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A MODIFIED GRAPHICAL METHOD OF ABSORPTION CORRECTION FOR THE DISPLACEMENT OF LINES IN A POWDER PHOTOGRAPH

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While working on the problem "Optical, chemical and x-ray studies of the mineral suites of some South Indian rocks," the author had to take a number of powder photographs and calculate the interplanar spacings and cell dimensions. It was found that the most important silicate minerals, such as garnets, pyroxenes and amphiboles, have fairly large linear absorption coefficients, μ, and hence can be called, following Peiser *et al.* (1955), "strongly absorbing specimens." Because of strong absorption, these substances give rise to errors in the measured Bragg angles owing to the displacement of powder lines. The aim of the present paper is to show that the graphical method, suggested by Azaroff and Buerger (1958) can be slightly modified for these "strongly absorbing specimens" and that this method gives more accurate values than that of Ramberg and Devore (1951).

In the course of this investigation all the powder photographs were taken in a 114.7 mm Seifert camera. Both Cu-Kα and FeKα radiations were used. The powder was packed in a Lindemann tube, whose wall thickness was very small. Much attention was not paid to the intensities of the lines. Only comparative intensities of the lines were taken into

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account to enable comparison with other data and indexing of the lines. But all the usual precautions were taken to measure accurately the distances between the lines. The correction for shrinkage was applied in the same manner as suggested by Ramberg and Devore (1951).

Peisser *et al.* (1955) recommend the use of Lindemann tubes with a diameter less than 0.5 mm in order to minimise the errors due to the absorption of the specimen. This worked out well for garnets which give very intense reflections and whose high-angle lines could be easily indexed. But in the case of pyroxenes and amphiboles only very few lines were observed and even they tended to merge in the background. Since a large number of observations of powder lines are required to determine accurately the cell dimensions from a powder photograph, Lindemann tubes with larger diameters, *e.g.*, 1 mm, had to be used for these ferromagnesian minerals. This correspondingly increased the errors due to the displacement of powder lines (see Buerger, 1942; Klug and Alexander, 1954; Peiser *et al.* 1955).

An attempt was made to correct for this error using Ramberg and Devore's method, which is here briefly described: First the distance between corresponding powder lines is measured and corrected for shrinkage. Supposing the corrected distance is X, then the Bragg angle θ is given by $(\mathrm{X}-\mathrm{L})/4$ where $\mathrm{L}=\mathrm{r}(1+\cos 2\theta')$, r being the radius of the specimen and θ' the measured glancing angle. Before applying to various minerals the accuracy of this method was tested with potassium chloride, whose cell dimensions have been accurately determined (ASTM Card No. 4-0587). It was found that especially in the region of low Bragg angles, there was a discrepancy between the values, arrived at by using the formula mentioned above and the values calculated for the respective planes, using the cell dimensions given. Tables I and II show the discrepancy in the values. This is considered a serious handicap especially when one has to index the powder lines in the high-angle region, using the values of the lower Bragg angles.

When potassium chloride was used as an internal standard, only a few of the most intense lines of the substance (*e.g.* pyroxene or amphibole) were seen, though all the lines of potassium chloride were observed. To surmount this difficulty, two Lindemann tubes having the same diameter were taken, one filled with potassium chloride and the other packed with potassium chloride and a pyroxene and exposed to *x*-rays. It was found that the net displacement of the corresponding lines of potassium chloride in the two photographs was the same within the limit of experimental error. Again, a powder specimen of lead nitrate (linear absorption coefficient for Cu-Kα 1040 cm^{-1}) having the diameter 1 mm was found

TABLE I. BRAGG ANGLES FOR KCl

Specimen diameter 1.0 mm. Radiation Cu-Kα

Measured	Calculated from ASTM Card	Corrected with graph (Fig. 1)	Corrected with Ramberg's formula
14° 30′	14° 11′	14° 12′	14° 16′
20 35	20 17	20 18	20 22
25 24	25 07	25 07	25 12
29 37	29 21	29 22	29 26
33 29	33 14	33 14	33 19
37 06	36 53	36 52	36 56
47 31	47 20	47 19	47 17
50 59	50 48	50 47	50 47
54 32	54 21	54 21	54 22

to show the same amount of displacement as that of potassium chloride (linear absorption coefficient for Cu-Kα 247 cm^{-1}) of the same diameter, for equal glancing angles. This indicates that once the linear absorption coefficient exceeds a particular value, the displacement of powder lines does not depend upon μ and hence any shift observed must be attributed to differing specimen thicknesses.

It was observed that, when a Lindemann tube of a diameter 1 mm was used, the powder lines were sharp for potassium chloride as well as for the minerals. The failure to observe the broadening of the powder lines and the observation of a displacement of the same depending upon the diameter of the specimen convey the impression that the x-rays are

TABLE II. BRAGG ANGLES FOR KCl

Specimen diameter 1.10 mm. Radiation Cu-Kα

Measured	Calculated from ASTM Card	Corrected with graph (Fig. 2)	Corrected with Ramberg's formula
14° 36′	14° 11′	14° 12′	14° 20′
20 39	20 17	20 16	20 25
25 28	25 07	25 06	25 15
29 42	29 21	29 21	29 28
33 34	33 14	33 15	33 23
37 12	36 53	36 52½	37 01½
47 35	47 20	47 18	47 27
51 04	50 48	50 49	50 57
54 34	54 21	54 20	54 29

reflected practically at the surface of the specimens of these "strongly absorbing substances." This seems to be in keeping with the statement of Peiser *et al.* (1955, p. 93) that for the strongly absorbing specimens "the position of maximum intensity in any normally accessible arc is almost identical with the position of the high angle edge of a corresponding arc, produced by a specimen of the same radius, but with a μ value approaching zero." Klug and Alexander (1954) also make a similar observation. On the basis of this observation it is assumed that absorption is practically complete in the case of these strongly absorbing substances.

Azaroff and Buerger state that if the product $\mu \cdot r$ for different specimens is kept constant, the absorption of the different samples is the same and that the spacing errors for all these specimens will also be the same. This implies that a powder specimen of potassium chloride (μ for Cu-Kα 247 cm^{-1}) must have a radius four times that of a powder specimen of lead nitrate (μ for Cu-Kα 1040 cm^{-1}), if it must show the same displacement for equal glancing angles. This is found to be contradictory to the above-mentioned observations, which show that specimens of potassium chloride and lead nitrate produce the same amount of error, if their radii are the same. This seems to indicate that this method cannot be applied to strongly absorbing samples, in the case of which absorption is practically complete.

It is now found that once the absorption coefficient exceeds a certain value, the absorption errors in the measured glancing angles depend on the diameter of the specimen. It is therefore concluded that if the radii of the specimens of these samples are kept constant, then they must show the same amount of error. Hence a graph (Fig. 1) is drawn for potassium chloride having the diameter 1 mm by following the procedure of Azaroff and Buerger. The ratio

$$R = \frac{\sin\theta \text{ theoretical}}{\sin\theta \text{ experimental}}$$

is first determined for it. A plot of R against

$$\frac{1}{2}\left[\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right]$$

was made and a straight line graph was obtained. Next the observed θ values of the pyroxenes and amphiboles, having the same diameter 1 mm were corrected, using this graph. The graph was checked once again by another photograph of potassium chloride with a diameter 0.98 mm. The glancing angles measured and those corrected with the graph (Fig. 1) and with Ramberg-Devore's formula are given in Table I. The procedure was repeated with potassium chloride with a specimen diameter

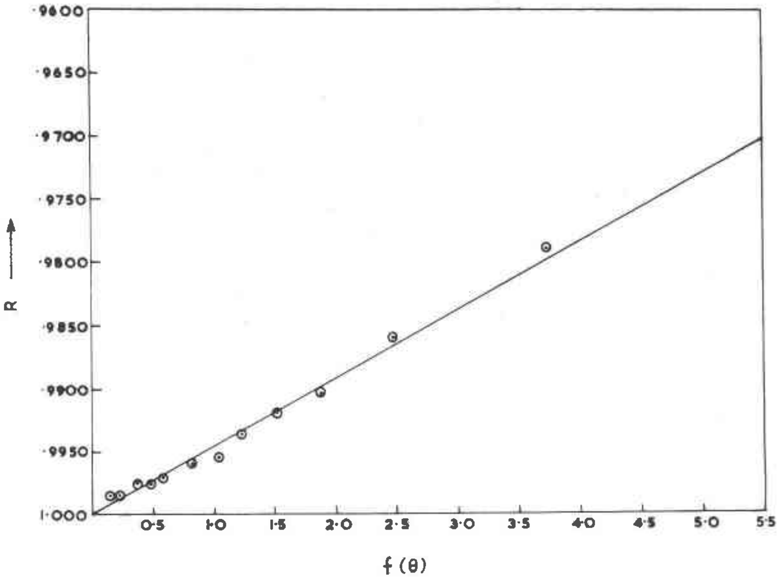

FIG. 1. Correction graph for diameter = 0.98 ± .02 mm.

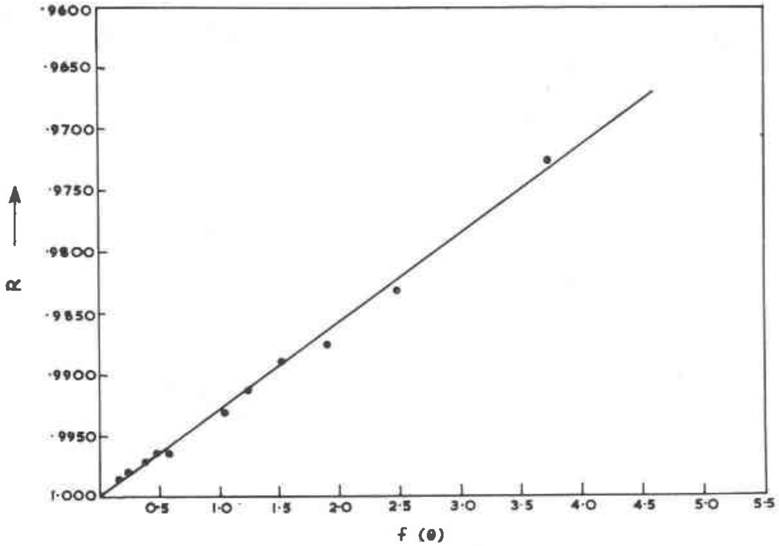

FIG. 2. Correction graph for diameter = 1.10 ± .02 mm.

TABLE III. BRAGG ANGLE FOR $Pb(NO_3)_2$

Specimen diameter 0.96 mm. Radiation Cu-Kα

Measured		Calculated from		Corrected with graph (Fig. 1)		Corrected with Ramberg's formula	
		ASTM Card					
11°	40′	11°	19′	11°	22′	11°	26′
16	27	16	07	16	09	16	14
19	19	19	00	19	01	19	06
20	11	19	53	19	53½	19	59
23	26	23	07	23	09½	23	14
25	38	25	20	25	21½	25	26
26	20	26	02	26	04	26	08
29	01	28	44	28	45½	28	50
30	56	30	39	30	40	30	46
33	58	33	43	33	42	33	47½
35	45	35	29	35	30	35	35½
36	19	36	04½	36	04½	36	09

1.10 mm and the corresponding values are given in Table II and the corresponding graph is given in Fig. 2.

Thus this method enabled the author to overcome two difficulties:

1. The error due to the displacement of the lines especially in the region of low-glancing angles.
2. The inability to get a number of intense lines from an amphibole or a pyroxene, when potassium chloride is mixed with it as an internal standard.

In order to test the validity of this graph for other substances, a lead nitrate specimen with a diameter 0.96 mm was exposed to Cu-Kα radia-

TABLE IV. BRAGG ANGLE FOR $Pb(NO_3)_2$

Specimen diameter 0.96 mm. Radiation Fe-Kα

Measured		Calculated from		Corrected with graph (Fig. 1)		Corrected with Ramberg's formula	
		ASTM Card					
12°	40′	12°	20′	12°	21′	12°	26′
20	44	20	24½	20	27	20	31½
24	28	24	08½	24	11½	24	15½
25	36	25	17	25	19½	25	24½
29	51	29	32½	29	34½	29	40
32	47	32	30½	32	31½	32	37
33	44	33	27½	33	29	33	34
37	25	37	09½	37	12	37	16
40	05	39	50½	39	51	39	56½

tion and the glancing angles were measured and corrected using the corresponding graph (Fig. 1). The measured values, the corrected values and the values calculated for the respective planes using the cell dimensions (given in ASTM Card No. 6-0151) are presented in Table III. It is evident from it that the graphical method gives better values.

In order to test the validity of the graph (Fig. 1) for other targets, the same procedure was repeated with lead nitrate (measured diameter, 0.96 mm) using Fe-Kα radiation. Table IV presents the measured values, the corrected values and the calculated values of the glancing angles.

CONCLUSIONS

These tables show that the graphical method is more accurate (particularly for low angles) than Ramberg and Devore's method, though the latter is simpler.

In the case of strongly absorbing substances, the absorption can be assumed to be practically complete. If the absorption is incomplete, then the absorption error will differ as a function of μ and a curve of the sort suggested by Azaroff and Buerger must be constructed.

These two graphs of correction can be applied to all radiations, provided the substance is strongly absorbing in that radiation.

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