
CONTRIBUTED PAPERS

A REVALUATION OF FILM METHODS IN X-RAY SCATTERING

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In considering the response of photographic film to X-rays, a relation between optical density and X-ray exposure, as well as a relation describing the accuracy of film measurements is derived. These relations are tested experimentally, and are found to be obeyed well. If the Detective Quantum Efficiency of an X-ray film is plotted versus exposure (Fig. 3), one finds a curve showing a broad maximum. The level of this maximum is close to the absorption factor of the AgBr on the film, which for most X-ray films, if used for Cu K α -radiation, is of the order of 0.4-0.5. At low exposures this ratio decreases, as small signals tend to get drowned in the fog, which is present on every film. At higher exposures, the ratio also decreases because of saturation of the AgBr-particles, but here the use of film is mainly limited by the highest optical density (3-4) which can be processed. The largest dynamic range is obtained for films containing relatively small AgBr particles, which may be characterized as slow films. Altogether, film is believed to be a good candidate for accurate data collection, especially if used in combination with Cu K α -radiation.

1. Introduction

For many years after the famous discovery of X-ray diffraction by von Laue in 1908, photographic films or plates have served as the only means for the detection of X-rays in diffraction experiments. In the early days of this science, when primarily information on the directions of the diffracted beams was desired, this method of registration was quite adequate. Later, with the growing interest of crystal structure analysis, also methods for intensity measurements by film methods were developed. These involved the use of densitometers, and the preparation of density-exposure scales for characterizing the films which were used. At the same time, ingenious instruments like the integrating Weissenberg- and Precession-cameras were introduced for obtaining integrated intensities of X-ray reflections from single crystals.

After the advent of the electronic counter in the late fifties, such procedures have almost completely been abandoned. In single crystal diffraction, electronic counters solved the problem of obtaining integrated intensities in a simple and natural way. In other branches of X-ray diffraction, like powder diffraction, scanning counters were introduced, and the use of film was largely confined to problems involving only qualitative intensity observations. However, it is to be noted that in a number of applications, scanning counters suffer from the serious disadvan-

tage that at each position only a small fraction of the diffraction pattern is measured, whereas the complete pattern, or a large part of it, might be recorded with a single film exposure. In powder diffraction the Bragg-Brentano diffractometer was developed, in which this loss of efficiency was compensated by a large gain in intensity by using focussing methods. In other areas, like small-angle X-ray scattering (SAXS), the use of the scanning counter has been justified by the claimed higher accuracy of the recorded data. However, this notion may have been based on intuition rather than on observations. At least, as to the authors knowledge, no considerations or observations which might substantiate such a conclusion, have been published.

Of late, so called-position sensitive counters (PSC's) have appeared on the market, which allow the location of single X-ray photons in one or two dimensions. In general, the introduction of these devices has been a great step forward in the instrumentation of X-ray diffraction. However, as will be discussed in section 5, the present types of PSC's show distinct limitations, because of which in many cases other means of detection may be preferred. In this respect also the film method must be considered as a serious candidate for quantitative X-ray registration. From a publication by Arndt, Gilmore and Wonnacot in 1977 [1], it might already be concluded that film methods are not fundamentally inferior to counter registration.

A further thorough investigation into the properties of film as a detection agent for X-rays was carried out in 1981 by Vonk and Pijpers [2]. In this communication, the results from the latter study are reviewed, and some consequences, which are of practical importance in the application of film methods, are presented.

2. Theoretical Considerations

2.1 Density-Exposure Relations

The action of X-ray on a photographic film is to turn silver bromide particles present in the film, into a state in which they can be reduced by the action of a suitable developer into silver *grains*. In the following, we will indicate such AgBr particles as being *excited*. A relation for the response of a film to X-rays may be derived by assuming that a certain number of photons is needed to excite one AgBr particle. Without loss of generality this number may be taken to be 1, which, according to our own observations, corresponds very closely to the actual situation. As a photon, hitting a silver bromide particle which has been excited before, has no further effect on this particle, an increment of the exposure E by dE photons/unit area causes the number n of excited AgBr particles per unit area to increase by

$$dn = a \frac{n_0 - n}{n_0} dE \quad (1)$$

Here, a is the absorption factor for the X-rays of the AgBr particles in the film, and n_0 is the total number of AgBr particles per unit area. Taking into account the boundary conditions, one finds the following solution of this equation:

$$n = n_0(1 - e^{-aE/n_0}) \quad (2)$$

As during the fixing of the film all non-excited AgBr particles are washed away, Eq.(2) might be used to determine the exposure E from the silver content of the developed film. To this end various analytical procedures, including X-ray fluorescence analysis [3], have been tried, but no practical procedures seem to have emerged. The only method commonly used for registering the effect of X-rays on a film still is to measure the transmission of a beam of visible light with the aid of a densitometer.

The response of a densitometer can be derived from the consideration that the fraction i/i_0 of the light, transmitted by the film, is equal to the fraction of the surface, which in projection parallel to the incident beam, is not covered by silver grains. As the thickness of the emulsion layers in most films is much larger

than the diameters of the individual silver grains, an increment dn of the silver grains may be assumed to correspond to a decrease of the uncovered area, which is proportional to this area, and thus to i/i_0 . Accordingly we find

$$d(i/i_0) = f \frac{i}{i_0} dn \quad (3)$$

where f is the effective surface, covered by one grain. The solution of this equation is

$$\frac{i}{i_0} = e^{-fn} \quad (4)$$

Using for the *optical density* the general expression

$$D = -\log_{10} \frac{i}{i_0} \quad (5)$$

we find from Eq. (4)

$$D = fn/2.3 \quad (6)$$

For obtaining a relation between density and exposure, Eqs. (2), (4) and (6) have to be combined. Introducing a close approximation, one finds

$$\frac{D}{E} = S_0 \left(1 - \frac{D}{2D_{\max}} \right) \quad (7)$$

where

$$S_0 = af/2.3 \quad (8)$$

is the *speed of the film*, and

$$D_{\max} = n_0f/2.3 \quad (9)$$

Here, D_{\max} accounts for the *saturation effect*, which is due to the circumstance that a AgBr particle, if once hit by a photon, can no longer contribute to an increase of the optical density.

From the derivation of Eq.(7) one may conclude that individual films may be characterized by their values of S_0 and D_{\max} . These values may be obtained with the aid of density-exposure scales from plots of D/E -versus- D . Such scales are prepared by exposing the film at different positions to the same X-ray intensity during different times. The X-ray intensity has to be measured separately with the aid of a counter of which the yield for the radiation under consideration has to be known. If, as is often the case, only relative intensity values are to be measured, the value of S_0 need not be determined, and values of E may be taken equal to the corresponding exposure times.

As is generally known, unexposed X-ray films show a spontaneous optical density, which is usually indicated as the *fog*. The value D_F of this density can be related, through Eq. (7), to a virtual X-ray exposure E_F , which would have caused the same density on a film showing no fog at all. We thus may write

$$E = E_{\text{eff}} + E_F \quad (10)$$

where E_{eff} is the actual effective X-ray exposure, which is to be determined.

2.2 Relations Regarding the Accuracy of Film Measurements

The above relations allow us to estimate the standard deviation $\sigma(D)$ of the optical density, corresponding with a certain exposure E . If we assume this deviation to be due to the stochastic nature of the X-ray beam only, we may equate the standard deviation in the number ns of photons, exciting the AgBr particles within a given area s of the film, to $(ns)^{1/2}$. Using Eqs. (6) and (8), we may then derive

$$\sigma(D) = \left(\frac{S_0 D}{as} \right)^{1/2} \quad (11)$$

To investigate the effect of saturation, we want an expression for $\sigma(E)$. Using the general relation

$$\sigma(E) = (dE/dD)\sigma(D)$$

we may obtain, with the aid of Eqs. (7) and (11), the following close approximation:

$$\sigma(Eas) = (Eas)^{1/2} \left(1 - \frac{D}{2D_{\text{max}}} \right)^{-3/2} \quad (12)$$

In this equation, Eas represents the total number of photons, absorbed by both the excited and the unexcited AgBr particles within the area s of the film. The equation shows that at low values of D , the standard deviation in this number, if determined by film methods, equals its square root. This is in agreement with our assumption that the stochastic nature of the X-ray emission process is responsible for the deviations in the measurements. At higher optical densities the saturation effect causes an increase of the standard deviation, as represented by the second factor at the r.h.s. of Eq. (12).

A convenient way of comparing the quality of various detecting systems was introduced by Gruner, Milch and Reynolds [4]. They define the *Detective Quantum Efficiency* DQE as the ratio between the signal-to-noise ratio of the output signal to the one of the input signal. Accordingly it is given by

$$DQE = \left| \frac{S_0}{\sigma(S_0)} \right|^2 / \left| \frac{S_i}{\sigma(S_i)} \right|^2 \quad (13)$$

where S_i and S_0 represent the magnitudes of the input and output signals respectively. In our case, the input signal consists of the number of $E_{\text{eff}}s$ photons, incident on the area s of the film, whereas the output signal corresponds to the value of Es as obtained from D with the aid of Eq. (7), after this is corrected for the fog. Combining Eqs. (11), (12) and (13), we find

$$(DQE)_{\text{film}} = a \frac{E_{\text{eff}}}{E_{\text{eff}} + E_f} \left(1 - \frac{D}{2D_{\text{max}}} \right)^3 \quad (14)$$

It is to be noted that the exposure times, needed to measure a signal with different detectors with the same accuracy using the same effective area s , varies according to $1/DQE$. The value of $DQE = 1$ pertains to an "ideal" detector, which shows no photon losses, and no instrumental background.

Another quantity, also involving the accuracy of the measurements, is the dynamic range of the detector, which can be defined as the ratio between the highest and the lowest exposures which can be recorded with it. For films, the highest limit is usually determined by the performance of the densitometer, which may be made to register optical densities as high as 3-4. At the low intensity side, small signals will tend to get drowned in the fog. From Eq. (12) one may derive for this limiting case the following approximation

$$\frac{\sigma(E_{\text{eff}})}{E_{\text{eff}}} = \frac{1}{E_{\text{eff}}} \left(\frac{E_F}{as} \right)^{1/2} \quad (15)$$

3. Testing of the Theoretical Expressions

3.1 Some Experimental Details

Materials. Tests on Eq. (7) were carried out on 6 different types of film, which were incidentally available to us at the time of the measurements. The films had been stored during different periods of time, so

Table 1 Survey of the films

Nr.	Type of film
1	Agfa-Gevaert Structurix D10
2	Ilford Ilfex 90
3	Kodak Industrex D54
4	Agfa-Gevaert Structurix D7
5	Kodak Industrex AA5
6	Kodak Industrex M5

the fog densities D_F to be quoted below (Table 2) can in no way be considered as being representative. The numbers by which the films are indicated, refer to the types quoted in Table 1.

The procedure for *processing* the films was the same for all types, and consisted of the following steps.

1. Developing for 5 min in Ilford RC51 developer, in a 21 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
3. Fixing at least 10min in a 10% sodium thio-sulphate solution
4. Washing for at least 30 min in running tap water
5. Rinsing with demineralized water
6. Drying

For obtaining the base material, which was used for determining the value of b in Eq. (5), a film was processed, with omission of the developing step.

The *densitometer* which was used for obtaining the optical densities, was of the type to be described in Appendix 1.

Density-Exposure scales were prepared with the monochromatic $\text{Cu K}\alpha$ -radiation, obtained by adjusting a powder diffractometer to the maximum of a broad reflection peak from an arbitrary sample, for which a platelet of polyethylene was used. The film was moved in steps through the position normally taken by the receiving slit, while the exposure times were increased according to an arithmetical progression. The intensity of the X-rays at the position of the film was recorded (after insertion of the receiving slit) with the aid of a proportional counter of known efficiency. The same set-up was used for measuring the absorption factors of the films. At a later stage, a special apparatus for preparing density-exposure scales was developed, which is described in Appendix II.

Uniformly exposed strips of film for *standard deviation measurements* were obtained with the aid of a Weissenberg camera, of which the point collimator was replaced by a slit collimator of 30cm 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 10kV, fell on a flat film mounted on the cart, which made an integral number of double trips during one exposure. After processing, the strips of film were scanned in the

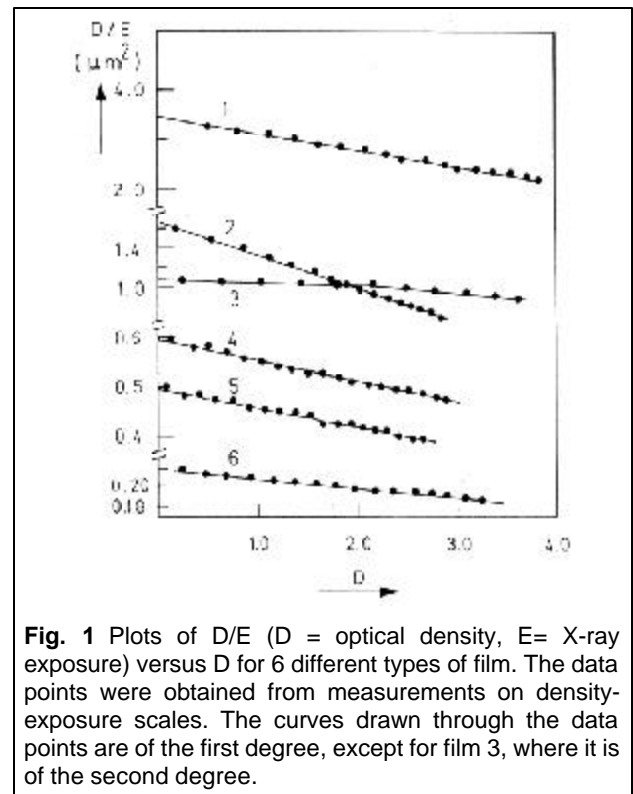


Table 2 Values of various quantities pertaining to six different types of X-ray film.

Type number	a	S_0 (μm^2)	D_{max}	D_F	E_F (μm^2)
1	0.48	3.44	4.3	0.187	0.054
2	0.26	1.67	2.5	0.075	0.045
3	0.53	1.1*	9.2*	0.252	0.229
4	0.39	0.59	6.9	0.139	0.253
5	0.43	0.50	6.2	0.059	0.118
6	0.41	0.22	11.1	0.017	0.077

* These values were obtained by fitting a first-degree curve to the data points; in Fig. 1 a second-degree curve is used.

densitometer so as to give 1000 independent readings, from which the standard deviation was determined.

3.2 Testing of the Density-Exposure Relation [Eq. (7)]

The results of the measurements on the density-exposure scales for the six different types of film are presented in Fig. 1 in the form of plots of D/E -versus- D . This figure shows that in general the linear relationship, predicted by Eq. (7), is well obeyed up to densities of 3-4. Only film 3 seems an exception in that the plot is distinctly curved. In Table 2 the values of S_0 and D_{max} found from these plots, together with the values of a , D_F and E_F , are presented.

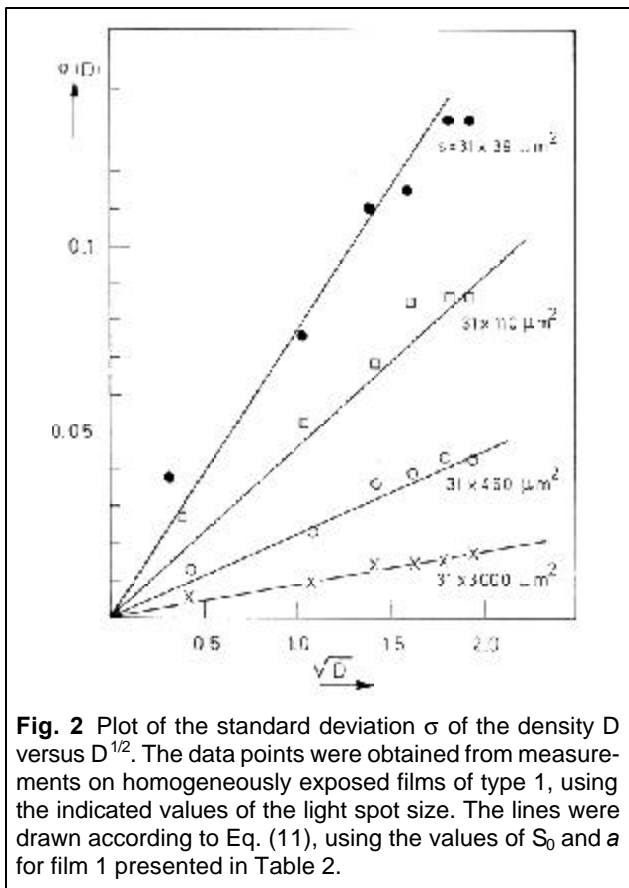


Fig. 2 Plot of the standard deviation σ of the density D versus $D^{1/2}$. The data points were obtained from measurements on homogeneously exposed films of type 1, using the indicated values of the light spot size. The lines were drawn according to Eq. (11), using the values of S_0 and a for film 1 presented in Table 2.

3.3 Testing of the Relation for the Standard Deviation [Eq. (11)]

A comparison between theoretical and observed standard deviations was made for strips of film of type 1, using different sizes of the light spot s in the densitometer. The results are shown in a plot of $\sigma(D)$ -versus $D^{1/2}$ in Fig. 2. Also shown in this figure are the theoretical lines derived from Eq. (11) with the aid of the values of S_0 and a listed in Table 2. Considering that in drawing these lines no parameters were adjusted, we find the agreement with the observed values quite satisfactory. Eq. (11) was derived on the basis of the assumption that the variations in the optical densities are completely due to the stochastic nature of the X-ray emission process. As this equation is found to be obeyed, we may conclude that no other important sources of error are to be considered, and that accordingly in this sense film is a good medium for the quantitative determination of X-ray intensities. This is born out by the $\log(DQE)$ -versus- $\log(E_{eff})$ curves calculated from Eq. (14) for a relatively fast film (nr. 1) and a relatively slow film (nr. 5) shown in Fig. 3. The curves show a broad maximum of which the level is determined by the absorption factor a of the film. At the left hand side the curves fall, because

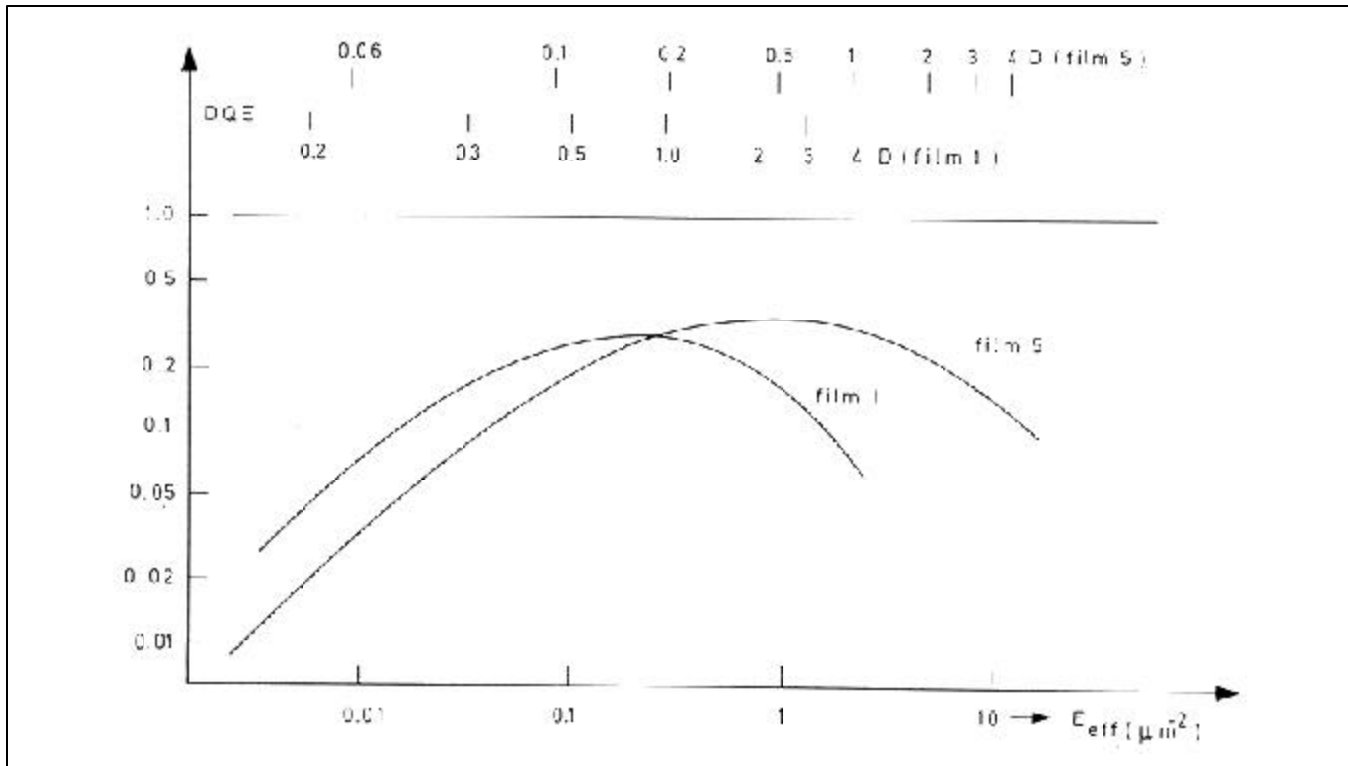


Fig. 3 Plots of $\log(DQE)$ -versus- $\log E_{eff}$ for films 1 and 5, as calculated from Eq.(14) with the values of a , E_F and D_{max} presented in Table 2 and the values of D calculated with the aid of Eq. (7). Also indicated in this figure are the density scales applying to the two films.

of the presence of the fog, and at the right hand side because of the saturation effect. According to Eq. (14) the positions of the curves at the left hand side vary with the virtual fog exposure E_F , and therefore depend on the age of the film. The two films of which the curves are shown in Fig. 3 had been stored during different lengths of time, which probably is the main reason for the divergence of the two curves at the left hand side.

4. Practical Considerations

4.1 Choice of the Type of Film

Of primary importance in the choice of a film for X-ray intensity measurements is the loading of the silver bromide. This determines the absorption factor for the radiation under consideration, which, according to Eq. (14), is proportional to the efficiency of the film. Furthermore, it may be seen from Eq. (9) that a low loading will also lead to a low value of D_{max} , and therefore to a more prominent saturation effect. As can be seen from Table 2, for most commercial films the absorption for Cu $K\alpha$ -radiation is of the order of 0.4-0.5, corresponding to a loading of 3-4mgr AgBr/cm². From Table 2 it furthermore follows that the absorption factor for film nr. 2 is exceptionally low. Accordingly, this type of film, although very well suited for visual inspection, is not to be recommended for intensity measurements. As the determination of the absorption factor of a film by the method described in section 3.1 is a relatively simple matter, this should be undertaken before deciding on the use of any new kind of film.

The second factor determining the behaviour of a film with respect to X-rays is the size of the AgBr particles. From Eqs. (8) and (9) one may deduce that, at a given loading, a small particle size will lead to a relatively low value of the speed S_0 , and a high value of the saturation coefficient D_{max} . Such films are favourable for reaching a high upper limit of exposures, as more X-ray photons can be accommodated before a certain optical density is reached. Comparing the slow film nr. 5 and the fast film nr. 1, for which the optical densities are also indicated in Fig. 3, we find that the ratio of the highest exposures which can be recorded with these two films is about 5-6. Assuming an allowed standard deviation of the lowest signals of 10%, and a densitometer light spot size s of 1 mm², one finds with the aid of Eq. (15) for the dynamic ranges the values of 2260 and 630 for the two films respectively.

From the foregoing it follows, that for quantitative intensity studies slow films are to be preferred over fast ones. Films of the types 4 and 5 mentioned in Table 2, are very suitable, provided the densitometer which is used in scanning the exposures can register relatively small variations of the optical densities. The use of still slower films, like nr. 6 in Table 2, is limited by the deviations in the densitometer response due to scratches and dust, and in general is not to be recommended.

4.2 Correction for the Fog

In Eq. (5) for the optical density, i_0 is the intensity of the light transmitted by the film under consideration, if this does not contain any silver grains. As indicated in section 3.1, such a film can be obtained by fixing it without previous development.

In preparing density-exposure curves, the difficulty arises that the value of E_F , which according to Eq. (10) should be added to the effective X-ray exposure, is not known at the outset of the calculations. However, by making the substitution $D = D_{eff} + D_F$ one may derive from Eq.(7) the following approximation:

$$\frac{D_{eff}}{E_{eff}} = S_0 \left(1 - \frac{D + D_F}{2D_{max}} \right) \quad (16)$$

Thus, from a plot of D_{eff}/E_{eff} versus $D + D_F$, which can be prepared from known experimental data, one may obtain preliminary values of S_0 and D_{max} , which can be used for obtaining E_F from D_F . It is to be noted that Eq. (16) can be used at relatively low values of D only.

In the correct use of film methods, the empty film as discussed above, should not only be used in preparing density-exposure scales, but also in all measurements of optical densities. Though the corresponding procedure is easily feasible, one may accelerate the measurements by equating i_0 in Eq. (5) to the light transmitted by the film at a position where it is fogged, but not has been exposed to X-rays. In this

Table 3 Absorption factor a of silver bromide for different types of radiation.

Film	Type of radiation		
	MoK α	CuK α	CoK α
1	.17	.48	.64
5	.15	.43	.58

case in Eq. (7) $E = E_{\text{eff}}$ and $D = D_{\text{eff}}$, and the observed optical density may be used directly for obtaining the effective X-ray exposure. This procedure involves an approximation, because of which slightly different values of E_{eff} will be obtained. The magnitude of the deviations will increase with the level of the fog density D_F .

4.3 Dependence of Film Response on X-ray Wavelength

This dependence is primarily determined by the value a of the absorption factor of the AgBr particles for the wavelength under consideration. According to Eq. (14), the efficiency of films is proportional to this quantity. The absorption factors for three common types of radiation, calculated for the films nr. I and 5, are presented in Table 3. This shows that one may expect films to be about 3 times less effective for MoK α -radiation, and to be 30% more effective for CoK α -radiation than for CuK α -radiation. The decrease of the absorption factor, occurring at decreasing wavelength, is beneficial, as it reduces the effect of the white radiation on the photographic film.

4.4 The Effect of a Sample Background

The diffraction curves of nearly all samples show a continuous sample background, on which the diffraction phenomena which are to be studied, are superimposed. A special position in this respect is taken by the SAXS curves recorded with the aid of slit collimation, in which case the sample background can be shown to be greatly enhanced with respect to the level obtained with pinhole collimation [2]. In general, if low signals are to be measured, long exposure times are needed to obtain a sufficient signal-to-noise ratio. If thereby the sample background is raised to a level, higher than the one of the fog, the occurrence of the fog will no longer be the limiting factor in obtaining the desired accuracy. This situation frequently occurs in the SAXS curves from particles in solution, or from solid polymers containing an appreciable fraction of amorphous material. Thus, film methods are specially suited for the registration of curves of such samples, if recorded with slit collimation.

4.5 The Scaling of Different Exposures

As indicated in section 4.1, the dynamic range of film measurements may be quite appreciable. If however it is insufficient for recording a complete scattering pattern, two or more exposures may be obtained, using different exposure times. The exposures may be scaled in such regions of the scattering pattern where two subsequent exposures show

intensity levels entailing relatively small errors. It was however found that if the optical densities are converted to X-ray intensities in the correct way, and if an X-ray generator of good stability is used, this matching is not necessary as the ratio of the two exposure times may be used as the scaling factor. In order to avoid any errors due to differences in processing, the two exposures should preferentially be made next to each other on one piece of film. The same precaution is needed if, as is common in SAXS, the exposure of an external standard is required for putting the X-ray intensities on an absolute scale. (It is noted that the use of the multiple film technique, which has been applied in single crystal diffractometry, does not lead to correct results if the incoming radiation is not strictly monochromatic).

4.6 Requirements Put to the Densitometer

The success of the film method depends to a large extent on the correct operation of the densitometer, which has to meet the following requirements.

1) In view of the circumstance that the relative variance of film measurements is inversely proportional to the effective light spot size s on the film (this follows directly from Eq. (12)), this size should be variable, so that it may be increased as far as the resolution allows. If the densitometer is to be used for powder patterns, or for slit-collimated SAXS patterns, the light spot on the film should be line-shaped, with a maximum height of the order of 1 cm.

2) Provisions must be made for allowing densities up to values of 3-4 to be read. This can be achieved in instruments having two apertures, of which one is in the incident light beam and the other in the transmitted beam. The configuration is explained more fully in Appendix I.

3) In view of the use of slow films, as advocated in section 4.1, small variations in the density level are significant. Accordingly, the electronics must allow density variations of the order of 0.001 to be read.

It seems that of the densitometers which are commercially available, only those of the drum scanning type may meet these requirements, provided the scanning facility is used for increasing the effective light spot size. Other types of available densitometers may be remodelled, for which those, which were originally meant for single crystal work, in some cases are specially suitable. Alternatively, a good densitometer can be composed in a relatively easy way from standard optical and electronic components. In Ap-

Table 4 comparison of various X-ray detectors.

Type of detector	Instrum. background	Upper detection limit	Resolving power	Absorption factor	Relative width of pulse energy distribution
<u>Scanning counters</u>					
Proportional (gas-filled)	0	10 ⁶ ph/s	—	0.65	0.3
Scintillation	1-10 ph/s	10 ⁷ ph/s	—	0.9	0.5
Li-doped Si	0	2000 ph/s (c)	—	1	0.02
<u>1-Dim. PSC's</u>					
Gas-filled	0	10 ⁴ -10 ⁵ ph/s	50-400 μm	0.65	0.3
Diode array	(a)	unlimited	25 μm	0.5	—
<u>2-Dim. PSC's</u>					
Gas-filled	0	10 ⁴ -10 ⁵ ph/s	1-2 mm	0.65	0.3
Vidicon	(b)	(b)	0.3 mm (d)	1.0	—
Film	0.05 ph/μm ²	10 ph/μm ²	2 μm	0.4-0.5	—

(a) Increases with number of scanning cycles; 0.05 ph/μm² is a typical value.

(b) Instrumental background as well as the saturation dose differ widely with the type of vidicon employed, and with experimental conditions.

(c) Larger counting rates primarily affect the width of the pulse energy distribution.

(d) The quoted value applies to the vidicon counter described by Milch, Gruner and Reynolds [8].

pendix I indications for constructing such an instrument are presented.

5. Comparison of Detecting Systems

In choosing a detecting system, many other factors than just the performance are usually of importance. As such one may mention the reliability, the ease of use, the degree of automatization which it allows, the maintenance required, and last but not least, the price. Here, we will leave out considerations regarding such arguments, but even then a comparison is difficult to make, as the various instruments show limitations of different kinds. In Table 4 some characteristic values of various parameters are quoted for different detectors; it should however be stressed that these figures are meant to give an indication only, and in no way can be considered as being representative. Furthermore, it is to be emphasized that, specially in the area of the PSC'S, developments are under way which can be expected to lead to important improvements.

The proportional and the scintillation scanning counters, mentioned in Table 4, doubtless are the most perfect types of detectors with respect to efficiency and dynamic range. Their DQE-values are of the order of their absorption factors for a very large range of intensity levels. The Li-doped Si detector has the great advantage of a very narrow energy distribution of the outgoing pulses, and thus is very suitable for applications in which there is insufficient monochro-

matization of the primary X-ray beam. Their main disadvantage is the necessity of keeping the detector cooled with liquid nitrogen even if it is not in operation. For a review of these devices, see ref. [5].

The time loss involved in the use of scanning counters has led to the introduction of PSC'S, of which those of the gas-filled type are the most common. As these counters show almost no instrumental background, they are very efficient in the detection of low signals, but their response to high intensities is hampered by their relatively long dead times. Part of this drawback is compensated by the circumstance that the dead time affects the losses at all data points in the same way, and thus does not influence the shape of a diffraction pattern. However it seems that because of the effect of near-coincidences and the occurrence of space charges [6] the count rate is still rather limited. The diode array counter does not suffer from these limitations, but seems to be encumbered by a relatively high noise, of which the level increases with the total dose of X-rays to which the counter has been exposed before. More details on this type of counter may be found in ref. [7].

The two-dimensional counter of the vidicon type still is in its infancy, and systematic information on its performance and its limitations is difficult to collect. They seem to work well in the recording of intensity data from protein single crystals [8], as well as in the

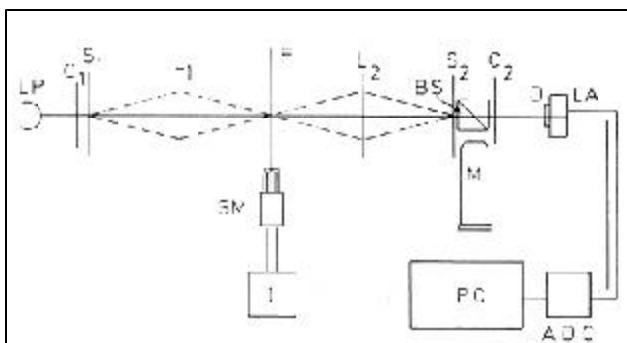


Fig. 4 Scheme of densitometer for the processing of photographic films. LP = lamp, C₁, C₂: condensor lenses, S₁, S₂: apertures, L₁, L₂: lenses, F=film, BS=beam splitter, D=detector, LA=logarithmic amplifier, ADC=analog-digital converter, PC=computer, I=interface, SM=stepping motor.

area of SAXS [9]. in the latter type of application, also 2-dimensional counters of the gas-filled type are in use [10]. Because of their poor resolving power, these counters however have to be applied in cameras of large dimensions. Here, a sample-to-counter distance of 10 m is not exceptional. As such, these counters are useful in combination with X-ray synchrotron sources, but again their relatively low maximum counting rate is a drawback.

The circumstance that film is not limited as to intensity values, but rather to exposures, makes it a good candidate for use with high intensity sources. However, mechanical provisions for the rapid changing of films must be provided for.

6. Conclusions

Films may serve well as two-dimensional detectors for the quantitative registration of X-ray intensities, provided they are processed with the aid of a good densitometer. From their DQE values it follows that at best they are but slightly inferior to the most common types of scanning counters. At low exposures, signals on film tend to get drowned in the fog, whereas at high exposures the use of films is limited by the maximum optical density, which can be processed (3-4). However, their dynamic range may still cover 3 decades. In this respect fine-grained films are better than coarse-grained ones. If signals are to be recorded which are superimposed on a relatively high sample background, films are less at a disadvantage with respect to scanning counters. Furthermore, high intensities may be measured without instrumental losses by simply reducing the exposure time. Combining these arguments with other advantages of the film method (reliability of performance, the

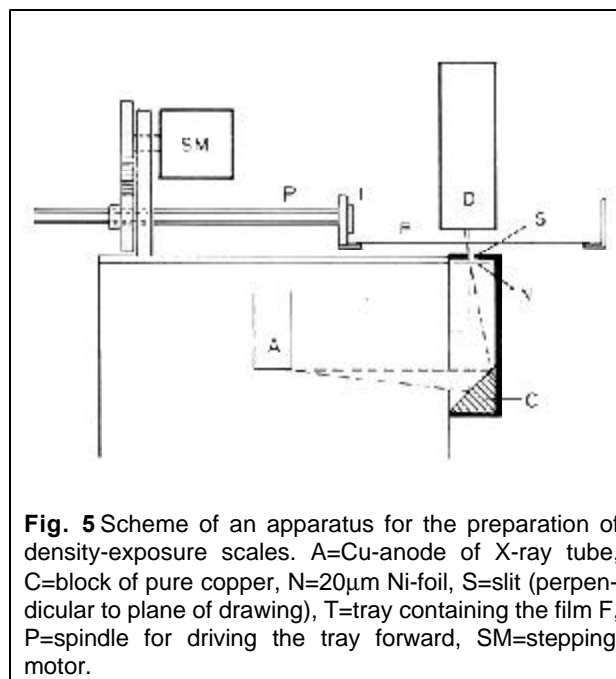


Fig. 5 Scheme of an apparatus for the preparation of density-exposure scales. A=Cu-anode of X-ray tube, C=block of pure copper, N=20 μ m Ni-foil, S=slit (perpendicular to plane of drawing), T=tray containing the film F, P=spindle for driving the tray forward, SM=stepping motor.

simple and elegant way of obtaining a permanent record, the little maintenance required, the low cost, etc.) one may consider film as a good candidate for X-ray intensity measurements.

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APPENDIX I

The Construction of a Densitometer

The lay-out for a densitometer suitable for the quantitative registration of X-ray intensities from films is presented in Fig. 4. The light beam from the lamp LP passes through an aperture S₁, of which an image is formed by the lens L₁ on the film F. This image is focussed by the lens L₂ at the position of the second aperture S₂. The images of S₁, S₂ and the film F can be viewed simultaneously through the beam splitter BS by the microscope M. The light beam also falls on photo diode D, of which the electric signal is fed to a logarithmic amplifier LA. This is coupled through an analog-digital converter ADC to a computer PC, which also takes care of the transport of the film with the aid of the stepping motor SM, and of the storing of the data. The rays of light emanating from the filament of the lamp are focussed by the condenser

C_1 at the position of L_1 , next by the lens L_2 at a position between L_2 and S_2 , and finally by the condenser S_2 on the detector D. At this position, the filament is imaged approximately at true size.

The second aperture should coincide closely with the image of the first aperture. Here, a small margin is allowed, which serves to reduce the sensitivity of the instruments to drifts in the alignment. The function of the second aperture is to prevent any light, not contributing to the image of S_1 at the position of S_2 , from reaching the detector. Such undesired illumination can be observed by viewing the image of S_1 through the microscope with aperture S_2 removed. It will be seen that the image of S_1 is surrounded by a relatively intense patch of light, probably resulting from light scattering at the edges of aperture S_1 . The aperture S_2 also serves to keep any stray light from the surroundings out of reach of the detector.

APPENDIX II

Apparatus for Making Density-Exposure Scales

A simple apparatus for making density-exposure scales, which can be used for obtaining values of S_0 and D_{\max} (see Eq. (7)), is sketched in Fig. 5. The X-rays from a vertically positioned X-ray tube with Cu anode A, operated at 20 kV, fall on a block of pure copper C. The fluorescent and diffracted rays pass through a 20 μm nickel foil N, and a slit S of approximately 0.5 mm width. They next fall on the wrapped film F, which is positioned in a small cart T of which the greater part of the bottom has been removed. The cart is moved horizontally in the direction perpendicular to the direction of the slit S with the aid of a stepping motor SM. This is programmed with the aid of a microcomputer to make the cart go forward in a linearly accelerated motion, which leads to a variation of the optical density of the developed film such as

occurs in an optical density wedge. The values of S_0 and D_{\max} are obtained from an analysis of the optical density as a function of the position on the film, for which purpose a program was written for the computer serving the densitometer. The absolute intensity of the X-ray beam, needed in the calculation of S_0 can be determined with the aid of the proportional counter D, after removing the film. If only relative intensities are to be measured by the film method, the measurements involving the detector may be left out.

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