

Rapid Calculation of X-ray Absorption Correction Factors for Cylinders to an Accuracy of 0.1%

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Accurate X-ray absorption correction factors A^* for cylindrical samples were calculated in the range of the product of linear absorption coefficient μ and cylinder radius R of $0 \leq \mu R \leq 2.5$ and in the range of Bragg angle θ of $0^\circ \leq \theta \leq 90^\circ$. A method of double numerical integration that is different from the method usually used resulted in a maximum error of 0.1% with the typical error being much less. A table of values of A^* was prepared, and simple equations were obtained for interpolation between values in the table to an accuracy of 0.1% or better. A full-range curve-fitting procedure that is accurate to 0.1% also was developed for routine use when many values of A^* must be calculated for a single sample.

Introduction

X-ray intensities now can be measured to a precision of one percent, or slightly better, in some cases. To make full use of precise intensities, various corrections should be made more carefully than in the past. Absorption correction factors for cylinders given in *International Tables for X-ray Crystallography* (1959) can have total errors of one percent in some cases (Dwiggins, 1972). The greatest error occurs for Bragg angles near 0° and for large values of μR . Because A^* can be calculated to any desired accuracy at Bragg angles of 0° and 90° (Dwiggins, 1972), one can check for the maximum error in the various numerical integration methods for obtaining A^* .

In the past it was most usual to evaluate that portion of the cylinder area (cross section) having scattering points between two close values of total path length L for the X-ray beam in the sample. This was first done using a geometrical construction and graphical integration; a computer was used for the integration in later work. Next, a mean path length L_a was assigned to the area between the two close values of L , and the contributions for all areas of the sample having different values of L_a were summed. References to much of this earlier work are given in *International Tables for X-ray Crystallography* (1959).

In this investigation a more direct approach that is well suited for use on a modern high-speed digital computer was desired. The first objective was to find a method for calculating A^* to an accuracy of 0.1% or better for any value of θ in the range of $0 \leq \mu R \leq 2.5$ in less than one second without excessive computer storage. Such a method would allow those using modern high-speed computers to calculate A^* directly in many cases. The second objective was to generate a table of values of A^* and to obtain simple equations that allow interpolation and full-range curve fitting as a function of μR and as a function of θ to an accuracy

of, at worst, 0.1%. This would allow high-accuracy values of A^* to be obtained very rapidly for routine work, and it would ensure that any possible error in the absorption-corrected intensities is caused by errors in experimental observables rather than in calculations. If one can estimate errors in the observables, then one can estimate errors in the absorption corrected intensities with assurance that calculation of A^* does not introduce more error of an unknown magnitude.

Theory

It is usual to express the equation for the absorption correction factor in Cartesian coordinates, and such an equation is given in *International Tables for X-ray Crystallography* (1959). If one transforms the equation to cylindrical coordinates and takes advantage of symmetry, the following equation is obtained:

$$A \equiv 1/A^* = \frac{4}{\pi} \int_{x=0}^1 \int_{\varphi=0}^{\pi/2} x \cosh(2\mu R x \sin \theta \sin \varphi) \times \exp(-\mu R[F_1 + F_2]) dx d\varphi$$

where,

$$F_1 = [1 - x^2 \sin^2(\theta + \varphi)]^{1/2} \quad (1)$$

$$F_2 = [1 - x^2 \sin^2(\theta - \varphi)]^{1/2}.$$

The term x is the contravariant component of the cylinder radius R , and the term φ is the polar angle. Equation (1) can be evaluated rapidly on a high-speed digital computer using Simpson's rule for double numerical integration.

Direct calculation of absorption correction factors

A double-precision computer program was written in Fortran IV, H-level, for solving equation (1) using Simpson's rule for the double numerical integration.

Table 1. Values of A^* for cylinders

μR	$\theta = 0^\circ$	$\theta = 5^\circ$	$\theta = 10^\circ$	$\theta = 15^\circ$	$\theta = 20^\circ$	$\theta = 25^\circ$	$\theta = 30^\circ$	$\theta = 35^\circ$	$\theta = 40^\circ$	$\theta = 45^\circ$	$\theta = 50^\circ$	$\theta = 55^\circ$	$\theta = 60^\circ$	$\theta = 65^\circ$	$\theta = 70^\circ$	$\theta = 75^\circ$	$\theta = 80^\circ$	$\theta = 85^\circ$	$\theta = 90^\circ$	
0.0	1.	1.	1.	1.	1.	1.	1.	1.	1.	1.	1.	1.	1.	1.	1.	1.	1.	1.	1.	1.
0.1	1.1843	1.1843	1.1842	1.1840	1.1838	1.1835	1.1832	1.1828	1.1823	1.1818	1.1813	1.1808	1.1802	1.1798	1.1793	1.1790	1.1787	1.1785	1.1785	1.1785
0.2	1.4009	1.4007	1.4002	1.3995	1.3984	1.3970	1.3953	1.3934	1.3912	1.3889	1.3865	1.3841	1.3818	1.3796	1.3777	1.3761	1.3749	1.3741	1.3739	1.3739
0.3	1.6548	1.6544	1.6531	1.6510	1.6481	1.6443	1.6398	1.6347	1.6290	1.6230	1.6169	1.6108	1.6049	1.5994	1.5946	1.5906	1.5876	1.5857	1.5851	1.5851
0.4	1.9522	1.9513	1.9485	1.9439	1.9376	1.9296	1.9201	1.9094	1.8979	1.8857	1.8733	1.8611	1.8495	1.8388	1.8293	1.8215	1.8157	1.8121	1.8108	1.8108
0.5	2.2996	2.2979	2.2926	2.2840	2.2721	2.2572	2.2398	2.2204	2.1996	2.1781	2.1564	2.1352	2.1152	2.0969	2.0809	2.0677	2.0579	2.0518	2.0497	2.0497
0.6	2.7047	2.7017	2.6926	2.6775	2.6570	2.6317	2.6023	2.5701	2.5359	2.5010	2.4662	2.4327	2.4012	2.3728	2.3480	2.3277	2.3126	2.3033	2.3001	2.3001
0.7	3.1762	3.1712	3.1561	3.1315	3.0982	3.0575	3.0111	2.9607	2.9081	2.8549	2.8028	2.7530	2.7068	2.6653	2.6295	2.6003	2.5784	2.5651	2.5606	2.5606
0.8	3.7236	3.7157	3.6919	3.6532	3.6015	3.5392	3.4691	3.3941	3.3169	3.2400	3.1656	3.0953	3.0307	2.9732	2.9239	2.8839	2.8542	2.8359	2.8297	2.8297
0.9	4.3578	4.3456	4.3093	4.2507	4.1733	4.0812	3.9792	3.8718	3.7629	3.6560	3.5538	3.4584	3.3717	3.2951	3.2299	3.1772	3.1383	3.1142	3.1061	3.1061
1.0	5.0907	5.0724	5.0185	4.9323	4.8196	4.6877	4.5439	4.3948	4.2461	4.1022	3.9664	3.8413	3.7286	3.6298	3.5462	3.4790	3.4295	3.3990	3.3886	3.3886
1.1	5.9356	5.9089	5.8305	5.7065	5.5466	5.3624	5.1649	4.9636	4.7660	4.5776	4.4022	4.2424	4.0998	3.9759	3.8717	3.7882	3.7269	3.6891	3.6763	3.6763
1.2	6.907	6.869	6.757	6.582	6.360	6.109	5.8436	5.5782	5.3219	5.0811	4.8598	4.6604	4.4842	4.3322	4.2051	4.1038	4.0295	3.9838	3.9682	3.9682
1.3	8.021	7.967	7.810	7.568	7.266	6.929	6.581	6.238	5.9125	5.6110	5.3376	5.0938	4.8805	4.6976	4.5456	4.4248	4.3365	4.2821	4.2636	4.2636
1.4	9.294	9.219	9.003	8.674	8.268	7.826	7.376	6.942	6.536	6.166	5.8341	5.5413	5.2873	5.0711	4.8922	4.7506	4.6471	4.5835	4.5619	4.5619
1.5	10.746	10.643	10.349	9.907	9.372	8.800	8.230	7.689	7.192	6.744	6.348	6.002	5.7036	5.4516	5.2441	5.0804	4.9609	4.8875	4.8625	4.8625
1.6	12.397	12.257	11.862	11.276	10.581	9.852	9.141	8.477	7.877	7.344	6.877	6.473	6.128	5.8385	5.6007	5.4136	5.2773	5.1935	5.1650	5.1650
1.7	14.267	14.080	13.555	12.788	11.897	10.982	10.106	9.304	8.589	7.963	7.420	6.955	6.561	6.231	5.961	5.7499	5.5960	5.5014	5.4691	5.4691
1.8	16.379	16.131	15.441	14.450	13.323	12.189	11.125	10.168	9.327	8.600	7.976	7.446	7.000	6.628	6.326	6.089	5.9166	5.8107	5.7746	5.7746
1.9	18.76	18.43	17.53	16.267	14.858	13.470	12.194	11.066	10.089	9.253	8.544	7.946	7.444	7.030	6.693	6.439	6.239	6.121	6.081	6.081
2.0	21.43	21.00	19.84	18.24	16.50	14.824	13.311	11.995	10.871	9.921	9.122	8.452	7.895	7.435	7.063	6.773	6.562	6.433	6.389	6.389
2.1	24.41	23.87	22.39	20.38	18.25	16.247	14.472	12.953	11.673	10.602	9.709	8.965	8.349	7.843	7.436	7.118	6.887	6.745	6.697	6.697
2.2	27.74	27.04	25.17	22.69	20.11	17.74	15.675	13.938	12.493	11.295	10.304	9.484	8.808	8.255	7.810	7.464	7.213	7.059	7.006	7.006
2.3	31.44	30.55	28.20	25.16	22.07	19.29	16.92	14.947	13.328	11.999	10.906	10.008	9.271	8.669	8.187	7.812	7.540	7.372	7.315	7.315
2.4	35.54	34.41	31.49	27.79	24.13	20.90	18.19	15.978	14.177	12.711	11.515	10.537	9.736	9.086	8.565	8.161	7.868	7.687	7.625	7.625
2.5	40.06	38.65	35.05	30.59	26.28	22.56	19.50	17.03	15.040	13.433	12.130	11.069	10.205	9.505	8.945	8.511	8.196	8.002	7.935	7.935

The program is simple, and only a small amount of computer storage is necessary. The increments in x and ϕ were taken as $\frac{1}{100}$ of the upper limits for x and ϕ given in equation (1), and these increments are sufficient for values of μR up to 2.5 if an accuracy of at least 0.1% is desired. The accuracy was checked by comparing computed results with the exact results at $\theta = 0^\circ$ for high values of μR where numerical integration methods, in general, give the most error in solving for A^* . Also, the number of increments was increased by a factor of four in a few test cases to make certain that the value of A^* did not change significantly. The time to calculate each value of A^* was 0.8 s using an IBM 370/165 computer. Copies of the computer program are available from the author.

Results and discussion of direct calculations

Table 1 gives values of A^* calculated at the same values of μR and θ as given in *International Tables for X-ray Crystallography* (1959).

In Table 2 comparison of a few of the new values of A^* is made with the exact values calculated at zero Bragg angle (Dwiggins, 1972) and with the values given in *International Tables for X-ray Crystallography* (1959). The error in all of the new values is under 0.1%.

Table 2. Values of A^* for cylinders, $\theta = 0^\circ$

μR	A^* , Exact†	A^* , New‡	% Error, New‡	% Error, Old§
0.1	1.18432	1.1843	0.0015	0.36
0.5	2.29961	2.2996	0.0005	0.42
1.0	5.09095	5.0907	0.0049	0.61
1.5	10.74774	10.7461	0.0153	0.80
2.1	24.42587	24.4137	0.0498	0.92
2.5	40.09687	40.0598	0.0925	0.74

† Dwiggins (1972).

‡ This paper.

§ *International Tables for X-ray Crystallography* (1959).

Inspection of equation (1) suggests that the greatest error should occur at zero Bragg angle for constant μR . Data similar to that given in Table 2, with the exception that $\theta = 90^\circ$, indicated that the error was less at 90° than at 0° and that μR could be 3.0 before 0.1% accuracy was exceeded.

Maintaining 0.1% accuracy, the range of μR can be extended to 5.0 by using 400 increments in x rather than 100. Such data were not obtained, except for a few test cases to make certain that the method would work, because it was thought that highly accurate values of A^* will be seldom needed for values of μR greater than 2.5. Use of samples that have a high value of μR when precise intensities are desired is usually not good practice because of the very large variation of A^* with Bragg angle at smaller values of the Bragg angle and because of the high precision with which the geometry of the sample must be known. However, should the need

arise, the computer program that is available can be used to obtain values of A^* for μR greater than 2.5 in a reasonable time and at a reasonable cost.

Interpolation and curve fitting

To use the values of A^* given in Table 1 for routine purposes, accurate curve-fitting and interpolation methods are needed. It was found that the same form of equations can be used for both interpolation and curve fitting.

The equation used to express $A \equiv 1/A^*$ as a function of μR at constant θ is:

$$A\{\mu R\} = \exp \left[- \sum_{i=0}^N K_i (\mu R)^i \right]. \quad (2)$$

The equation used to express A as a function of θ at constant μR is:

$$A\{\theta\} = \sum_{i=0}^M L_i \sin^{2i} \theta. \quad (3)$$

The terms K_i in equation (2) are constants at fixed θ and the terms L_i in equation (3) are constants at fixed μR .

To use either equation (2) or (3) for three-point interpolation, then $M=N=2$. Known values of A^* for three consecutive tabulated values of either μR or θ are taken from Table 1 with the value of μR or θ of the unknown being in the range of the three values selected. The constants K_i or L_i then are calculated from a set of three equations of the form given in equation (2) or (3).

The accuracy of the interpolation method was found to be better than 0.1% by comparing A^* values obtained between two of the points used to obtain the constants K_i or L_i with values of A^* that were calculated directly. The interpolation method is most useful for calculating only a few values of A^* with a desk calculator or small computer.

In the usual experiment the value of μR is fixed, and calculation of A^* as a function of θ is desired. When many values of A^* are to be calculated, a full-range curve-fitting procedure allows calculations to be made more rapidly than does the direct-calculation method and avoids storing massive tables of A^* in the com-

puter, as the interpolation method does. The curve-fitting procedure will next be described.

Equations (2) and (3) can be used for full-range curve fitting with $M=6$ and $N=5$. Six standard values of μR are selected. These are 0, 0.3, 0.7, 1.5, 2.0, and 2.5. Also, seven standard values of θ are selected. In degrees, these are 0, 15, 30, 45, 60, 75, and 90.

The calculation of preliminary data that never has to be repeated is next described. A set of six equations is solved for six K values for each of the standard values of θ using the standard values of μR . When this stage is completed one has, neglecting K_0 values that are all zero, five values of K for each standard θ , or a total of 35 K constants. These constants are stored in a computer subprogram along with the standard values of μR and θ .

When it is desired to solve for A^* , the following procedure is used. First, the values of A^* for the exact value of μR of the experiment are obtained for each of the standard angles from equation (2) and the stored K values, resulting in seven values of A^* at the standard angles. Next, a set of seven equations of the type of equation (3) is solved for L values with the seven values of A^* just calculated at the standard angles. Finally, the values of L just obtained can be used in equation (3) to obtain a very large number of values of A^* at any angles for the exact value of μR of the experiment.

The curve-fitting method was used to calculate A^* at all points listed in Table 1. In all cases, the error was well under 0.1% on comparison with A^* values listed in Table 1.

All of the calculations required for full-range curve-fitting are done using a computer subprogram that is available written in H-level Fortran IV. All necessary constants are included in this subprogram. It is necessary to supply only μR and values of θ from a main program. The subprogram calculates A^* and returns this value to the main program.

References

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