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The Absorption Factor for Rod-Mounted Specimens in the Powder Method of X-ray Analysis

By Eva Møller
Chemical Laboratory, University of Copenhagen, Denmark
and E. Jensen
Chemical Laboratory of the Royal Veterinary and Agricultural College, Copenhagen, Denmark

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A method for calculating absorption factors for rod-mounted specimens in the powder method of X-ray analysis is described. Tables are given for the absorption factor as a function of θ and μr for different rod materials and values of (core radius)/(specimen radius).

The influence of the variables on the intensity ratio of two lines is discussed and information is given on the choice of experimental conditions for obtaining more accurate intensity ratios. Rod-mounted specimens are just as good as homogeneous specimens for many analytical purposes.

Claassen (1930) and Bradley (1935) have developed methods for calculating absorption factors in homogeneous cylindrical powder specimens. In cases where accurate measurements of relative intensities are wanted, however, the specimens are often not homogeneous, but mounted on rods of glass or other materials. A calculation of absorption factors for such specimens has been carried out and the results are given here.

According to Claassen, the absorption factor of a homogeneous specimen may be written

$$A = \frac{1}{\pi r^2}\iint \exp\,[-\mu a]\,ds\,, \qquad (1)$$

where

s = a cross-section area of the specimen,
r = radius of the specimen,
μ = linear absorption coefficient of the powder, and
a = path length of a parallel X-ray beam through the powder.

Equation (1) can be solved either numerically (Bradley) or by graphical integration (Claassen). If the latter is used (1) may be written

$$A = \frac{1}{\pi r^2}\sum \exp\,[-\mu a]\Delta s\,. \qquad (2)$$

For a specimen mounted on a glass rod we have, similarly,

$$A = \frac{1}{\pi(r^2-r_g^2)}\sum \exp\,[-(\mu a+\mu_g a_g)]\Delta s\,,$$

where

r_g = radius of the glass rod,
μ_g = linear absorption coefficient of the glass,
a_g = path length of a parallel X-ray beam through the glass rod, and
Δs is an area element of the reflecting powder with such properties that $\exp\,[-(\mu a+\mu_g a_g)]$ is nearly constant for reflections within Δs.

The absorption factor of a homogeneous specimen is a function of the Bragg angle θ and μr. In the case of an inhomogeneous specimen, however, the absorption factor also depends on the ratio r_g/r and on μ_g.

The method for calculating the contributions to the absorption factor depends on whether the X-ray beam traverses the core 0, 1 or 2 times (the areas I, II and III in Fig. 1).

In case I, Claassen's method was used except for the area *ABCA*, where the Bradley method was applied for $\mu r > 1$ because of its greater accuracy under these conditions. In cases II and III, the Claassen method was used with modifications in the construction of the curves limiting Δs.

For case II this construction is illustrated in Fig. 2. Let $OA = qa_1$, and $OB = (1-q)a_1$, where a_1 is the path length of a parallel beam through the powder before it passes the core, a_2 the path length after it has passed the core. Further, let S be the point of intersection of two circles, the first with radius r and centre at A, the second with radius r_g and centre at B. If q varies between 0 and 1, then S will describe a curve *CD* containing the points for which the distances of primary and reflected beam from the outer to the inner circle have the sum a_1.

Let us consider a segment of the powder ring bounded by *CD* and a similar curve corresponding to the path length $a_1+\Delta a_1$. Rays reflected from an element of area Δs within such a segment pass through a small strip of the core with path lengths between a_g and $a_g+\Delta a_g$, and afterwards through the powder ring the second time with path lengths between a_2 and $a_2+\Delta a_2$. The increments Δa_1, Δa_g, Δa_2 determining Δs are chosen so small that $\exp[-(\mu(a_1+a_2)+\mu_g a_g)]$ is approximately constant for the corresponding Δs. The middle path length through powder and glass, respectively, was used in our calculations.

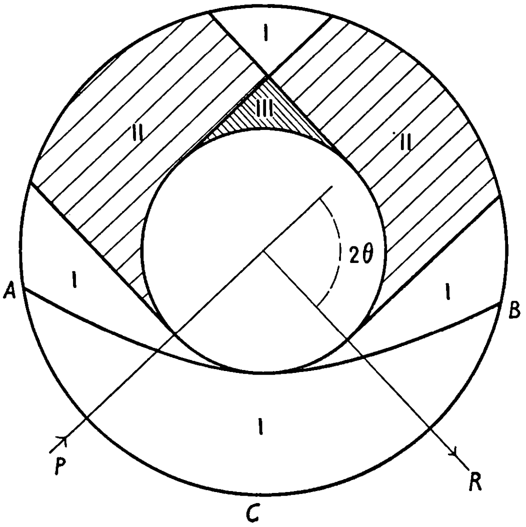

Fig. 1. Cross-section of a rod-mounted specimen. P indicates the direction of primary beam, R the direction of reflected beam. The X-ray beam traverses the core 0, 1 and 2 times by reflexions within the areas I, II and III respectively.

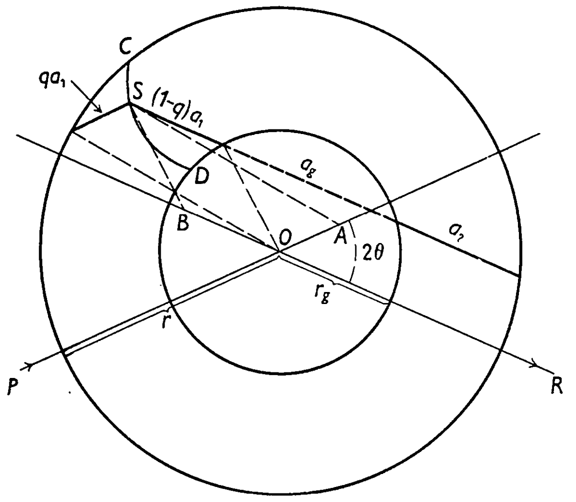

Fig. 2. Geometrical construction of a reflecting point S for which the distance of primary and reflected beams from the outer to the inner circle have a given sum a_1.

The construction of elements in case III is analogous except that the circle with centre at A has radius r_g.

The elements of area Δs were estimated by means of a planimeter or by counting squares on scale paper. The calculated absorption factors for different sets of θ, μr, r_g/r and μ_g are given in Table 1. In our investigations we generally use r_g about 0·1 mm. and, as it is possible with this value to keep the ratio r_g/r very close to 0·5, most of the absorption factors are calculated with this ratio. The three μ_g values 5, 30 and 200 correspond approximately to the linear absorption coefficient in Co $K\alpha$ radiation for hair, Lindemann glass and common glass respectively.

Absorption factors corresponding to values of θ, μr, r_g/r and μ_g between those given in Table 1 can be estimated with reasonable accuracy by graphical interpolation. The relationship between absorption factor and $\sin^2\theta$ turns out to be nearly linear, as was the case for a homogeneous specimen. For variations in r_g/r, linear interpolation can be used; this is the case also for variations in μ_g if $\mu_g > 100$ and, for small ranges, when $\mu_g < 100$, e.g. for small variations in the composition of the core substance or for substitution of copper for cobalt radiation. For $\mu r > 10$ the relative absorption factors are equal to those given by Bradley.

The accurate ratio between intensities of two different lines is a quantity frequently wanted in X-ray investigations. In a given diagram this ratio will be proportional to the ratio between the respective absorption factors $A(\theta_1)$ and $A(\theta_2)$, and consequently a function of μr, μ_g, r_g/r and the θ values. The ratio $A(\theta_1)/A(\theta_2)$ can be calculated by means of Table 1.

It is in practice difficult to make a specimen with a given packing density and r, that is with given values of μr and r_g/r.

We have calculated how much the intensity ratio $I(\theta_1)/I(\theta_2)$ varies with a 10% variation in μr, and a 5% variation of r_g/r in the range $0{\cdot}4 < r_g/r < 0{\cdot}5$, for different sets of μ_g, μr and $\theta_1-\theta_2$. The difference $\theta_1-\theta_2$ is used as variable because the variation of $I(\theta_1)/I(\theta_2)$ depends very much on this quantity. An abstract of the results is given in the Tables 2 and 3.

It is always preferable to choose θ_1 and θ_2 as close to each other as possible. For $\mu r < 1$ and all values of θ_1 and θ_2 with $(\theta_1-\theta_2) < 15°$, or for $\mu r > 10$ and all values of θ_1 and θ_2 greater than 15° with $(\theta_1-\theta_2) < 15°$, the corrections in $I(\theta_1)/I(\theta_2)$ for variations in μr and r_g/r are very small and can in most cases be neglected. For $2 < \mu r < 10$ it is usually necessary to determine the values of μr and r_g/r carefully for each specimen and to correct $I(\theta_1)/I(\theta_2)$ accordingly. It may be added that for large μr values the relative variation in $I(\theta_1)/I(\theta_2)$ is considerably greater if $0° < \theta < 45°$ than if $45° < \theta < 90°$.

The rod material should be chosen so that small fluctations in μr and r_g/r induce the smallest possible variation in $I(\theta_1)/I(\theta_2)$. For specimens having $\mu r < 0{\cdot}1$, hair or Lindemann glass is the best material. If $\mu r > 0{\cdot}1$ the kind of rod material is less important, and in many cases an ordinary glass rod is preferable to, or just as good as, other rods.

A few values are given in Table 2 also for a homogeneous specimen. It is to be noted that the influence of variations in μr on the relative variation in $I(\theta_1)/I(\theta_2)$ is just as large as, or larger than, for rod-mounted specimens.

Table 1. *Absolute absorption factor 100A for different sets of* μr, μ_g, θ *and* r_g/r

$r_g/r = 0·4$

	$\mu r =$	0·1	0·5	0·75*	1·0	1·5*	2·0	2·5*	3·0*	4·0	6·0	8·0	10·0
$\mu_g=200$	$\theta = 0^\circ$	55·9	31·7	22·4	16·0	8·9	4·5	2·68	1·55	0·67	0·201	0·080	0·039
	$\theta = 22\frac{1}{2}^\circ$	56·8	33·2	24·3	18·2	10·7	6·7	4·7	3·42	2·03	1·08	0·71	0·53
	$\theta = 45^\circ$	57·6	36·8	28·6	23·0	15·5	11·2	8·5	6·8	4·77	2·92	2·09	1·62
	$\theta = 90^\circ$	72·1	47·3	37·2	31·6	23·2	18·1	14·6	12·3	9·42	6·30	4·73	3·79
$\mu_g=30$	$\theta = 0^\circ$	75·9	43·5	30·8	22·2	11·2	6·2	3·56	2·13	0·80	0·194	0·078	0·039
	$\theta = 22\frac{1}{2}^\circ$	76·4	45·4	32·8	24·1	13·0	8·1	5·4	3·80	2·14	1·08	0·71	0·53
	$\theta = 45^\circ$	76·6	46·6	35·1	27·2	17·3	12·1	9·1	7·2	4·81	2·92	2·09	1·62
	$\theta = 90^\circ$	79·3	50·5	40·0	32·9	23·6	18·4	14·9	12·5	9·42	6·30	4·73	3·79
$\mu_g=5$	$\theta = 0^\circ$	85·0	49·0	35·6	25·1	12·8	7·0	3·98	2·31	0·86	0·186	0·076	0·0385
	$\theta = 22\frac{1}{2}^\circ$	84·9	50·2	36·2	26·5	15·3	9·4	6·1	4·15	2·19	1·07	0·71	0·53
	$\theta = 45^\circ$	85·1	50·8	38·0	29·1	18·4	12·5	9·3	7·3	4·83	2·92	2·09	1·62
	$\theta = 90^\circ$	85·8	53·5	42·3	34·1	24·3	18·6	15·0	12·6	9·44	6·30	4·73	3·79

$r_g/r = 0·5$

	$\mu r =$	0·1	0·5	0·75*	1·0	1·5*	2·0	2·5*	3·0*	4·0	6·0	8·0	10·0
$\mu_g=200$	$\theta = 0^\circ$	48·6	28·7	21·0	15·2	8·6	4·8	2·95	1·80	0·76	0·240	0·090	0·044
	$\theta = 7\frac{1}{2}^\circ$	48·9	28·8	21·0	15·4	8·6	5·0	3·10	1·97	0·90	0·354	0·190	0·124
	$\theta = 15^\circ$	49·3	29·4	21·7	16·2	9·3	5·8	3·8	2·65	1·48	0·75	0·45	0·317
	$\theta = 22\frac{1}{2}^\circ$	49·8	30·7	22·7	17·8	10·6	7·0	5·0	3·68	2·24	1·23	0·80	0·59
	$\theta = 45^\circ$	51·1	34·7	28·2	23·0	16·4	12·1	9·3	7·6	5·23	3·28	2·33	1·81
	$\theta = 60^\circ$	55·6	39·7	33·0	27·5	20·4	15·6	12·6	10·5	7·58	4·89	3·57	2·81
	$\theta = 90^\circ$	68·6	47·3	39·5	33·0	26·0	19·8	16·1	13·8	10·51	7·07	5·30	4·24
$\mu_g=30$	$\theta = 0^\circ$	72·6	43·8	32·0	23·8	13·3	7·6	4·4	2·68	1·08	0·227	0·088	0·044
	$\theta = 7\frac{1}{2}^\circ$	72·4	43·9	32·0	23·8	13·5	7·8	4·7	2·88	1·19	0·346	0·189	0·124
	$\theta = 15^\circ$	72·4	44·1	32·2	24·2	13·9	8·4	5·2	3·45	1·75	0·74	0·45	0·317
	$\theta = 22\frac{1}{2}^\circ$	72·6	44·8	33·4	25·4	15·0	9·4	6·4	4·4	2·46	1·22	0·80	0·59
	$\theta = 45^\circ$	72·8	46·5	36·3	28·9	19·5	13·6	10·4	8·0	5·34	3·27	2·34	1·81
	$\theta = 60^\circ$	73·7	48·7	38·0	31·2	22·3	16·3	12·9	10·6	7·62	4·89	3·57	2·81
	$\theta = 90^\circ$	77·1	51·5	42·0	34·8	26·0	20·1	16·2	13·9	10·53	7·07	5·30	4·24
$\mu_g=5$	$\theta = 0^\circ$	84·5	51·7	38·5	28·4	16·0	9·1	5·2	3·18	1·26	0·207	0·085	0·043
	$\theta = 7\frac{1}{2}^\circ$	84·5	51·3	38·5	28·2	16·0	9·2	5·4	3·28	1·36	0·334	0·187	0·124
	$\theta = 15^\circ$	84·4	51·6	38·4	28·7	16·4	9·8	6·2	4·0	1·93	0·708	0·45	0·317
	$\theta = 22\frac{1}{2}^\circ$	84·2	51·8	38·8	29·7	17·3	10·6	7·0	4·8	2·61	1·20	0·80	0·59
	$\theta = 45^\circ$	84·6	53·3	41·4	32·1	20·7	14·4	10·6	8·2	5·39	3·26	2·34	1·81
	$\theta = 60^\circ$	85·0	54·6	43·0	33·9	23·6	16·9	13·3	10·9	7·65	4·89	3·87	2·81
	$\theta = 90^\circ$	85·8	56·0	45·0	36·9	26·4	20·6	16·3	14·0	10·56	7·07	5·30	4·24

$r_g/r = 0·6$

	$\mu r =$	0·1	0·5	0·75*	1·0	1·5*	2·0	2·5*	3·0*	4·0	6·0	8·0	10·0
$\mu_g=200$,	$\theta = 22\frac{1}{2}^\circ$	42·6	27·8	21·7	17·3	11·0	7·4	5·3	4·0	2·54	1·50	0·95	0·70
$\mu_g=30$,	$\theta = 22\frac{1}{2}^\circ$	67·8	44·6	34·8	27·2	16·9	11·0	7·8	5·4	3·05	1·47	0·94	0·70
$\mu_g=5$,	$\theta = 22\frac{1}{2}^\circ$	82·3	54·7	43·4	33·9	21·4	13·5	9·1	6·4	3·41	1·41	0·94	0·70

* Estimated by graphical interpolation.

Table 2. *Maximum percentage variation in* $I(\theta_1)/I(\theta_2)$ *for a* 10% *variation of* μr *calculated for* $r_g/r=0·5$ *and different sets of* μr, $\theta_1-\theta_2$ *and kinds of rod materials*

	Common glass			Lindemann glass			Hair			Homogeneous specimen		
$\theta_1-\theta_2$	$7\frac{1}{2}^\circ$	15°	$22\frac{1}{2}^\circ$	$7\frac{1}{2}^\circ$	15°	$22\frac{1}{2}^\circ$	$7\frac{1}{2}^\circ$	15°	$22\frac{1}{2}^\circ$	$7\frac{1}{2}^\circ$	15°	$22\frac{1}{2}^\circ$
$\mu r = 0·1$	1	2	1	1	I	1	1	1	1	—	—	—
$\mu r = 1$	1	2	3	1	3	2	1	2	1	2	2	2
$\mu r = 1·5$	1	2	4	2	3	3	1	2	3	—	—	—
$\mu r = 2$	3	5	6	3	4	5	2	4	5	4	7	9
$\mu r = 4$	9	11	15	10	12	17	7	14	16	6	11	17
$\mu r = 6$	8	17	17	10	18	17	10	18	16	8	14	—
$\mu r \geqq 10$*	2	3	2	2	3	2	2	3	2	2	3	2

* Excluding values corresponding to $\theta < 15^\circ$.

Table 3. *Maximum percentage variation in* $I(\theta_1)/I(\theta_2)$ *for a* 5% *variation of* r_g/r *in the range* $0{\cdot}4 < r_g/r < 0{\cdot}5$ *calculated for different sets of* μr, $\theta_1-\theta_2$ *and kinds of rod materials*

	Common glass		Lindemann glass		Hair	
$\theta_1-\theta_2$	22½°	45°	22½°	45°	22½°	45°
$\mu r = 0{\cdot}1$	1	2	1	1	1	1
$\mu r = 1$	1	2	1	1	1	1
$\mu r = 2$	1	2	2	3	4	4
$\mu r = 4$	1	2	4	5	6	8
$\mu r = 6$	1	2	1	1	1	1

By substitution of a glass rod, say, for a hair the intensities are decreased if equal times of exposure are applied. For μr values less than 4 the intensities are decreased 40–50% at small θ values ($\theta = 7\frac{1}{2}°$) and about 10% at large θ values ($\theta = 90°$).

The intensities in question are, however, usually within such a range that the intensity ratios are estimated with almost the same accuracy for the two rod materials.

The tables of absorption factors have been used in an investigation of the quantitative determination of quartz in clay materials (Jensen, 1951, p. 65). The quartz content was determined by mixing the sample with a known amount of magnesium oxide and comparing the intensity ratio $I(\theta_1)/I(\theta_2)$ with similar ratios obtained from standard quartz–magnesium oxide mixtures (the internal standard principle). Variations in mineralogical composition of the samples in question caused deviation in μr up to 0·5 from those of the standard mixtures. A deviation of that magnitude required, according to Table 1, in some cases a correction amounting to 5% of the result. The analytical error of the quartz content after correction for absorption was 4–5%. Thus the correction has increased the analytical accuracy considerably.

As a last example on application of the tables an investigation of the relative intensities of hexametylenetetramine may be mentioned. The powder was mounted on a glass rod and the relative intensities were estimated by the multiple-film method and corrected according to Table 1. The resulting relative F values, multiplied by a suitable factor, turned out to lie between the absolute F values determined by Brill, Grimm, Hermann & Peters (1939) (single crystal measurements) and those determined by Wyckoff & Corey (1934) (measurements on single crystal and on powder).

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Remarques sur la Technique d'Observation des Spectres *K* de l'Aluminium*

PAR Y. CAUCHOIS

Laboratoire de Chimie physique, Faculté des Sciences, 11 *rue Pierre-Curie, Paris* 5e, *France*

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An account is given of improvements to a previously described vacuum bent-crystal spectrograph for soft X-rays. The special features necessary for studying aluminium K spectra are the use of crystals of mica or of gypsum (free from aluminium), and the replacement of the usual aluminium window either by thin lithium foils (down to 0·01 mm. thick) or by butterfly wings. Beryllium foils at present available are still too thick for use as windows, except for studying aluminium-rich samples.

Le spectre K de l'aluminium métallique a déjà été étudié par divers expérimentateurs: cela s'explique par le bon comportement de ce métal comme anticathode et la bonne position du spectre dans l'échelle des longueurs d'onde (vers 8 Å), pour la spectroscopie cristalline, sous une dispersion en énergie suffisamment élevée. Mais les alliages d'aluminium offrent un domaine d'étude encore à peine exploré. L'état chimique ou d'alliage peut influencer fortement la bande de conductibilité $K\beta$, et même les émissions $K\alpha$. Il est donc utile de disposer d'une technique expérimentale adaptée spécialement à l'analyse du spectre K de l'aluminium, pur, en composé ou en alliages, et de bien préciser les conditions d'expérience, ce qui n'a pas toujours été le cas dans la littérature sur ce sujet.

Pour la bande $K\beta$, la discontinuité et toute la partie

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