Supplementary Material

1. Derivation of path length for diffraction from inside a circle of unit radius.

The incident beam at angle θ is diffracted from point B with coordinates (x, y), Figure S1. The total path length inside the circle is:

$$l = AB + BC$$

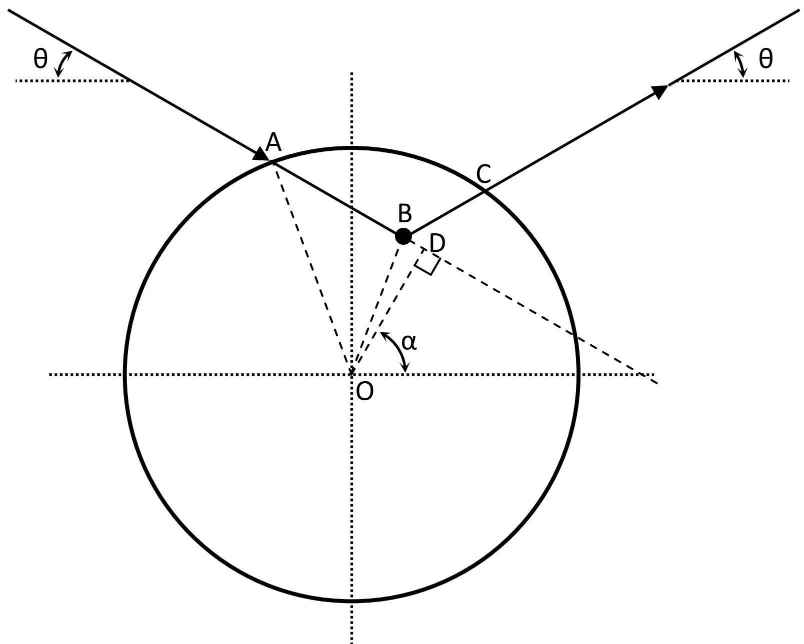

Figure S1. Cross-section of a cylindrical sample showing diffraction from an element at point B with coordinates (*x*,*y*). The dashed lines are constructions to aid calculating the total path length through the sample.

To find the incident beam pathAB, recall the perpendicular equation for a straight line in Cartesian geometry:

$$P = y \sin\alpha + x \cos\alpha$$

where P is the perpendicular distance from the origin to the line (OD in Figure S1). Since $\alpha = 90° - \theta$, the perpendicular distance is:

$$\begin{aligned} OD &= y \sin(90 - \theta) + x \cos(90 - \theta) \\ &= y \cos\theta + x \sin\theta \end{aligned}$$

Distance OA is the radius = 1, therefore:

$$\begin{aligned} AD &= \sqrt{OA^2 - OD^2} \\ &= \sqrt{1 - (y \cos\theta + x \sin\theta)^2} \end{aligned}$$

The distance BD can be obtained from the right-angled triangle ODB:

$$
\begin{aligned}
BD^2 &= OB^2 - OD^2 \\
&= (x^2 + y^2) - (y\cos\theta + x\sin\theta)^2 \\
&= x^2 + y^2 - x^2\sin^2\theta - 2xy\sin\theta\cos\theta - y^2\cos^2\theta \\
&= x^2(1 - \sin^2\theta) - 2xy\sin\theta\cos\theta + y^2(1 - \cos^2\theta) \\
&= x^2\cos^2\theta - 2xy\sin\theta\cos\theta + y^2\sin^2\theta \\
&= (x\cos\theta - y\sin\theta)^2 \\
BD &= \pm(x\cos\theta - y\sin\theta)
\end{aligned}
$$

We want $AB = AD - BD$, so a positive value for BD would indicate D lies further along the incident beam path from B, as is the case in Figure S1 above. To find out which root is correct, consider $\theta = 45°$ where $\sin\theta = \cos\theta$. BD should be positive for values of $y > x$. Therefore the correct root is $y\sin\theta - x\cos\theta$ and:

$$
\begin{aligned}
AB &= AD - BD \\
&= \sqrt{1 - (x\sin\theta + y\cos\theta)^2} + x\cos\theta - y\sin\theta
\end{aligned}
$$

A similar treatment of the diffracted beam (where $\propto = 90° + \theta$) gives:

$$BC = \sqrt{1 - (y\cos\theta - x\sin\theta)^2} - x\cos\theta - y\sin\theta$$

Therefore the overall path length through the sample is:

$$l = \sqrt{1 - (x\sin\theta + y\cos\theta)^2} + \sqrt{1 - (y\cos\theta - x\sin\theta)^2} - 2y\sin\theta$$

This is the formula given by Bond, although Bond considered a beam path from top to bottom rather than left to right, and so x and y are transposed.

2. Derivation of path length through a circle of unit radius for diffraction from outside that circle.

Figure S2 below depicts this situation for an incident beam which traverses a chord through a circle of unit radius before being diffracted from a point B at coordinates (x, y) outside the circle. This is the situation for a sample coated on the outside of a glass fibre, for example. The equations derived above cannot be used to calculate this path length because the values inside the square root functions can become negative for some values of x, y and θ.

Calculation of the path length is straightforward. From the description above, we know that the length OD is given by:

$$OD = y\cos\theta + x\sin\theta$$

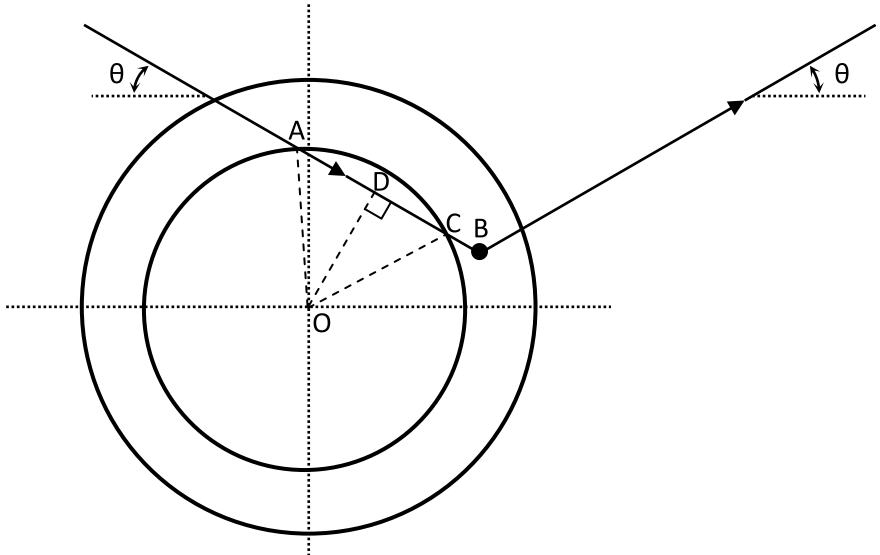

Figure S2 Cross-section of an annular geometry where the sample is in the region between the two circles. In our calculations we have assigned the inner circle a radius of 1. Dashed lines are constructions to aid calculation of the path length through the inner circle.

Lengths OA and OC are both radii and therefore have length = 1. The path length AC is the sum of two identical sides of right-angled triangles and can be calculated using Pythagorus's theorem:

$$\begin{aligned} AC &= AB + BC \\ &= 2\sqrt{1 - (y\cos\theta + x\sin\theta)^2} \end{aligned}$$

The diffracted beam can be treated in the same fashion, and results in a path length of:

$$Diffracted\ path = 2\sqrt{1 - (y\cos\theta - x\sin\theta)^2}$$

In the case depicted in Figure S2 this equation gives a real number although clearly the diffracted beam does not traverse the inner circle. The equation gives the chord length for the projected beam through the inner circle. In an automated calculation we need to determine whether the beam actually traverses the inner circle and therefore whether a path length should be calculated. For the incident beam this can be accomplished by:

1. Ensuring that the perpendicular distance OD is less than the radius of the inner circle, i.e.
$$(y\cos\theta + x\sin\theta)^2 < 1$$
2. Ensuring that diffraction occurs from a point further along the beam path than point D (Figure S2).

The second of these conditions can be checked by calculating the distance DB maintaining correct sign conventions for coordinates and angles. The condition will be fulfilled if $DB > 0$ (we have assumed that diffraction from only points between the two circles is being considered). The distance is calculated with reference to Figure S3 below.

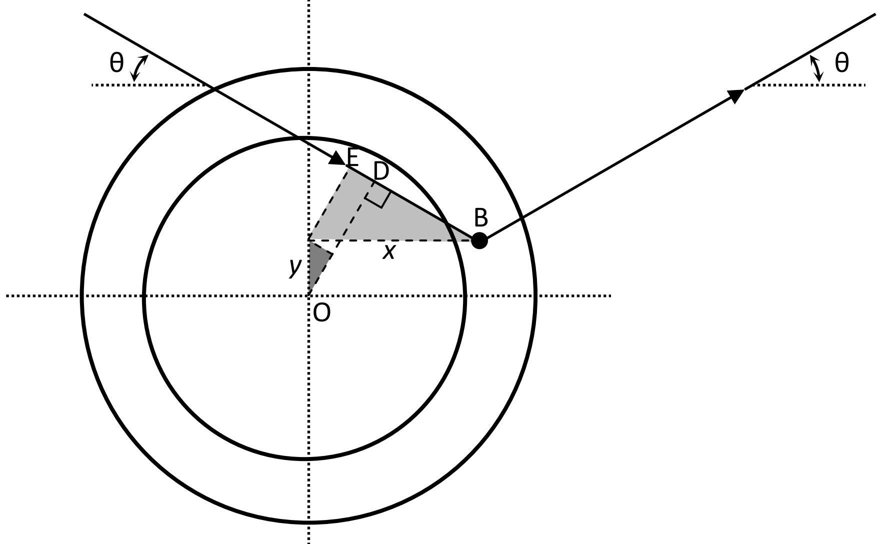

Figure S3 **Geometry for calculating the distance (DB) between the position of diffraction and the intersection of the incident beam and a perpendicular line passing through the origin.**

Both the shaded triangles in Figure S3 have an internal angle equal to θ; one has a hypotenuse of *x*, the other *y*. Our condition is:

$$
\begin{aligned}
DB &> 0 \\
\Rightarrow EB - ED &> 0 \\
\Rightarrow x\cos\theta - y\sin\theta &> 0
\end{aligned}
$$

For the diffracted beam, the conditions required to determine that the inner circle has been traversed are:

$$
\begin{gathered}
(y\cos\theta - x\sin\theta)^2 < 1; \text{and} \\
x\cos\theta + y\sin\theta < 0
\end{gathered}
$$