**ABSORB: An Absorption Correction Program for Crystals Enclosed in Capillaries with Trapped Mother Liquor***

**BY GEORGE T. DEITTA**

*Medical Foundation of Buffalo, Inc., 73 High Street, Buffalo, NY 14203-1196, USA*

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**Abstract**

A computer program to calculate the contributions of crystal, capillary and a simple model of mother liquor to the overall absorption of X-rays has been written. It is based on the Gaussian quadrature method of integration; the crystal is described by the polyhedral faces bounding it, the capillary by its diameter, thickness and orientation with respect to the diffractometer axes and the mother liquor by the crystal faces that trap it between crystal and inner capillary wall. The program is written in Fortran for a VAX 11/780 computer and incorporates tables of mass absorption coefficients for silver, molybdenum and copper radiations for easy calculation of linear absorption coefficients.

**Introduction**

Various techniques to evaluate and correct for the effects of absorption are available to the crystallographic community. Classical methods require a precise description of the crystal geometry and contents; the Gaussian quadrature method was introduced by Busing & Levy (1957) and the two-dimensional treatment in analytical form described by Howells (1950) was extended to three dimensions by de Meulenaer & Tompa (1965). These techniques have been more expansively described by Coppens (1970) and Alcock (1970). Semiempirical methods do not require specific information about the absorbing media but do require additional diffraction data to model the absorption process. Kopfmann & Huber (1968) and North, Phillips & Mathews (1968) showed that ψ-scan information could be used to model a transmission surface approximately. Huber & Kopfmann (1969) and Flack (1974) proposed further refinements in the analysis of ψ-scan data. Taking a different tack, Rae & Dix (1971) proposed a method that requires the measurement of two data sets, in differing diffraction geometries. Truly empirical methods, requiring only the unique diffraction data and a structural model, have been described by Katayama, Sakabe & Sakabe (1972) and by Walker & Stuart (1983). These methods are amenable to least-squares treatment.

A driving force in the development of the semiempirical techniques has been the demands of macromolecular crystallography. A typical situation may find a crystal enclosed in a thin-walled glass capillary. Adhering to it, or trapped by one or more faces, is mother liquor that serves to hold the crystal in place and preserve it from drying. A ray incident on a small volume element within the crystal must traverse three different absorbing media (ignoring the saturated vapor space within the capillary) on its trajectory to the element, namely the capillary wall, the mother liquor and the crystal itself, Fig. 1. The difficulty of describing accurately all the elements of the absorption process, and particularly the mother liquor, contrasts with the relative ease in recording additional diffraction data, particularly ψ-scan data.

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A computer program has been written to model and correct for the absorption processes at work in the conceptually simple case of a crystal bounded by plane faces enclosed in a capillary with mother liquor trapped between one or more faces and the inner capillary wall. The approach is classical; the crystal is treated in the Gaussian approximation weighted by the absorption contributions of the capillary and trapped liquid. The capillary contribution is calculated by the method of Wells (1960); no assumptions concerning the orientation of the capillary with respect to the rotation axis of the diffractometer or the location of the crystal within it are made. In the present export version of the program only the mother liquor trapped between a face and the capillary wall is treated; adhering droplets that only partially obscure the crystal are ignored. A completely general treatment of the mother liquor is the subject of continuing work.

The method

The crystal is described in the usual way (see, for example, Coppens, 1970): it is assumed to be a convex polyhedron bounded by plane faces with no re-entrant angles. Each face is described by its Miller indices and by the perpendicular distance from a fixed point within or on the surface of the crystal to the plane of the face. The orientation of the crystal is given by the diffractometer orientation matrix (code available for Nicolet P3/F and Enraf-Nonius CAD4 geometry).

The capillary is assumed to be a right cylinder of known diameter, thickness and chemical composition. The orientation and position of the capillary axis vis à vis the diffractometer $\varphi$ axis are specified by two angles, $\tau$ and $\sigma$, and two offsets, $\Delta X_k$ and $\Delta Y_k$. The angles are those required to bring the capillary axis parallel to the $\varphi$ axis, while the offsets are those required to bring the two axes into coincidence, Fig. 2.

The mother liquor is described by the faces that trap it between crystal and capillary inner wall. The linear absorption coefficient of the mother liquor must be hand calculated from its presumed known chemical composition and density.

The absorption correction itself employs the Gaussian quadrature integration technique, it being straightforward to extend the calculation to account for the capillary and mother liquor contributions. A clear exposition of the general strategy is given by Wuensch & Prewitt (1965). For each point on the Gaussian grid ruled out within the crystal, path lengths through the crystal and to the inner and outer capillary walls (Busing & Levy, 1957; Wells, 1960) are evaluated. For each crystal face that traps mother liquor, Fig. 3, the dot product $\mathbf{S} \cdot \mathbf{U}_f^*$ (or $\mathbf{S}_0 \cdot \mathbf{U}_f^*$), where $\mathbf{S}$ is the unit vector defining the diffracted beam direction (or reverse primary beam direction for $\mathbf{S}_0$), and $\mathbf{U}_f^*$ is the unit vector perpendicular to the $f$th trapping face, is evaluated. If the dot product is negative the beam is obtuse to that face and can neither enter nor exit through it. If the dot product is positive the path length $B_i$ from the grid point to the plane $f$ of the $i$th trapping face is evaluated.†

If $B_i$ exceeds the distance from the grid point (e.g. $l$, $J$ or $K$ of Fig. 3) to the inner capillary wall $W_1$ then this ray intersects the plane of the mother liquor outside the capillary (a mathematically consistent but

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†It is necessary to make a distinction between the crystal face itself and the plane of the crystal face. When a crystal face is specified as a 'trapping face' this implies that mother liquor is bounded by the inner capillary wall and the plane of that face.

‡In fact, the values of $B$ for all the faces for each point in the crystal must be evaluated in order to find the minimum path length through the crystal and thus identify the face of entrance or exit. These values are stored for analysis of the mother-liquor path length.

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![Fig. 2. Specification of the capillary orientation parameters. For the Nicolet (née Syntex) diffractometer the $\varphi$ axis is set perpendicular to the telescope axis at $\varphi = 335^\circ$. At $\varphi = 25^\circ$ a positive displacement of the capillary axis along $X(\Delta X_k > 0)$ is seen as an offset of the capillary to the left. At $\varphi = 115^\circ$ a positive displacement of the capillary axis along $Y(\Delta Y_k > 0)$ is also seen as an offset of the capillary axis to the left (not shown). For the CAD-4 at $\kappa = 134.9^\circ$ the $\varphi$ axis is perpendicular to the telescope axis, but rather than being vertical in the field of view it is horizontal. At $\varphi = 10^\circ$ a positive X displacement is seen as an offset of the capillary axis to the top. At $\varphi = 280^\circ$ a positive Y displacement is seen as an offset of the capillary axis to the top also (both not shown). The angles $\varphi$ and $\tau$ are offsets in degrees of the $\varphi$ and $Z_k$ axes. With the notch of a Huber or Supper goniometer head to the right of the viewer, the top arc is perpendicular to the line of sight. If the capillary is inclined top to the left, bottom to the right, as in the figure, $\tau > 0$. With the notch facing the viewer, the bottom arc is perpendicular to the line of sight. If the capillary is inclined, again as seen in the figure, $\tau > 0$. Note that the $\varphi$ axis intercepts the center of mass of the crystal.](image-url)
physically uninteresting result). For \( B_i < W_i \) the path length through the mother liquor is \( t_a = W_i - B_i \). All the planes with \( B_i < W_i \) are evaluated and the maximum value of \( t_a \) is the path length through the mother liquor.

The partial transmission factor \( A_j \) for the \( j \)th point on the Gaussian grid is given by

\[
A_j = w_j \cdot \exp[-\mu_s t_{x_j}] \cdot \exp[-\mu_k t_{k_j}] \cdot \exp[-\mu_s t_{s_j}],
\]

where \( w_j \) is the compound Gaussian weight equal to the fractional volume of the crystal that the \( j \)th point represents; \( \mu_s \), \( \mu_k \) and \( \mu_s \) absorption coefficients, and \( t_{x_j}, t_{k_j} \) and \( t_{s_j} \) are the total path lengths (diffracted plus reverse primary), through crystal, capillary and mother liquor, respectively.

**Measuring the thickness of a capillary wall**

As glass capillaries are fairly expensive it seems worthwhile to devise a simple and non-destructive technique for measuring the thickness of the capillary wall, \( t \). Apart from the funnel at its base and bulbous glob of glass at its tip a capillary is to a good approximation a right circular cylinder of measurable length \( l \), mass \( m \), density \( \rho \) and outer diameter \( d_o \). The volumes of the outer-wall cylinder \( V_o \) and inner-wall cylinder \( V_i \) are given by

\[
V_o = \pi d_o^2 l / 4, \\
V_i = \pi d_i^2 l / 4,
\]

where \( d_i \) is the inner-wall diameter and \( t = (d_o - d_i) / 2 \). The volume of glass is

\[
V_g = V_o - V_i = m / \rho.
\]

Solving for \( t \) we get

\[
t = d_o / 2 - [d_o^2 / 4 - (m / \rho \pi l)]^{1/2}.
\]

A '0.5 mm Glaskapillare' capillary (D'Antonio & Konnert, 1979) was selected at random from a batch supplied commercially and the tip and funnel gently pinched off. Its length was measured under a low-power microscope, its outer diameter measured under a 40× microscope top and bottom, its density was taken as the value reported by D'Antonio & Konnert but could have been measured by flotation using the left-over funnel, and its mass was measured on a Cahn electrobalance, giving values \( l = 54.36(5) \) mm, \( d_o = 0.46(1) \) mm, \( m = 2.91(2) \) mg, and \( \rho = 2.44(1) \) mg mm\(^{-3} \). The calculated thickness is \( t = 0.0157(4) \) mm (the nominal thickness is 0.01 mm), in good agreement with the transmission of X-rays through the capillary wall. Another capillary from the same batch was viewed at 100× in a scanning electron microscope (not shown). The view down the capillary axis showed that the wall thickness is highly uniform, the cross section highly circular, and the wall thickness 0.016 mm, in line with the results of the non-destructive measurements.

**The program**

The program is written in standard ANSI Fortran 77 for a VAX 11/780 computer (32 bit word size). It is modularly constructed and is broken into two main parts, which share many of the same subroutines. The first part (ABSORB1) is a menu-driven editor, which constructs and tests a file that contains all the pertinent information to estimate the absorption correction. The second part (ABSORB2) reads the data file created by ABSORB1 and applies an absorption correction to the diffraction data.

Included in the programs are a number of useful tables, such as the mass absorption coefficients of the glass capillaries are slightly tapered from base to tip.

†Actually most capillaries are slightly tapered from base to tip.
Table 1. Composition of some glasses in percentage by weight

<table>
<thead>
<tr>
<th>Component</th>
<th>Glaskapillaren*</th>
<th>Pyrex 7740†</th>
<th>AR glass‡</th>
<th>Fused quartz†</th>
<th>Lindemann‡</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>67.74</td>
<td>80.5</td>
<td>69</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>B₂O₃</td>
<td>1.24</td>
<td>12.9</td>
<td>1</td>
<td>1</td>
<td>82.1</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>3.59</td>
<td>2.2</td>
<td>4</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Na₂O</td>
<td>16.22</td>
<td>3.8</td>
<td>13</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td>2.17</td>
<td>0.4</td>
<td>2</td>
<td>1</td>
<td>2.6</td>
</tr>
<tr>
<td>BaO</td>
<td></td>
<td>1</td>
<td>4</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>7.11</td>
<td>–</td>
<td>4</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>0.18</td>
<td>–</td>
<td>2</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>TiO</td>
<td>0.25</td>
<td>–</td>
<td>–</td>
<td>1</td>
<td>15.3</td>
</tr>
<tr>
<td>LiO₂</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2.6</td>
</tr>
<tr>
<td>BeO</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>

†Shand (1958).

Table 2. Linear absorption coefficients for some glasses

Linear absorption coefficients are in mm⁻¹ calculated from the compositions in Table 1, the densities in Table 2, and the mass absorption coefficients of Hubbell et al. (1974) using the mixing rule (Stout & Jensen, 1968).

<table>
<thead>
<tr>
<th>Glass</th>
<th>ρ*</th>
<th>μAg</th>
<th>μMo</th>
<th>μCu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glaskapillaren</td>
<td>2.44</td>
<td>0.538</td>
<td>1.058</td>
<td>10.870</td>
</tr>
<tr>
<td>Pyrex 7740</td>
<td>2.23</td>
<td>0.375</td>
<td>0.733</td>
<td>7.600</td>
</tr>
<tr>
<td>AR glass</td>
<td>2.52</td>
<td>0.700</td>
<td>1.360</td>
<td>13.398</td>
</tr>
<tr>
<td>Fused quartz</td>
<td>2.20</td>
<td>0.411</td>
<td>0.807</td>
<td>15.201</td>
</tr>
<tr>
<td>Lindemann</td>
<td>1.77</td>
<td>0.094</td>
<td>0.161</td>
<td>1.484</td>
</tr>
</tbody>
</table>

*Densities for particular glasses from references cited in Table 1.

Discussion

Insofar as the crystal part is concerned the program has been tested against the standard values of Alcock (1974) and of Flack, Vincent & Alcock (1980). Various hand calculations for limiting cases of the capillary position and the mother-liquor absorption have been verified.

A few remarks about the applicability of the program are in order. No matter how precisely geometrical information can be measured it is always good practice to keep absorption to a minimum. In this regard the wavelength dependence of the linear absorption coefficients μ₀, μ₆ and μ₄ is well known. It should also be recognized that it is worthwhile to match carefully the capillary size to the crystal (ΔX ≈ ΔY ≈ 0), to align the capillary axis parallel to the φ axis (φ = φ₀) whenever possible, and to wick away all unnecessary mother liquor, especially mother liquor adhering to the crystal but not trapped by a face.

In test calculations under favorable conditions, such as when capillary dimensions are well matched to fairly regular crystal habits, it is clearly the case that the contribution of the capillary to the overall absorption is fairly isotropic, even for copper radiation. Test cases where the conditions are much less favorable, for example the case of a thin plate enclosed in a large-diameter capillary whose axis is severely inclined to the diffractometer φ axis, show the capillary contribution to be markedly anisotropic. Apart from those unfavorable cases it might seem expedient to disregard the capillary correction, or perhaps to use a much more economical analytical correction for the capillary absorption, such as the one described by Watkin (1975). However, the capillary correction is the necessary vehicle for the mother-liquor correction, which even for the ideal match of crystal and capillary can be quite severe.

When many crystals of differing morphologies, or ill-defined morphologies, must be treated for an individual problem these classical techniques may prove too arduous for the most dedicated of experimentists. However, when accuracy is important and conditions permit, these techniques may prove useful.

Copies of the program and a detailed description of the particulars of the input are available from the author.

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References

HAMILTON, Table 2.1C, pp. 61–66. Birmingham: Kynoch Press.