The Use of Film Methods in Small-Angle X-ray Scattering

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Abstract

Various sources of random deviations occurring in the determination of X-ray intensities with the aid of film methods are discussed and corresponding mathematical expressions are derived. From a comparison with experimental values of the standard deviations obtained from measurements on homogeneously exposed films, it follows that the deviations are primarily caused by the variations of the X-ray photon flux due to the stochastic nature of the X-ray emission process. The accuracy attainable with most X-ray films is found not to be limited by saturation of the number of excited AgBr particles occurring at increasing exposures, but at low exposures film methods are at a disadvantage because of the presence of fog. If, however, small signals superimposed on a high sample background have to be measured, relatively high exposures are required; in this case film registration is found to be much faster than methods involving step-scanning counters, and in general little slower than registration with the aid of a position-sensitive counter. It is also shown that the dynamic range of the film method may be extended without sacrificing accuracy by resorting to slower films.

Introduction

Since the advent in the nineteen fifties of reliable counters, the use of films in X-ray diffraction techniques has been reduced considerably, but not to zero. Generally speaking, film methods are still used in those instances where the radiation to be measured can be registered simultaneously within a wide range of scattering angles. Examples are the recording of powder patterns by such instruments as the Debye–Schererrer camera, the Guinier camera, the flat-film camera, and the recording of reflections from protein crystals with the aid of the precession or rotation camera. Here, the replacement of the film by a scanning counting detector would lead to much longer exposure times and therefore seems illogical. An exception in this respect is the measurement of slit-smeared small-angle X-ray scattering (SAXS) patterns: although the entire pattern is simultaneously available, it is usually measured with the aid of a step-scanning counter. Here the time loss may be motivated by the higher accuracy and larger dynamic range of the counter; however, such arguments are probably in most cases based on intuition rather than on observations. Actually, although the effect of X-rays on photographic material is well understood (see, for example, the review of Corney, 1966), and furthermore a wealth of data on X-ray films is available from two investigations, sponsored by the IUCr (Commission on Crystallographic Apparatus of the IUCr, 1956; Morimoto & Uyeda, 1963), a quantitative comparison of film and counter methods seems not to have been made until 1977 (Arndt, Gilmore & Wonacott, 1977).

In the present study we will first extend the relations given in the publications mentioned above by taking into account the saturation of the AgBr layers which occurs at increasing exposures. Next, these relations will be tested with the aid of the new experimental data, and finally the use of films in SAXS will be compared with methods involving step scanning as well as position-sensitive counters.

Experimental

Materials

The films used in this investigation were selected from a number which were incidentally available to us at the time when the experiments started. As it was not the purpose of this work to compare the different types of films, they were not treated with special precautions; thus they were all processed according to the standard procedure described below, disregarding the recommendations of the manufacturers. Furthermore, at the time the measurements were made the films were of very different ages, and the figures concerning the optical density of the fog can in no way be considered to be representative. The numbers 1–6 by which the films are indicated in this paper refer to the following types: (1) Agfa-Gevaert Structurix D10; (2) Ilford Ilfex 90; (3) Kodak Industrex D54; (4) Agfa-Gevaert Structurix D7; (5) Kodak Industrex D54; (4) Agfa-Gevaert Structurix D7; (5) Kodak Industrex AAS; (6) Kodak Industrex M5.

Processing

The standard procedure, applied to all films, consisted of:

1. Developing for 5 min in Ilford RC 51 developer, in a 2 l tank at 293 K, with gentle shaking of the film at intervals of 1 min. The developer was renewed every 14 days;
2. Stopping in 3% acetic acid;
Densitometry

The densitometer was a home-built conventional-type instrument, in which the film was placed at the midpoint between two identical objective lenses with a numerical aperture of 0.18; the light source illuminating the entrance slit was a halogen lamp burning on a highly stabilized power supply; after passing a receiving slit the transmitted light fell on a photomultiplier tube, the signal of which was fed to a logarithmic amplifier, giving its output in digital form on a cassette recorder. The table on which the film was mounted between two glass plates could be moved with the aid of stepping motors, which were commanded by a microcomputer programmed to make various sorts of scans.

Density-exposure scales

These scales were made with Cu Kα radiation obtained from the 110 reflection of a polyethylene sample in a vertical Philips diffractometer. In order to broaden the homogeneous region of the reflected beam, the sample was mounted in transmission. The intensity in this region of the beam was determined by a proportional counter, the efficiency of which, according to the calculations of the manufacturer (Philips), was assumed to be 65%. By way of a check, in one experiment four different counters of the same type were compared; the results were found to agree within 2%. For making a density-exposure scale the counter slit assembly was replaced by a piece of film, which was exposed at different places for different times.

The same set-up was used for measuring the absorption factors of the various films.

Standard deviation measurements

Uniformly exposed strips of film were obtained with the aid of a Weissenberg camera, whose point collimator was replaced by a slit collimator of 300 mm length, the longitudinal direction of the slit being vertical. The Ni-filtered X-ray beam, which was supplied by a Cu X-ray tube operated at 10 kV, and therefore could be expected to be almost monochromatic, fell on a flat film that was mounted on the cart, which made an integral number of double trips during one exposure.

The strips of film thus obtained were scanned in the densitometer in 1000 steps of 40 μm. At the position of the film the rectangular light spot had a width of 31 μm in the scanning direction, while different heights were applied. The densitometer readings were divided into groups of 50 successive values; the standard deviations within the individual groups were determined, which were then used to calculate the standard deviation for all measurements on one strip. The same procedure was applied to the unexposed films and the base materials.

Homogeneity of the silver bromide layers

The film to be investigated was mounted at the sample position of a Kratky small-angle-scattering camera, in which the height of the primary beam was confined by lead curtains placed just in front of the film. After passing the film, the beam, which was generated by an X-ray tube with Cu anode, was reflected on a proportional counter by a graphite monochromator tuned to Cu Kα radiation. The film was moved manually to different positions; from the transmission factor at these positions the weight w of the silver bromide layer per mm² was calculated. In determining the standard deviation of w, the procedure described in the previous subsection was applied, with the exception that here 120 measurements were made, which were divided into groups of 20 values.

Theoretical

General

The response of X-ray films will be quantitatively described by comparing the accuracy of an X-ray signal, as measured with the aid of the film method, with the one obtained by means of an 'ideal' counter. This is a counter which shows no instrumental background, and of which the efficiency γ is constant over the entire exposure range. We assume the counter and the film are exposed to the same number of $E_{\text{eff}}$ quanta per μm²; then the counter will register a number $E_{\text{eff}} \gamma$ of quanta, where s is the cross section of the counter aperture. The film, after being processed, will show an optical density $D$ defined by $D = \log_{10}(i_0/i)$, where $i$ and $i_0$ are the intensities of the light beam in the densitometer after passing through the exposed film and the base material, respectively. In order to secure the same resolution in the two experiments, the cross section of the light beam at the position of the film (to be indicated in the following as the 'light spot size') is taken equal to that of the aperture used in the counter measurement. The total density $D$, which is composed of a contribution $D_{\text{eff}}$ from the X-ray exposure and a contribution $D_F$ from the fog, is converted to a total exposure $E$, which in turn is separated into the contributions $E_{\text{eff}}$ and $E_F$, where $E_F$ is a virtual X-ray exposure corresponding to $D_F$.

We furthermore separate the effective exposure and the corresponding density according to $E_{\text{eff}} = E_S + E_B$ and $E_{\text{eff}} = E_S + E_B$, into contributions pertaining to the signal (subscript S) and a sample background (subscript B) respectively.

In comparing the two detection systems use will be made of the so-called detective quantum efficiency (DQE), introduced by Gruner, Milch & Reynolds (1978), which is defined as the ratio of the squares of the relative standard deviations $\sigma$ of the in- and out-put signals $U_i$ and $U_o$: 
The quantity we wish to obtain is the ratio \( R \) of the standard deviations at equal exposures of the film and counter methods, which is given by

\[
R = \frac{(DQE)_c}{(DQE)_f}^{1/2}. \tag{1}
\]

Here, the subscripts \( c \) and \( f \) refer to counter and film respectively. It can be shown that \( R^2 \) is equal to \( t_f/t_c \), which is the ratio of the exposure times needed to obtain the same accuracy in using film and counter methods.

If it is assumed that the input signal obeys Poisson statistics and that \( E_B \) can be determined with much better accuracy than \( E_S + E_b \), one may derive

\[
(DQE)_c = \gamma E_S/(E_S + E_B). \tag{2}
\]

In determining \( (DQE)_c \), the total variance \( \sigma^2 \) pertaining to film measurements will be considered to be given by

\[
\sigma^2 = \sigma^2_{\text{eff}} + \sigma^2_0
\]

where \( \sigma_{\text{eff}} \) corresponds to the statistical variations in the effective exposure \( E_{\text{eff}} \), and \( \sigma_0 \) to the ‘noise’ resulting from the density variations of the fogged film. Furthermore we write

\[
\sigma^2_{\text{eff}} = \sigma^2_S + \sigma^2_B
\]

and

\[
\sigma^2_0 = \sigma^2_F + \sigma^2_G
\]

where the subscripts \( S, B, F \) and \( G \) refer to the signal, the sample background, the fog and the gelatine layers plus base material respectively. Also we will take into account a standard deviation \( \sigma \) resulting from the short-range non-uniformity of the AgBr layers covering the film.

**Density-exposure relations**

In order to find an expression for \( (DQE)_c \), we first need a relation between the X-ray exposure and the resulting optical density of a film. In the following a simple derivation of such a relation is presented, which for the greater part parallels the one given by Frieser & Klein (1958) for electron radiation, but differs from it in that on the basis of microscopic observations, we distinguish between the AgBr ‘particles’ in the original film, and the silver ‘grains’ in the developed film. In order to facilitate comparison with the data presented in the report on the second investigation of the IUCr mentioned above (Morimoto & Uyeda, 1963), we will, if not indicated otherwise, use the same symbols as those used in that report.

Let a film contain \( n_0 \) AgBr particles per \( \mu m^2 \), of which at a certain time during the exposure \( n \) have been excited by X-rays; only the excited particles are supposed to give rise to Ag grains during the developing process. By increasing the exposure by \( dE \) photons \( \mu m^{-2} \), the number of excited particles per \( \mu m^2 \) will increase by

\[
dn = m a \frac{n_{0} - n}{n_{0}} dE.
\]

Here, \( m \) is the number of particles excited by one photon, \( a \) is the fraction of the radiation absorbed by the AgBr particles (both excited and unexcited) and \( (n_0 - n)/n_0 \) obviously presents the fraction of unexcited particles. Using the condition that \( n = n_0 \) if \( E = 0 \), one finds by integration

\[
n = n_0 \{ 1 - \exp (- maE/n_0) \}. \tag{3}
\]

In considering now the light transmission of the developed film, we assume that during the developing process on average \( k \) excited particles lead to the formation of one silver grain. Furthermore, the fraction \( i/i_0 \) of the light transmitted by the film is considered to be equal to the fraction of the surface which in projection perpendicular to the plane of the film is not covered by silver grains. An increment of \( dn \) excited particles per \( \mu m^2 \) will lead to an increase of \( dn/k \) silver grains; as the thickness of the sensitive layers generally is much larger than the diameter of the grains, a fraction \( i/i_0 \) of these may be assumed to fall within the uncovered part of the surface, leading to a decrease of this fraction given by

\[
d(i/i_0) = - f(i/i_0) (dn/k).
\]

Here \( f \) is the effective cross section for light absorption of one silver grain. Together with the condition that \( i = i_0 \) if \( n = 0 \), this leads to

\[
i/i_0 = \exp (- fn/k)
\]

or

\[
D = fn/(2.3k). \tag{4}
\]

Combining this with (3) one obtains the following relation between density and exposure

\[
D = D_{\text{max}} \{ 1 - \exp (- S_0 E/D_{\text{max}}) \}, \tag{5}
\]

where

\[
S_0 = ma f/(2.3k) \tag{6}
\]

and

\[
D_{\text{max}} = n_0 f/(2.3k). \tag{7}
\]

This relation as such is not well suited for the purpose of calibrating films with the aid of density-exposure scales; however, by two successive series developments one may obtain as a good approximation:

\[
D/E = S_D = S_0 \{ 1 - D/(2D_{\text{max}}) \}. \tag{8}
\]

Here the symbol \( S_D \) indicates the speed of the film at density \( D \). [In the report of Morimoto & Uyeda (1963) the speed was defined as the value of \( D/E \) at \( D = 1 \).] The factor \( 1 - D/(2D_{\text{max}}) \) describes the decrease of the film speed due to the increasing number of particles already excited at increasing exposure, and as such will be indicated as the saturation factor.

According to (8), in calibrating a film one may use a plot of \( D/E \) versus \( D \), where \( D \) and \( E \) are experimental values determined with the aid of a density-exposure
scale. Here, a difficulty is that at the outset the value of the virtual exposure $E_F$ pertaining to the fog, which according to the foregoing is to be added to the X-ray exposure $E_{\text{eff}}$, is not yet known. However, by making the substitutions $D = D_{\text{eff}} + D_F$ and $E = E_{\text{eff}} + E_F$ one may derive from (8) the following approximation:

$$ D_{\text{eff}}/E_{\text{eff}} = S_0\{1 - (D + D_F)/(2D_{\text{max}})\}. \quad (9) $$

Thus from a plot of $D_{\text{eff}}/E_{\text{eff}}$ versus $D + D_F$, which can be made from the available data, preliminary values of $S_0$ and $D_{\text{max}}$ may be obtained, from which $E_F$ can be calculated.

**Standard deviations of film measurements**

Considering the effect of statistical variations of the exposure, we notice that the number of photons registered on the area $s$ of the film equals $ns/m$, with a standard deviation of $(ns/m)^{1/2}$. Together with (4) and (6) this leads to

$$ \sigma(D) = (S_0D/(ns))^{1/2}. \quad (10) $$

For finding $\sigma(E)$ we use the relation $\sigma(E) = (dE/dD)\sigma(D)$, from which, with the aid of (8), the following approximation may be derived:

$$ \sigma(E_{\text{as}}) = (E_{\text{as}})^{1/2}\{1 - D/(2D_{\text{max}})\}^{-3/2}. \quad (11) $$

In this equation $E_{\text{as}}$ is the number of photons absorbed in the film in the area of the light spot; according to the first factor on the right-hand side, the standard deviation of this number to a first approximation is equal to its root, which is to be expected from the assumptions used in deriving (11). The second factor results from the saturation factor; in Fig. 1 its value is plotted as a function of $D$ for various values of $D_{\text{max}}$.

The value of $E$ that is to be used in (11) comprises a contribution $E_F$ due to the fog. However, the processes causing the fog are different from those described above; moreover, the variations in the density of the fogged film also comprise the variations in the optical density of the gelatine layers and the base material, as expressed by $\sigma_G$. It is therefore not to be expected that application of (10) to the fog density $D_F$ will give the correct value of $\sigma_F(D)$. For this reason, in calculating the standard deviation, we will substitute for $D_F$ a value $D_N$, representing a density which by application of (10) would lead to the observed value of $\sigma_N(D)$. This density will be related by (8) to an equivalent exposure $E_N$. Similarly, the standard deviation $\sigma_F$ will be connected with an equivalent exposure $E_G$.

The non-uniformity of the AgBr layer can be considered to be brought about by variations in the number $n_0$ of AgBr particles per $\mu m^2$. Taking into account that the absorption factor $a$ is also affected by such variations, we find by differentiating (8) with respect to $n_0$ the following expression for the ratio of the relative variations in $E$ and $n_0$:

$$ -dE/E \frac{dn_0}{n_0} = -\frac{1 - aD/(2D_{\text{max}})}{a}\ln(1-a) + \frac{D/(2D_{\text{max}})}{1-D/(2D_{\text{max}})}. \quad (12) $$

The first term on the right-hand side of this equation depends on the type of film only and for most films is of the order of 0.7; the second term increases with increasing saturation, but usually is below 0.5. Thus one may conclude that the value of $E$ as obtained from film measurements varies about proportionally with the local density of the AgBr layer. It is however to be noticed that with increasing loading of the film, $a$, and usually also $D_{\text{max}}$, increase, which results in a reduced sensitivity of $E$ to variations in $n_0$.

Using the above results we find, after rearranging (11) with the aid of (2) and (8), the following expression involving $R$ as defined by (1):

$$ R^2 = \frac{R^2}{a} \left(1 + \frac{E_N}{E_{\text{eff}}} \right) \left(1 + \frac{S_0E}{2D_{\text{max}}} \right)^3 + T, \quad (13) $$

where $E = E_S + E_B + E_F$. The term $T$ represents the contribution due to the non-uniformity of the AgBr layers, which can be calculated with the aid of (12). In (13) all exposures refer to the values used in applying film methods; from these the exposures that have to be used for obtaining the same accuracy when applying an ideal counter can be found by multiplication by $1/R^2$.

**Systematic errors**

Of the conceivable sources of systematic errors, those resulting from variations in the film response due to aging, to differences in processing, etc. can be met by making a density–exposure scale on a piece of the film to be used for the measurements, and processing the two parts of the film together. (Such measures will be necessary only if very accurate results are required; in general the use of a previously made density–exposure scale will suffice.) The only systematic errors which cannot be avoided are those resulting from long-range inhomogeneities in the covering of the film, which again we consider to be representable by variations in $n_0$; thus in calculating the effect of such variations, (12) applies.

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Fig. 1. Plot showing the effect of the saturation factor on the accuracy of film readings as a function of the density $D$ for various values of the parameter $D_{\text{max}}$. 
Dynamic range

The dynamic range of a measuring instrument may be defined as the ratio of the highest to the lowest signal that can be measured with a certain precision without changing the measuring conditions and adjustments of the instrument. If non-essential limitations are left out of consideration, the lowest effective exposure that can be measured by the film method must have a certain ratio to the standard deviation $\sigma(E)$ of the background on which it is superimposed. The highest intensity will either be set by the saturation effect as described by (11), or by some shortcoming of the densitometer, e.g. the dark current of the photomultiplier.

In general, the dynamic range of any instrument will depend on the various measuring conditions, which therefore have to be specified. The conditions pertaining to the use of film and counter methods are found to be of a different nature, because of which a quantitative comparison of the dynamic ranges cannot be made. However, in considering the film method one may discuss the effect of various measures on the dynamic range, which for this purpose may be put on a relative scale.

Results

Evaluation of literature data

In comparing the properties of X-ray films Morimoto & Uyeda (1963) also determined the so-called Selwyn granularity $G_S$ at $D = 1$, which is related to the standard deviation $\sigma(D)$ at this value of $D$ by

$$G_S^2 = 2\sigma^2(D)_{D=1}.$$  

On the basis of the values obtained from 43 different types of film they found the following empirical relation:

$$G_S^2 = 3.6S_1/A,$$

where $A$ is the fraction of Cu Kα radiation absorbed by the entire film (base + AgBr layers). Combination of these two equations yields

$$\sigma(D)_{D=1} = 1.34\{S_1/(As)\}^{1/2}.$$  

This result may be compared with a similar expression that can be derived by combining (10) and (8) and substituting $D = 1$:

$$\sigma(D)_{D=1} = \{S_1/\alpha(1-1/2D_{max})\}^{1/2}.$$  

From our data and those presented by the above authors, it follows that on average $a = 0.71A$ and $(1-1/2D_{max}) = 0.91$, which reduces the previous relation to

$$\sigma(D)_{D=1} = 1.24\{S_1/(As)\}^{1/2}.$$  

Comparison with the empirical equation shows that the present treatment not only leads to the correct functional relationship but also to a value of the numerical constant differing by only 8%. This is a first indication that the standard deviation of X-ray intensities as obtained by the film method is determined primarily by the statistical variations of these intensities.

![Fig. 2. Plots of the speed $S_0 = D/E$ ($D =$ density, $E =$ exposure) versus $D$ for various films. The data points were obtained from measurements on density-exposure scales. The curves, which were drawn to give the best fit to the data points, were of first degree, except for film 3, where it was of second degree. Notice that in the vertical direction different scales have been used.](image)

Table 1. Values of various quantities pertaining to six different types of X-ray film

<table>
<thead>
<tr>
<th>Type number</th>
<th>$a$</th>
<th>$S_0$ ($\mu m^2$)</th>
<th>$D_{max}$</th>
<th>$D_F$ ($\mu m^2$)</th>
<th>$E_F$ ($\mu m^2 \times 10^4$)</th>
<th>$E_{s}$ ($\mu m^2$)</th>
<th>$E_{as}$ ($\mu m^2$)</th>
<th>RDR</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.48</td>
<td>3.44</td>
<td>4.3</td>
<td>0.187</td>
<td>0.054</td>
<td>0.12</td>
<td>0.029</td>
<td>0.120</td>
</tr>
<tr>
<td>2</td>
<td>0.26</td>
<td>1.67</td>
<td>2.5</td>
<td>0.075</td>
<td>0.045</td>
<td>0.34</td>
<td>0.030</td>
<td>0.141</td>
</tr>
<tr>
<td>3</td>
<td>0.53</td>
<td>1.1</td>
<td>9.2</td>
<td>0.252</td>
<td>0.229</td>
<td>1.43</td>
<td>0.050</td>
<td>0.151</td>
</tr>
<tr>
<td>4</td>
<td>0.39</td>
<td>0.59</td>
<td>6.9</td>
<td>0.139</td>
<td>0.253</td>
<td>0.34</td>
<td>0.154</td>
<td>0.509</td>
</tr>
<tr>
<td>5</td>
<td>0.43</td>
<td>0.50</td>
<td>6.2</td>
<td>0.059</td>
<td>0.118</td>
<td>0.34</td>
<td>0.154</td>
<td>0.310</td>
</tr>
<tr>
<td>6</td>
<td>0.41</td>
<td>0.22</td>
<td>11.1</td>
<td>0.017</td>
<td>0.077</td>
<td>0.34</td>
<td>0.149</td>
<td>0.388</td>
</tr>
</tbody>
</table>

* These values were obtained by fitting a first-degree curve to the data points; in Fig. 2 a second-degree curve is shown.
tensities. A similar conclusion was reached by Arndt, Gilmore & Wonacott (1977), who, however, did not take into account the factors $a/A$ and $(1 - 1/2D_{\text{max}})$ mentioned above.

Density–exposure scales

The results of the measurements of density–exposure scales made on six different types of film are presented in the form of $D/E$ versus $D$ plots in Fig. 2. This figure shows that in general the linear relationship predicted by (8) is well obeyed up to densities of about 3; only film 3 seems an exception. In Table 1 the values of $S_0$ and $D_{\text{max}}$ found from these plots are presented together with the values of $D_F$ and $E_F$ and other data to be discussed later.

From Table 1 it can be seen that the values of $a$ and $D_{\text{max}}$ pertaining to the film of type 2 are exceptionally low. Accordingly this film, although very well suited for purposes involving visual inspection only, is less recommended for intensity measurements. In the following it will therefore be left out of the considerations.

Standard deviations of film readings

The determinations of the standard deviations of the density on homogeneously exposed strips of X-ray film were made on film of type 1 only. As described more fully in the experimental section, each value of the observed total standard deviation $\sigma(D)$ was determined from 1000 independent readings. Such measurements were also made on the fogged films of all types to obtain $\sigma(D)$, as well as on the base materials to obtain $\sigma(D)$. The corresponding equivalent exposures $E_N$ and $E_G$ are entered in Table 1, together with the light spot sizes used in making these measurements. The values of $\sigma(D)$ obtained from the type 1 film were corrected for inhomogeneities of the base material by $\sigma^2(D) = \sigma^2(D) - \sigma^2(D)$. The results of these measurements, which were made with four different light spot sizes, are presented in a plot of $\sigma(D)$ versus $D^{1/2}$ in Fig. 3; also shown in this figure are the theoretical lines derived from (10) with the aid of the value of $S_0$ obtained from the density exposure scale and the value of $a$ quoted in Table 1. Considering that in drawing these lines no parameters were adjusted, the agreement with the measured values is very satisfactory. Only the data points at the lowest $D$ values, which correspond with the fog, are systematically above the theoretical values; this may be connected with the afore-mentioned difference in nature of the processes which are responsible for the occurrence of the fog.

The divergent response of the fogged films may also be recognized by considering the values of $E_F$, $E_N$ and $E_G$ of the various films presented in Table 1: whereas one might expect $E_N$ to be equal to $E_F + E_G$, it is found that in all cases $E_N$ is appreciably larger.
The agreement shown by Fig. 3 fully confirms the supposition expressed above, that the granularity observed on X-ray films is primarily caused by the local variations of the X-ray photon flux. A similar conclusion, which was also confirmed by experiments, had been reached with respect to the effect of electron radiation on photographic material by Frieser & Klein (1958), and had been supposed to apply to X-rays as well (Corney, 1966).

In view of these results it is to be expected that the effect of inhomogeneities of the AgBr layers on \( \sigma(D) \) may be neglected. This is born out by the determination of these inhomogeneities with the aid of an X-ray beam of fifty-fold cross section; the measuring points were chosen at 10 \( \times \) 10 positions on a rectangular lattice covering a 300 \( \times \) 400 mm piece of film. A plot of the relative deviations \( \Delta n_0/n_0 \) from the average is shown in Fig. 5; the maximum deviation was 1.7\%\( _o \), the standard deviation 0.7\%\( _o \). Of special interest in the use for SAXS is the derivative \( dn_0/(n_0 dx) \), where \( x \) is the coordinate along an arbitrary straight line on the film; this was found to be 0.018°\( _o \) per mm on average, the maximum being 0.052°\( _o \) per mm. According to the discussion given in connection with (12), these figures would in general also apply to the long-range deviations of the intensities obtained with the aid of this film. Of course, these values cannot be considered to be representative of films in general, or even for the present type of film; they may, however, serve to give an idea of the systematic errors in film measurements that can be expected. In connection with this it should be mentioned that the deviations found here are definitely smaller than the values obtained by comparing the variations in optical densities of uniformly exposed films in the investigations of the Commission on Crystallographic Apparatus of the IUCr (1956) and Morimoto & Uyeda (1963), which corresponded to standard deviations of the order of 2°\( _o \).

They are, however, in qualitative agreement with the results of similar experiments made by Arndt, Gilmore & Wonacott (1977).

**Dynamic ranges**

For reasons of apparatus performance the highest useful density \( D_h \) generally is of the order of 3–4. By considering the curves presented in Fig. 1 and the \( D_{max} \) values quoted in Table 1 one may see that, except for the film of type 2, the use of densities of such values is not yet seriously interfered with by the saturation effect, and that therefore the exposure \( E_h \) corresponding to \( D_h \) by \( E_h = D_h/S_h \) may be considered to represent the upper limit.

The values of the relative dynamic range (RDR) presented in the last column of Table 1 are proportional to the ratio \( E_h/\sigma_s(E) \), where \( \sigma_s(E) = E_s/as \) and \( D_h = 3 \). The values of RDR show that at a given value of \( s \) considerable increase of the dynamic range can be obtained not only by increasing the light spot size used in the densitometer, but also by resorting to slower films. As the speed of the film does not enter into (11) representing the accuracy of the intensity as measured by the film method, this can be obtained using the same exposure times without sacrificing accuracy. Apart from the weaker impression slower films make on visual inspection, the only disadvantage of these films is the circumstance that they put higher demands on the densitometer. Such demands may, in general, easily be met by modern equipment.

The increase of the dynamic range that can be attained by decrease of the film speed is limited by the occurrence of deviations due to external sources, of which the presence of dust particles usually is the most important one. When using films of type 6 already stringent precautions to avoid dust are required, and it is not expected that the use of still slower films would be advantageous.
Discussion

The curves presented in Fig. 4 show a broad minimum, in which the ratio \( R^2 \) between the exposure times needed to obtain equal accuracy when using film and counter methods, according to (13), approaches the value \( \gamma/a \); in general this value may be close to unity. At higher exposures \( R^2 \) rises because of the saturation effect, but this rise does not exceed a factor of about 2. At lower exposures, however, and in the absence of a sample background, \( R^2 \) rises continuously with decreasing exposure, as the density resulting from the signal gets more and more drowned in the fog. The region of exposures in which films can compete with counters can be seen to have a lower limit at about \( \frac{1}{2} E_N \), where, according to Fig. 4, the ratio \( R^2 \) for the type 1 film, will be \( 10^4 \), with a relative standard deviation of 1%. Therefore, if a higher relative standard deviation of the lowest signal is permitted, counters will clearly have an advantage. A similar calculation to the one just given shows that, if a relative standard deviation of 10% is allowed, the factor \( R^2 \) for the type 1 film is about 40. As this is of the order of the number of steps used in scanning through a complete slit-smeared SAXS curve, films and step-scanning counters may in this case be about equivalent as regards the total exposure time. When using a linear position-sensitive counter (PSC) one may of course entail the full gain of time corresponding to the factor of 40.

However, in many SAXS curves the smallest signal to be measured is superimposed on a much higher background of sample scattering. This situation occurs in the analysis of the scattering of particles in dilute solutions, as well as in the investigation of a transition layer in polymeric two-phase structures. Here a relatively high accuracy of the background intensity is required, which may well correspond to a relative standard deviation of 1%. In that case, in using the film method under the conditions described above, the exposure of the background has to be greater than \( \frac{1}{2} E_N \). where, according to Fig. 4, the ratio \( R^2 \) for films of both types is between 2 and 5. The profit that can be gained by using instead of these films an ideal PSC is therefore limited; here a step-scanning counter will of course be much slower than film registration.

The occurrence of a high sample background is a feature connected with the use of slit geometry in SAXS. This may be seen by considering by way of example a pinhole SAXS pattern, consisting of a Gaussian origin peak corresponding to particles with a radius of gyration of 10 nm, superimposed on a constant background. One may easily calculate that in the smeared pattern, as obtained with a conventional Kratky camera, in which the length profile of the primary beam in the plane of registration at 200 mm from the sample is a trapezoid of 40 mm width at half height, the background-to-peak ratio is 26 times the corresponding ratio in the original pattern.

In order to appreciate the significance of the sample background, in Fig. 4 curves corresponding to various values of \( E_B \) are presented. As regards the value of \( \frac{1}{2} E_N \), which can be considered as a lower limit of the background exposure for which film methods are useful, one may see from the values given in Table 1 that in practice this is about equal to \( E_F \), the exposure corresponding to the fog density.

In Table 2 the background intensities from various liquids and polymers, as measured under the conditions mentioned in the legend of this table, are presented. By comparing these with the values of \( \frac{1}{2} E_N \) pertaining to the film of type 1, one may conclude that under these conditions and for this film the accuracy of 1% is reached in exposure times ranging from about \( \frac{1}{2} \) h for some organic liquids to about 2 h for aqueous solutions.

As the limited dynamic range of X-ray films may require a second shorter exposure, the effective exposure time in using the film method may have to be extended with respect to the time used in the calculations of the curves presented in Fig. 4. From the considerations concerning the accuracy of film methods presented in this paper one may conclude that, if stable X-ray equipment is used, and if both exposures are made on the same piece of film and developed together, the corresponding scaling factor may be taken equal to the ratio of the exposure times. As no overlapping exposure intervals are required, this ratio may be taken as high as 10:1, which does not seriously prolong the effective exposure time.

Apart from considerations involving accuracy and dynamic range the choice between counter and film methods will often be affected by more qualitative arguments. An obvious advantage of counters is the possibility of the direct processing of digital information to digital results, obviating the complications.

Table 2. Background intensities \( I_B \) of various solvents and polymers, measured at a scattering angle of 0.05 rad, expressed in the number of Cu Kα quanta \( \mu m^{-2} h^{-1} \)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (mm)</th>
<th>( I_B ) (( \mu m^{-2} h^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>1.1</td>
<td>0.035</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.1</td>
<td>0.109</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>1.1</td>
<td>0.094</td>
</tr>
<tr>
<td>Dodecane</td>
<td>2.6</td>
<td>0.143</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.6</td>
<td>0.126</td>
</tr>
<tr>
<td>Polyethylene, ( \varphi = 0.85 )*</td>
<td>1.4</td>
<td>0.029</td>
</tr>
<tr>
<td>Polyethylene, ( \varphi = 0.45 )</td>
<td>1.6</td>
<td>0.035</td>
</tr>
<tr>
<td>Polyethylene, ( \varphi = 0.1 )</td>
<td>2.2</td>
<td>0.094</td>
</tr>
</tbody>
</table>

Measuring conditions: Kratky camera, as described in text, entrance slit 80 \( \mu m \); sample-counter distance 200 mm; radiation from tube with Cu target, operated at 35 kV, 45 mA; Ni-filtered.

* \( \varphi \) = crystallinity.
involved in the dark-room processing of films, in operating a densitometer and in making density-exposure scales. Furthermore, the possibility of applying electronic discrimination to a counter signal in order to simulate monochromatization may be of importance. In considering a PSC, one must also take into account the difference in resolution obtainable by the two methods: whereas films allow a resolution of a few μm, the values for one-dimensional PSC's reported in scientific literature range from 50 to 400 μm; for the two-dimensional counter operated at Oak Ridge the resolution amounts to 1 mm (Hendricks, 1976, 1978).

The resolution can be improved by increasing the sample-counter distance, which, however, is at the expense of economy in general. A further restriction in exposure scales. Furthermore, the possibility of applying film methods for measuring X-ray intensities is determined by the following factors: (a) the stochastic nature of the X-ray emission process, (b) the saturation of the AgBr layers occurring at increasing exposure, and (c) the presence of the fog.

In considering the time needed to register a complete SAXS pattern with a certain accuracy and at a certain resolution, we find the exposure $E_B$ of the sample background to be of prime importance. If this is allowed to be well below the exposure $E_F$ corresponding to the fog density, films are much slower than PSC's, but may compete with step-scanning counters. This situation will generally occur in the registration of SAXS patterns with the aid of pinhole collimation. If, however, $E_B$ is of the order of $E_F$, films will be much faster than step-scanning counters, and may compete with PSC's. This situation will often be met in the recording of slit-smeread SAXS patterns from solutions or from solid polymers.

The dynamic range pertaining to the film method can be extended without sacrificing accuracy by resorting to slower films.

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References


