SMALL ANGLE X-RAY SCATTERING FROM DEPOSITS IN COTTON

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INTRODUCTION

Apart from the lumen which occurs in many natural fibres, fibrous materials in general appear to be threaded by a system of sub-microscopic pores or capillaries in which foreign substances such as dyes, metals and salts can be deposited. Such deposits have been intensively studied by X-ray diffraction methods [Kratky and Mark (1937); Kratky and Schossberger (1938)] which reveal that in many cases the foreign substance crystallises inside the fibre, sometimes exhibiting preferred orientation [Radhakrishnan and Vaidya (1957); Ramachandran and Ambady (1955)]. The sizes of the crystallites have been computed from X-ray line breadths and are found to be of the order of 100 Å [Frey-Wyssling (1937)]. One might at first assume, as has been done hitherto, that the cavities in which the crystallites are lodged are also of the same order of size. However, the possibility cannot be ruled out that the deposited particles are in the form of multi-crystalline aggregates with larger dimensions than inferred from X-ray line breadths. Measurements of small-angle X-ray scattering from the treated fibres would be quite informative in regard to particle size and its heterogeneity as well as particle shape. On this account, certain studies have been undertaken of the small angle X-ray scattering (hereafter abbreviated to SAS) from fibres of cotton and viscose in which some metals and inorganic salts were deposited. These studies comprise qualitative estimates of the shape factor (from the overall scattering pattern) and when possible, computations of size distribution (from measurements of equatorial scattered intensity). Owing to the very similar nature of the results obtained with cotton and viscose, only the results for cotton are reported in this paper.

SAMPLE PREPARATION

The fibres used in this study consisted of dewaxed Sea Island cotton as well as viscose staple. Silver, the sulphides of mercury and lead as well as
lead iodide and lead chromate (Ag, HgS, PbS, PbI₂, PbCrO₄) were deposited in these fibres by means of a simple technique which will be described elsewhere by another group of workers (Iyer et al., unpublished). The "dyed" fibres were rendered free of superficially adhering material by soaping at boil, drying and repeated combing. In the case of lead iodide the soaping at boil was omitted because this salt is somewhat soluble in hot water. Gravimetric determinations showed that in all cases the amount of salt deposited came to only a few percent of the weight of fibres.

**Wide Angle Diffraction**

Diffraction patterns given by the treated cotton fibres using Ni-filtered copper radiation are shown in Fig. 1. Apart from the cotton pattern, there are lines which belong to recognized lattices of the deposits concerned. The line breadths have been measured with the help of a diffractometer and have been used to estimate crystallite sizes, which were found to lie between 100 and 250 \(\AA\).

In the case of lead chromate and lead iodide, Fig. 1 shows that there is a tendency to preferred orientation, though this is much less pronounced than has been observed with other fibre-salt systems [Ambady (1959)]. The precise nature of orientation of lead chromate is somewhat confusing on account of the overlap of reflections. On the other hand, in the case of lead iodide, the C-axis tends to be perpendicular to the fibre axis.

**Photography of Overall Small Angle X-Ray Scattering Pattern**

Nickel-filtered X-rays from a copper tube were collimated by two pinholes set apart so that the divergence of the emergent beam was about \(2 \times 10^{-3}\) radians. A bundle of parallel fibres was placed immediately after the second pinhole. The scattering pattern was recorded on flat films, a cup-shaped stop serving to keep out the primary beam. This beam stop had to be somewhat large in order to avoid beam spill-over, so that the smallest angle of scattering in these photographs was about 4 milliradians. In addition to the treated fibres, the scattering from untreated cotton was also photographed. This required about 6 times the level of exposure generally used for the treated fibres. The patterns obtained from the treated and untreated fibres are reproduced in Fig. 2 with a magnification of 3·5.

**Measurements of Equatorial Scattered Intensity**

These measurements were taken with copper radiation from a stabilised X-ray generator. The primary beam was collimated by two line slits and
was incident on the specimen after passing through a third guard slit. The specimen was in the form of a bundle of parallel fibres which could be moved into and out of the beam. A Geiger counter detector with a line slit served to measure the scattered intensity. In front of this counter was put a rotatable filter-holder containing balanced filters of nickel foil and cobalt acetate powder, either of which could be swung into the beam. A subsidiary Geiger counter was also employed as a monitor to measure the wide-angle X-ray diffracted intensity from the strong (002) interference of cellulose. Either counter could be connected in turn to a Philips diffractometer circuit panel. The camera constants (slit widths and placements) were worked out according to the principles set forth by Guinier and Fournet (1955). The camera was fabricated in the authors' laboratory. Two values of beam divergence (i.e., two sets of slit widths) were used in order to measure the scattering in the angular range of 0.5 to 20 milliradians. At each angle the scattered intensity was measured in turn through nickel and cobalt filters, according to the "bracketing technique" for pure CuKα [Compton and Allison (1935)]. The amount of absorption by the sample and the "profiles" of the direct beam along the length and width of the slits were also measured. Finally, the intensity of the (002) interference from the substrate was determined for purposes of monitoring the small angle scattering.

**CORRECTIONS AND SCALE FACTOR**

A number of corrections were necessary before the data could be used for analysis of particle size distribution. The corrections were for (a) the dead time of the counter [Klug and Alexander (1954)], (b) the absorption of X-rays by the sample, which would vary between samples, (c) the "smearing effect" caused by slits of finite length and width. The first two corrections are of a standard form. The correction for slit length was effected by means of the DuMond formula [DuMond (1947)] which was found to be applicable in this case because the intensity of the primary beam was sensibly constant along the slit length:

\[
\mathcal{I}(h) \propto - \int_0^\infty \frac{d}{d \sqrt{h^2 + z^2}} J(\sqrt{h^2 + z^2}) \, dz
\]

(1)

where \( J(h) \) and \( \mathcal{I}(h) \) are the intensities before and after correction respectively and

\[
h = \frac{4\pi \sin \theta}{\lambda} \approx \frac{4\pi \theta}{\lambda}.
\]

(2)
The differentiation and integration in eq. (1) were carried out by standard techniques in numerical analysis.

The correction for the smearing effect of slit width involves the deconvolution of the integral

$$\mathcal{I}(h) = \int_{-\infty}^{\infty} G(x) I(h-x) \, dx$$

where $I(h)$ is the corrected intensity and $G(x)$ represents the beam profile, which in the present case was found to be symmetric around $x$ equal to zero.

Instead of handling equation (3) by the usual method of Fourier Transforms [Beeman et al. (1957)], we have used an elegant result due to a colleague in this laboratory (Rao, unpublished) which, when reduced to the present case, states that

$$I(h) = \mathcal{I}(h) \left[1 - \frac{\mu_2}{2!} \mathcal{I}^2(h) - \left\{ \frac{\mu_4}{4!} - \left( \frac{\mu_2}{2!} \right)^2 \right\} \mathcal{I}^4(h) \ldots \right]$$

where

$$\mu_{2n} = \frac{\int_0^{\infty} x^{2n} G(x) \, dx}{\int_0^{\infty} G(x) \, dx}.$$  

The moments of $G(x)$ and the differential coefficients of $\mathcal{I}(h)$ were evaluated by standard methods of numerical analysis. It was found that the infinite series on the right-hand side of equation (4) converged rapidly and higher terms than those written down were not needed. The reliability of equation (4) was checked by substituting the values of $I(h)$ in equation (3) and evaluating the convolution integral. The original values $\mathcal{I}(h)$ were recovered with negligible error.

The values of $I(h)$ so obtained for the untreated and treated fibres were multiplied by scale factors which were chosen to correspond to a constant value of the (002) diffracted intensity from the cotton substrate, this too being corrected for the absorption factor by the sample in the (002) direction. The final values of intensity are shown in Fig. 3.

**PARTICLE SHAPE FACTOR**

Referring to Fig. 2, it will be seen that the overall SAS pattern from untreated cotton is continuous and pronouncedly elliptical. The
minor axis of the ellipse was found to be parallel to the length of the fibres. This continuous small angle scattering is exhibited by many textile fibres and is attributed to the presence of capillaries or pores within the fibre substance [Statton (1956)]. The ellipticity of the SAS pattern results from the fact that such pores tend to possess their maximum extension in a direction parallel to the fibre axis.

![Equatorial SAS from cotton fibres containing inorganic deposits. The full curves represent the experimental data after slit corrections, while the points represent calculated intensities.](image)

**Fig. 3.** Equatorial SAS from cotton fibres containing inorganic deposits. The full curves represent the experimental data after slit corrections, while the points represent calculated intensities.

A similar elliptical shape is shown by cotton containing deposits of lead chromate and lead iodide. However, it is clear from the conditions of exposure that most of the scattered intensity is due to the deposits and not to the substrate fibre. Thus it appears that particles of lead chromate and lead iodide, as crystallised in cotton, are also elongated in the direction of the
fibre axis. These are the salts which show preferred orientation in the wide-angle photographs. Thus preferred orientation appears to be connected with preferred growth along a particular set of crystallographic directions.

With the cubic crystals silver and mercuric sulphide on the other hand, no ellipticity is found in the scattering pattern and only a slight trace in the case of lead sulphide. The particles must therefore be either isodiametric or, if elongated, randomly oriented, though a pronounced elongation does not appear to be likely.

**Particle Size Distribution**

Fig. 3 shows the scattered intensity, plotted on a logarithmic scale, as a function of the scattering angle, or rather, of the parameter $h$ (Å$^{-1}$). These Joerchel plots [Joerchel (1957)] have been reproduced here rather than the more usual Guinier plots of log $I(h)$ versus $h^2$ in order not to compress unduly the data at very small angles. The upward concavity in Fig. 3 becomes even more pronounced when the Guinier plots are drawn. This suggests that there is considerable heterogeneity in particle size [Guinier and Fournet (1955)]. The problem of estimating the extent of heterogeneity from the intensity curves would be well-nigh hopeless but for the fact that a number of simplifying approximations can be assumed. These approximate assumptions are as follows:

1. The component of scattered intensity due to the substrate itself is negligible, so that the scattering can be thought of as due to foreign particles of high electron density embedded in a solid matrix of cellulose. Figure 3 shows that this assumption becomes increasingly valid at higher angles of scattering. For instance, from $h$ equal to $5 \times 10^{-3}$ Å$^{-1}$ and onwards, the scattering from untreated cotton is nearly a decade down in intensity compared to the treated fibres.

2. The scattering from different particles can be considered to be independent. This is because the total mass of foreign material deposited amounts to only a few percent of the mass of the substrate. Since the deposits have high specific gravity, the fraction of volume that they occupy in the fibre would be still less. Thus interparticle interference need not be taken into account.

3. In the case of the cubic crystals, the overall SAS pattern is isotropic. Thus the equatorial scattering is the same as the scattering at any azimuth,
In such cases, a good approximation for the scattering from a single particle would be given by Guinier's formula:

$$i_v(h) \propto V^2 \exp\left(-\frac{h^2 R_o^2}{3}\right)$$

where $V$ is the volume of the particle and $R_o$ its radius of gyration [Hosemann and Bagchi (1962); Guinier and Fournet (1955)]. Assuming that the particles are essentially isodiametric, the radius of gyration can be replaced by an equivalent sphere radius $R$, which would modify equation (6) into

$$i_v(h) \propto V^2 \exp\left(-\frac{h^2 R^2}{3}\right).$$

Taking a system of independent scattering particles of the same chemical composition, but varying radii, the angular dependence of scattered intensity could be written in the form [Jellinek et al. (1946)]

$$I(h) = C \int_0^\infty W(R) R^3 \exp\left(-\frac{h^2 R^2}{3}\right) dR$$

where $W(R)$ is the frequency function by mass, i.e., $W(R) \, dR$ is the fraction by mass of particles having radii in the range $(R \pm \frac{1}{2} dR)$ and $C$ is a constant for a given scattering system.

It is not possible to make a rigorous and direct inversion of equation (8) in order to recover $W(R)$ from $I(h)$. For certain assumed types of frequency function (Gaussian, Maxwellian, etc.), equation (8) can be directly integrated and by comparing the result with the experimental $I(h)$, the parameters of $W(R)$ can be evaluated [Shull and Roess (1947); Hosemann (1951)]. Such methods have been tried out in the present case, but without success. Recourse was therefore had to a graphical filtration technique [Jellinek et al. (1946)] whereby it is possible to decompose $I(h)$ into a series of Guinier terms

$$I(h) = \sum_{j=1}^n K_j \exp\left(-\frac{h^2 R_j^2}{3}\right).$$

Details of conducting this filtration procedure are to be found in the literature [Jellinek et al. (1946); Klug and Alexander (1954)]. It will only be remarked here that all the graphical procedures mentioned in these references have been replaced in the present work by analytical methods of greater precision.
Fig. 4. Frequency functions by mass of sizes of deposits in cotton.
Physically, equation (9) means that the small angle scattering from the system can be simulated by spheres with a discrete distribution of radii, particles of radius $R_j$ accounting for a fraction by mass proportional to $K_j/R_j^8$. In terms of a continuous distribution $W(R)$, earlier workers had assumed:

$$W(R_j) = \left(\frac{K_j}{R_j^8}\right) \sum \frac{K_j}{R_j^8}. \tag{10}$$

This assumption has no formal justification, particularly when the $R_j$ are not equispaced. Actually it is clear from a consideration of mean value theorems on the integrals of products of two functions [Whittaker and Watson (1952)] that

$$K_j = \int_{a_j}^{a_{j+1}} W(R) R^3 dR. \tag{11}$$

where

$$a_j < R_j < a_{j+1} \tag{12}$$

but the $a$'s cannot be uniquely assigned. It was assumed as a working approximation that

$$a_j = \frac{1}{2} (R_{j-1} + R_j). \tag{13}$$

from equation (11) we now have

$$\sum_{j=1}^{a_{j+1}} K_j = \int_{0}^{a_{j+1}} W(R) R^3 dR. \tag{14}$$

Thus by plotting the sums of $K_j$ against the $a_{j+1}$, it was possible to obtain a graph of the cumulative function

$$S(R) = \int_{0}^{R} W(x) x^3 dx. \tag{15}$$

The function $W(R)$ could now be recovered by numerical differentiation. But since $S(R)$ tended to increase rapidly with $R$, the numerical values were kept in manageable proportions by use of the formula

$$W(R) = \left[ \frac{d}{dR} + \frac{3}{R} \right] \frac{S(R)}{R^3}. \tag{16}$$

The procedures outlined above are necessarily approximate. However, they sufficed to give a starting curve which could be successively refined by
recalculating the scattered intensity $I(h)$ and modifying $W(R)$ in order to improve the agreement. In the course of these refinements by trial it became clear that the angular dependence of scattered intensity was very sensitive to slight changes in the assumed $W(R)$ curve. Thus it was not difficult, though tedious, to arrive at the shape of this curve with some precision.

The frequency functions by mass $W(R)$ are plotted in Fig. 4 for the deposits silver, mercuric sulphide and lead sulphide. The values of scattered intensity at selected angles, re-calculated from $W(R)$ by use of equation (8), are shown as points in Fig. 3. It will be seen that the agreement over nearly 5 decades of intensity is everywhere within a fraction of a decade.

**DISCUSSION**

The functions $W(R)$ shown in Fig. 4 for three deposits are all characterised by a mode at 100 Å or below and a long tail to the right. Thus while the modal diameter of the particles is 100 to 200 Å, a considerable fraction by mass (though much less by number) is distributed among very large particles. It is likely that large particles are not lodged within the fibre substance, but in the lumen of the cotton fibre as well as in cavities or striations which occur on the fibre surface. If this be the case, the question of distribution of pore sizes within the fibre substance is still open.

Another reservation about the presence of very large particles arises when we remember that while the scattering due to large particles is very strong at small angles, so is the scattering due to the substrate, *i.e.*, untreated cotton, and no provision has been made for allowing for this effect. Thus the tendency for $W(R)$ to rise at large $R$, which is noticed with lead sulphide, may be partly an artifact due to the strong cotton scattering at small angles.

A third factor to be considered is the limitation of small angle scattering theory. It is well known [Beeman *et al.* (1957)] that as $hR$ increases beyond unity, the Guinier approximation becomes increasingly poor for particles of increasing eccentricity such as spheres *versus* spheroids, etc. Thus contributions to $I(h)$ at large $h$ from large particles may be wrongly given by equation (8). However, in the absence of specific information about particle shape, and particularly under the assumption that the particles are nearly isodiametric, equation (6) is the most obvious one to use. It may be remarked in passing that two other approaches were tried out. In one case
the particles were assumed to be spheres and the exact expression for scattered intensity was used in equation (8).

\begin{align*}
  i_v(h) & \propto V^2 \Phi^2(hR) ; \\
  \Phi(x) & = \frac{3 (\sin x - x \cos x)}{x^3}
\end{align*}

(16)

A modified method of graphical filtering was developed to obtain W(R). The results were substantially similar to those shown in Fig. 4.

In another approach it was assumed that the particles were spheroids with moderate eccentricity and random orientation. By comparing plots of log I versus log h with the log I versus log (h) plots for spheroids [Beeman et al. (1957)] it appeared that sharper size distributions than in Fig. 4 would account for the scattered intensity.

Taking all these limitations into account, it would be prudent to regard the information in Fig. 4 as only qualitative, notwithstanding its excellent correspondence with the intensity data under the given assumptions. One can say with confidence that the majority (by number) of particles deposited on cotton fibres have diameters of 200 Å and below, which is the same order of size as given by line breadth measurements. However, there are some very much larger particles as well. If they were single crystallites, they would have inflated the average size as obtained from line breadths. They are therefore likely to be polycrystalline aggregates.

The analysis given above could not be conducted in the case of elongated, orienting particles such as lead chromate and lead iodide. This is because the accurate measurement of scattered intensity requires the use of line slits. The equatorial scattering then becomes smeared by scattering at other azimuths as well and the important corrections for slit length and width are no longer meaningful.

**Summary**

Small angle scattering patterns have been photographed from cotton (and viscose) fibres containing deposits of silver, mercuric sulphide, lead sulphide, lead chromate and lead iodide. These patterns have shown that deposits of the cubic crystals are nearly isodiametric and randomly oriented. On the other hand, particles of lead chromate and lead iodide are elongated, with the longer direction tending to be oriented along the fibre axis. These conclusions are in agreement with evidence on orientation secured from wide-
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angle diffraction. In the case of the randomly oriented deposits, extensive measurements have been made of the angular dependence of equatorial scattered intensity. Distributions of particle size have been computed which will synthesize back the scattered intensity. Some limitations of such calculations have been pointed out. It has been concluded, however, that the majority of particles are crystallites with dimensions of 200 Å or less. There are a few particles with very much larger dimensions. These may be polycrystalline aggregates which are lodged in the fibre lumen rather than in cellulosic substance.

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EXPLANATION OF PLATES

PLATE III

Fig. 1. Wide angle diffraction from cotton fibres containing various inorganic deposits:
(a) Raw Cotton; (b) Cotton/PbCrO₄; (c) Cotton/PbI₄; (d) Cotton/Ag; (e) Cotton/HgS;
(f) Cotton/PbS.

PLATE IV

Fig. 2. Small angle X-ray scattering from cotton fibres containing various inorganic deposits:
(a) Raw Cotton; (b) Cotton/PbCrO₄; (c) Cotton/PbI₄; (d) Cotton/Ag; (e) Cotton/HgS;
(f) Cotton/PbS.
FIG. 2