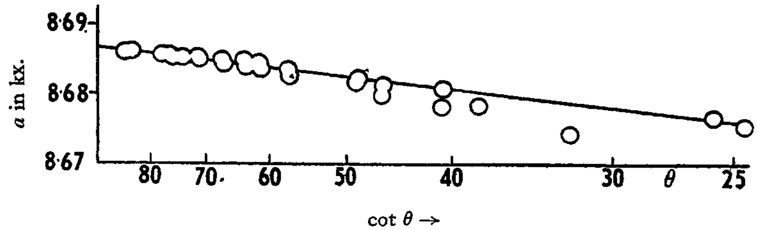


Figure 6. Medium thickness diluted specimen.
Large-scale plot of *a* against $\cot\theta$ for lines with $\theta > 25°$.

The extrapolated value of *a* is 8·6867 kx., which is higher than that obtained above. It was noticed that the $\cot\theta$ plot tended to emphasize the effect of random errors in measurement, giving a slightly more "scattered" plot than the one against $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$.

The enclosure of specimens in thin-walled silica or Lindemann-glass tubes does not appear to cause any new errors.

§ 5. EFFECT OF WRONG CAMERA ANGLE

The effect of an error in θ_k, the camera angle, is to cause a flexure in the plot of *a* vs. $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$ at high angles. Figures 7 *a* and 7 *b* show this effect on data obtained from specimen (*b*). The *a* values used were calculated using θ_k in error by 0·1 % in a positive and negative sense. A positive error in θ_k causes an upward flexure, and *vice versa*. The symmetry of the two effects confirms the accuracy of determination of the camera angle ($\theta = 86°{\cdot}693$) by Wilson and Lipson (1941).

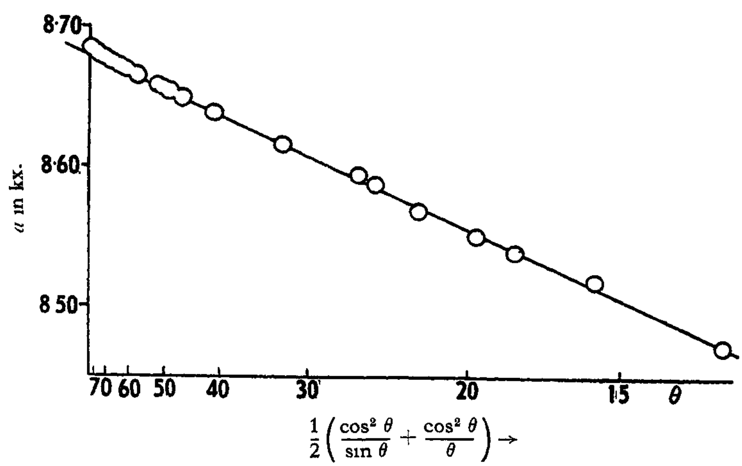


Figure 7 *a*. θ_k in error by +0·1 %.

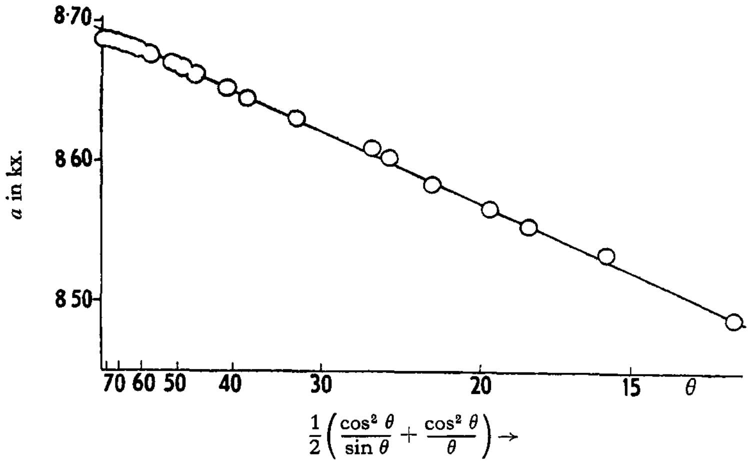


Figure 7 *b*. θ_k in error by $-0{\cdot}1$ %.

Figure 7. Effect of wrong camera angle, θ_k.

Plots of a against $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$ for thick diluted specimen.

These authors also discussed the source of error and showed that errors in a due to this cause are proportional to $\theta\cot\theta$. It is advisable to use a camera which can record lines with θ approaching 85°, otherwise the flexure in the plot may be unobservable and an unsuspected source of error be present.

§6. METHOD OF CALIBRATING CAMERA

The recommendation of Wilson and Lipson (1941) is to calibrate by direct measurement. Some cameras are so constructed, however, that this is impossible, and θ_k must then be derived from the high-angle lines on a quartz photograph. The basis of the method as described by Bradley and Jay (1933) is to derive values of θ_k from each high-order reflection and then to use an extrapolation technique. These authors showed that,

if $$\frac{\delta a}{a}\propto\cos^2\theta,$$

then $$\frac{\delta\theta_k}{\theta_k}\propto\frac{\sin 2\theta}{2\theta}.$$

Hence the true value of θ_k is found by plotting the apparent values against $\frac{\sin 2\theta}{2\theta}$ and extrapolating linearly to zero (corresponding to $\theta=90°$).

We have shown that with well-constructed cameras absorption is the main source of error, and that

$$\frac{\delta a}{a}\propto\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}.$$

In this case it is easily proved that

$$\frac{\delta\theta_k}{\theta_k}\propto\frac{\cos\theta}{\theta}\left(1+\frac{\sin\theta}{\theta}\right).$$

Hence a plot of θ_k against $\frac{\cos\theta}{\theta}\left(1+\frac{\sin\theta}{\theta}\right)$ should give a straight line, and extrapolation to zero value of this function (corresponding to $\theta=90^\circ$) should give the correct value of θ_k. Table 2 gives the values of $\frac{\cos\theta}{\theta}\left(1+\frac{\sin\theta}{\theta}\right)$ for the angles of reflection for quartz recommended by Wilson and Lipson (1941).

We have tried out this method of extrapolation on the results of Wilson and Lipson for films 873, 876, 877, which were all taken with the camera we used. The values derived for θ_k were 86°·687, 86°·694, 86°·704; mean $\theta_k=86°·695$,

Table 2

Values of $\frac{\cos\theta}{\theta}\left(1+\frac{\sin\theta}{\theta}\right)$ for quartz. Cu radiation, 18° C.

Line	θ (°)	$\frac{\cos\theta}{\theta}\left(1+\frac{\sin\theta}{\theta}\right)$	Line	θ°	$\frac{\cos\theta}{\theta}\left(1+\frac{\sin\theta}{\theta}\right)$
$412\alpha_1$	61·304	0·817	$502\alpha_1$, $225\alpha_1$	71·632	0·443
$412\alpha_2$	61·567	0·806			
$305\alpha_1$	63·631	0·723	$502\alpha_2$, $225\alpha_2$, $331\alpha_1$	72·065	0·430
$305\alpha_2$	63·920	0·711			
$116\alpha_1$	65·613	0·647			
$116\alpha_2$	65·931	0·636	$331\alpha_2$	72·509	0·417
$501\alpha_1$, $501\alpha_2$, $404\alpha_1$, $404\alpha_2$	very faint		$420\alpha_1$	73·319	0·392
			$420\alpha_2$	73·803*	0·378
			$315\alpha_1$	75·092*	0·341
$206\alpha_1$	68·217	0·555	$315\alpha_2$, $421\alpha_1$	75·606	0·327
$206\alpha_2$	68·578	0·542			
			$421\alpha_2$	76·138	0·312
$413\alpha_1$	68·951	0·530	$234\alpha_1$	76·772	0·295
$413\alpha_2$	69·326	0·517	$234\alpha_2$	77·394	0·278
$330\alpha_1$	70·162	0·490	$216\alpha_1$	78·552	0·248
$330\alpha_2$	70·562	0·477	$216\alpha_2$	79·280	0·230

* These angles are given erroneously in table 4 of Wilson and Lipson's paper (1941), owing to a proof error.

mean deviation $=0°·006$. The above authors, using a $\frac{\sin 2\theta}{2\theta}$ plot, had obtained 86°·688, 86°·697, 86°·709; mean $\theta_k=86°·698$, mean deviation $=0°·007$. The camera angle derived by direct measurement is 86°·693, which is taken as the correct value. It will therefore be seen that the $\frac{\cos\theta}{\theta}\left(1+\frac{\sin\theta}{\theta}\right)$ plot gives a more accurate result for θ_k in this case.

We should like to emphasize the recommendations of Wilson and Lipson that cameras should be calibrated by direct measurement wherever possible. When quartz *has* to be used, we would advise that at least three photographs be taken.

§ 7. RECOMMENDATIONS ON PROCEDURE

It is obvious that if a number of factors are contributing to the error, each of the factors having a different dependence on θ, no satisfactory linear plot of a vs. $f(\theta)$ can in general be obtained. The eccentricity error can, however, be almost entirely avoided by using a well-made camera, which should be a *sine qua non* in an investigation claiming the highest accuracy. The principal remaining source of error is then due to absorption, and linear extrapolation over a wide range becomes possible. It may not always be easy to assess the importance of eccentricity in the camera being used. In such cases it is advisable to calibrate the camera for extrapolation, following a procedure similar to that described in this paper. That is to say, the extrapolation function best suited to the particular camera should be derived empirically.

The first general recommendation, then, is to minimize the possible sources of error by using a well-designed and accurately constructed camera. Secondly, whether the Bradley-Jay or van Arkel arrangement is used, the method of film measurement using a camera angle described by Bradley and Jay (1932) and by Lipson and Wilson (1941) should be employed as it avoids uniform film-shrinkage errors. It is necessary, however, to know the camera angle accurately. We have shown in this paper that the effect of 0·1% error in the camera angle is easily noticed in an extrapolation, and Wilson and Lipson observed it with an error of only 0·06%. Hence the linearity of the plot at very high angles should provide another check on the accuracy of calibration of the camera. Thirdly, care should be taken to avoid "hot spots" on the target and to use an effectively circular focal spot.

Four conditions need to be considered in deciding on an extrapolation procedure :

(*a*) It should give a consistent value for a whatever the nature of the specimen.

(*b*) The low-angle limit of linearity of the plot should be as low as possible.

(*c*) The compression of the high-angle points towards the extrapolation limit should be considerable.

(*d*) The slope of the extrapolation should be as small as possible.

It is clear from the above results that a thick absorbing specimen gives an accurate linear plot of a vs. $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$ down to the lowest recorded values of θ. This advantage is somewhat outweighed by the greatly increased slope of the extrapolation. A thinner specimen of "optimum" absorption will, on the other hand, give rise to a very small extrapolation slope. The plot in general will not be linear over the whole range, but a plot of a vs. $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$ will be accurately linear down to an angle of *about* 30°. This is a very much lower limit than is possible with a plot against $\cos^2\theta$. Although a plot against $\cot\theta$ for such a specimen *may* have a greater range of linearity, it has the disadvantage that the high-angle points are not brought very close to the extrapolation limit. It also tends to accentuate the effect of random errors. Further, it has been demonstrated for such a specimen that the plot against $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$ gives a value for a very close to the mean obtained from a number of specimens.

In order to obtain highest accuracy it is therefore recommended:

(*a*) To make a thin specimen of "optimum" absorption.

(*b*) To choose x radiation of the right wave-length to give high-angle lines; in particular, to ensure that at least one line has $\theta > 80°$. The closer this final line is to $\theta = 90°$, the greater the accuracy, no matter what extrapolation method is used.

(*c*) To plot apparent a against $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$ and to extrapolate linearly to zero value of this function. Lines with θ values as low as 30° can be included in the plot. This means that a far greater number of lines than usually considered can justifiably be used, giving the extrapolation greater certainty.

In critical cases it may be advisable to make a number of specimens of different thickness and absorption and to take the mean value of the results.

It must be emphasized that these recommendations have effect only when the eccentricity error is negligible, and we have urged that cameras be so designed and constructed that this is so. If, however, the effect of eccentricity is very much greater than that of absorption, a plot against $\cos^2\theta$ would be more correct. It is our experience that this is rarely the case, i.e. that absorption is usually the more important source of error.

If the problem is such that a reasonably accurate value of the cell dimension has to be derived from a few low-angle lines only, it would be preferable to make a thick absorbing specimen and again to use the $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$ plot. The reason for this is that the extrapolation will have greater certainty than would be the case for the low-angle lines of a thin specimen. At the same time, it should be borne in mind that a thick specimen causes a considerable diminution in intensity of low-angle lines.

Our recommendations may be criticized on the grounds that they are based on the examination of one substance only, Cu_9Al_4. There is, however, no reason for supposing any uniqueness of behaviour for this substance in the derivation of accurate unit-cell dimensions. Also, the different types of specimens prepared were chosen so as to give a considerable variation in properties.

A table of $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$ calculated for every tenth of a degree is appended (table 3). The calculations in this paper were carried out on a Marchant electric calculating machine with automatic division.

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Table 3

Table of $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$

θ	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
°										
10	5·572	5·513	5·456	5·400	5·345	5·291	5·237	5·185	5·134	5·084
11	5·034	4·986	4·939	4·892	4·846	4·800	4·756	4·712	4·669	4·627
12	4·585	4·544	4·504	4·464	4·425	4·386	4·348	4·311	4·274	4·238
13	4·202	4·167	4·133	4·098	4·065	4·032	3·999	3·967	3·935	3·903
14	3·872	3·842	3·812	3·782	3·753	3·724	3·695	3·667	3·639	3·612
15	3·584	3·558	3·531	3·505	3·479	3·454	3·429	3·404	3·379	3·355
16	3·331	3·307	3·284	3·260	3·237	3·215	3·192	3·170	3·148	3·127
17	3·105	3·084	3·063	3·042	3·022	3·001	2·981	2·962	2·942	2·922
18	2·903	2·884	2·865	2·847	2·828	2·810	2·792	2·774	2·756	2·738
19	2·921	2·704	2·687	2·670	2·653	2·636	2·620	2·604	2·588	2·572
20	2·556	2·540	2·525	2·509	2·494	2·479	2·464	2·449	2·434	2·420
21	2·405	2·391	2·376	2·362	2·348	2·335	2·321	2·307	2·294	2·280
22	2·267	2·254	2·241	2·228	2·215	2·202	2·189	2·177	2·164	2·152
23	2·140	2·128	2·116	2·104	2·092	2·080	2·068	2·056	2·045	2·034
24	2·022	2·011	2·000	1·989	1·978	1·967	1·956	1·945	1·934	1·924
25	1·913	1·903	1·892	1·882	1·872	1·861	1·851	1·841	1·831	1·821
26	1·812	1·802	1·792	1·782	1·773	1·763	1·754	1·745	1·735	1·726
27	1·717	1·708	1·699	1·690	1·681	1·672	1·663	1·654	1·645	1·637
28	1·628	1·619	1·611	1·602	1·594	1·586	1·577	1·569	1·561	1·553
29	1·545	1·537	1·529	1·521	1·513	1·505	1·497	1·489	1·482	1·474
30	1·466	1·459	1·451	1·444	1·436	1·429	1·421	1·414	1·407	1·400
31	1·392	1·385	1·378	1·371	1·364	1·357	1·350	1·343	1·336	1·329
32	1·323	1·316	1·309	1·302	1·296	1·289	1·282	1·276	1·269	1·263
33	1·256	1·250	1·244	1·237	1·231	1·225	1·218	1·212	1·206	1·200
34	1·194	1·188	1·182	1·176	1·170	1·164	1·158	1·152	1·146	1·140
35	1·134	1·128	1·123	1·117	1·111	1·106	1·100	1·094	1·098	1·083
36	1·078	1·072	1·067	1·061	1·056	1·050	1·045	1·040	1·034	1·029
37	1·024	1·019	1·013	1·008	1·003	0·998	0·993	0·988	0·982	0·977
38	0·972	0·967	0·962	0·958	0·953	0·948	0·943	0·938	0·933	0·928
39	0·924	0·919	0·914	0·909	0·905	0·900	0·895	0·891	0·886	0·881
40	0·877	0·872	0·868	0·863	0·859	0·854	0·850	0·845	0·841	0·837
41	0·832	0·828	0·823	0·819	0·815	0·810	0·806	0·802	0·798	0·794
42	0·789	0·785	0·781	0·777	0·773	0·769	0·765	0·761	0·757	0·753
43	0·749	0·745	0·741	0·737	0·733	0·729	0·725	0·721	0·717	0·713
44	0·709	0·706	0·702	0·698	0·694	0·690	0·687	0·683	0·679	0·676
45	0·672	0·668	0·665	0·661	0·657	0·654	0·650	0·647	0·643	0·640
46	0·636	0·632	0·629	0·625	0·622	0·619	0·615	0·612	0·608	0·605
47	0·602	0·598	0·595	0·591	0·588	0·585	0·582	0·578	0·575	0·572
48	0·569	0·565	0·562	0·559	0·556	0·553	0·549	0·546	0·543	0·540
49	0·537	0·534	0·531	0·528	0·525	0·522	0·518	0·515	0·512	0·509
50	0·506	0·504	0·501	0·498	0·495	0·492	0·489	0·486	0·483	0·480
51	0·477	0·474	0·472	0·469	0·466	0·463	0·460	0·458	0·455	0·452
52	0·449	0·447	0·444	0·441	0·439	0·436	0·433	0·430	0·428	0·425
53	0·423	0·420	0·417	0·415	0·412	0·410	0·407	0·404	0·402	0·399
54	0·397	0·394	0·392	0·389	0·387	0·384	0·382	0·379	0·377	0·375

Table 3 (*continued*)

θ	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
55	0·372	0·370	0·367	0·365	0·363	0·360	0·358	0·356	0·353	0·351
56	0·349	0·346	0·344	0·342	0·339	0·337	0·335	0·333	0·330	0·328
57	0·326	0·324	0·322	0·319	0·317	0·315	0·313	0·311	0·309	0·306
58	0·304	0·302	0·300	0·298	0·296	0·294	0·292	0·290	0·288	0·286
59	0·284	0·282	0·280	0·278	0·276	0·274	0·272	0·270	0·268	0·266
60	0·264	0·262	0·260	0·258	0·256	0·254	0·252	0·250	0·249	0·247
61	0·245	0·243	0·241	0·239	0·237	0·236	0·234	0·232	0·230	0·229
62	0·227	0·225	0·223	0·221	0·220	0·218	0·216	0·215	0·213	0·211
63	0·209	0·208	0·206	0·204	0·203	0·201	0·199	0·198	0·196	0·195
64	0·193	0·191	0·190	0·188	0·187	0·185	0·184	0·182	0·180	0·179
65	0·177	0·176	0·174	0·173	0·171	0·170	0·168	0·167	0·165	0·164
66	0·162	0·161	0·160	0·158	0·157	0·155	0·154	0·152	0·151	0·150
67	0·148	0·147	0·146	0·144	0·143	0·141	0·140	0·139	0·138	0·136
68	0·135	0·134	0·132	0·131	0·130	0·128	0·127	0·126	0·125	0·123
69	0·122	0·121	0·120	0·119	0·117	0·116	0·115	0·114	0·112	0·111
70	0·110	0·109	0·108	0·107	0·106	0·104	0·103	0·102	0·101	0·100
71	0·099	0·098	0·097	0·096	0·095	0·094	0·092	0·091	0·090	0·089
72	0·088	0·087	0·086	0·085	0·084	0·083	0·082	0·081	0·080	0·079
73	0·078	0·077	0·076	0·075	0·075	0·074	0·073	0·072	0·071	0·070
74	0·069	0·068	0·067	0·066	0·065	0·065	0·064	0·063	0·062	0·061
75	0·060	0·059	0·059	0·058	0·057	0·056	0·055	0·055	0·054	0·053
76	0·052	0·052	0·051	0·050	0·049	0·048	0·048	0·047	0·046	0·045
77	0·045	0·044	0·043	0·043	0·042	0·041	0·041	0·040	0·039	0·039
78	0·038	0·037	0·037	0·036	0·035	0·035	0·034	0·034	0·033	0·032
79	0·032	0·031	0·031	0·030	0·029	0·029	0·028	0·028	0·027	0·027
80	0·026	0·026	0·025	0·025	0·024	0·023	0·023	0·023	0·022	0·022
81	0·021	0·021	0·020	0·020	0·019	0·019	0·018	0·018	0·017	0·017
82	0·017	0·016	0·016	0·015	0·015	0·015	0·014	0·014	0·013	0·013
83	0·013	0·012	0·012	0·012	0·011	0·011	0·010	0·010	0·010	0·010
84	0·009	0·009	0·009	0·008	0·008	0·008	0·007	0·007	0·007	0·007
85	0·006	0·006	0·006	0·006	0·005	0·005	0·005	0·005	0·005	0·004
86	0·004	0·004	0·004	0·003	0·003	0·003	0·003	0·003	0·003	0·002
87	0·002	0·002	0·002	0·002	0·002	0·002	0·001	0·001	0·001	0·001
88	0·001	0·001	0·001	0·001	0·001	0·001	0·001	0·000	0·000	0·000

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