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**The effects of surface roughness and porosity on X-ray integrated intensities for carbonyl iron powder.** BY T. PAAKKARI AND P. SUORTTI, *Department of Physics, University of Helsinki, Helsinki 17, Finland*

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The possibility of correcting X-ray integrated intensities for the effects due to sample porosity and to surface roughness is studied by making use of fluorescent radiation from the sample. Corrections of the values of atomic scattering factors recently measured by Paakkari & Suortti have proved that a small amount of reduction from the free atom values found previously does not seem to exist, or at least it is comparable to experimental errors.

In a recent absolute measurement of the atomic scattering factor of iron (Paakkari & Suortti, 1967) the effects due to porosity and surface roughness were concluded to be negligible as a result of observations of the variation of the integrated intensity of the 110 reflexion with the apparent density of the sample. The purpose of this paper is to point out that the fact that these results were independent of packing density and surface treatment was partly due to the effect of preferred orientation rather than to the absence of the effects of porosity and surface roughness.

The intensity of fluorescent X-rays is not affected by preferred orientation. Therefore its measurement is a suitable means for studying granularity effects. This technique is, strictly speaking, applicable only if the absorption coefficients for the incident,  $\mu$ , and fluorescent,  $\mu^*$ , radiation are identical (de Wolff, 1956). The effects due to porosity and surface roughness depend on the fact that on the average the emergent absorption path lengths are longer than the corresponding entering absorption path lengths. By assuming an exponential distribution for such a difference in the path lengths, DeMarco & Weiss (Weiss, 1966) obtained an expression for the factor  $R$  for the reduction of a Bragg intensity in the case when the absorption coefficients are different:

$$R = 1 - \frac{\mu + \mu^*}{2\mu^*} (1 - R^*), \quad (1)$$

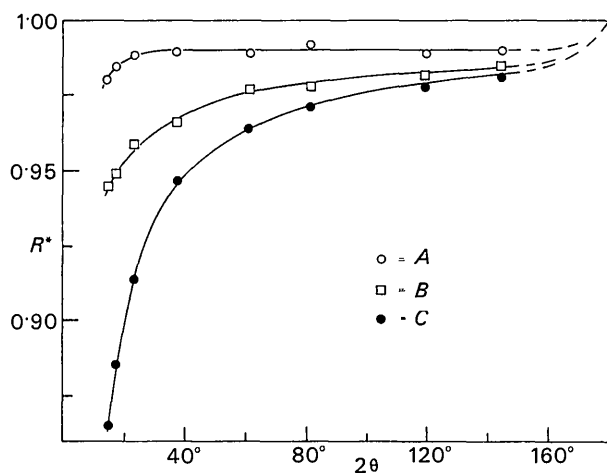


Fig. 1. The ratio  $R^*$  of the fluorescent intensity from powder samples to that from a polished bulk sample as a function of the scattering angle. The powder samples were pressed at 1000  $\text{kp}\cdot\text{cm}^{-2}$ . *A*, pressed against a polished steel plate; *B*, like *A* but the surface was treated with fine emery papers; *C*, against a plate with random roughness of 20–40  $\mu$ .

where  $R^*$  is the ratio of the fluorescent intensity from a porous sample to that from a polished bulk sample.

Measurements of fluorescent intensity were carried out under similar experimental conditions to the previous measurements of Bragg intensity, except that monochromatic Mo  $K\alpha$  was used as exciting radiation and a pulse height analyser was used so as to accept only Fe  $K$  components. All measurements were made relative to a well polished iron plate of high purity. This plate was also used for checking whether the fluorescent intensity is independent of Bragg angle by a continuous scan and with a monochromator after the sample.

Fig. 1 gives the measured values of  $R^*$  for three different samples, each of which was pressed with 1000  $\text{kp}\cdot\text{cm}^{-2}$  and made of the same carbonyl iron powder as used for determining the absolute scale. The relative density of these samples was 0.55. Sample *A* was pressed against a well polished steel plate, and measurements were made on this untreated, very smooth, surface. The fluorescent intensity from this sample shows angular dependence only in the range  $2\theta < 25^\circ$ . The surface of sample *B* was treated with fine emery papers and sample *C* was pressed against a plate exhibiting irregular roughness of about 20–40  $\mu$ . The results show that the effect due to the rough surface is strongly dependent on angle (cf. de Wolff, 1956).

The validity of equation (1) can be studied by comparing integrated intensities from samples which possess different porosity and surface roughness but similar preferred orientation. Samples *A* and *C*, which differ mainly only in surface roughness, were chosen for this purpose. The ratios,  $I(A)/I(C)$ , measured for four low order reflexions with correction by Fig. 1 and equation (1), are given in the third column of Table 1. All deviations from unity are within the experimental error (about  $\pm 1\%$ ) which supports the application of equation (1) for present case.

The values of  $R^*$  for sample *B* can be used to correct the experimental Bragg intensity data given by Paakkari & Suortti (1967), because it is identical with one of the samples

Table 1. *The values of absolute atomic scattering factors of iron  $f_{\text{PS}}$ , given by Paakkari & Suortti (1967), corrected for the effects of granularity after Fig. 1 and equation (1)*

The corrected values are in the column  $f_{\text{PS}}^{\text{c}}$ . The theoretical values  $f_{\text{th}}$  are taken from the paper of Freeman & Watson (1961).

<i>hkl</i>	$2\theta(^{\circ})$	$I(A)/I(C)$	$f_{\text{PS}}$	$f_{\text{PS}}^{\text{c}}$	$f_{\text{th}}$
110	20.2	1.003	18.19	18.50	18.51
200	28.7	1.010	15.19	15.41	15.27
211	35.4	1.005	13.01	13.17	13.13
220	41.1	0.992	11.60	11.74	11.61
310	46.2	—	10.47	10.58	10.49

(B) leading to the same value of the absolute scale obtained in that work and is also identical with the sample on which the relative measurements were carried out. It is worth noting that the pressure values given in that work were the values of total forces on a sample of area of 2 cm<sup>2</sup>. The corrected values,  $f_{ps}^c$ , are given in Table 1. As the result of the correction, the small amount of reduction which was found in the previous study does not seem to exist, or at least it is comparable to the experimental errors.

A careful treatment of the effects of porosity and surface roughness is important in order to give more reliability to the experimental values of X-ray structure factors obtained

with powders. An effort to correct for these effects by a parameter determined by measurements of fluorescent intensity from copper powder samples of different particle size is in progress.

#### References

- FREEMAN, A. J. & WATSON, R. E. (1961). *Acta Cryst.* **14**, 231.  
 PAAKKARI, T. & SUORTTI, P. (1967). *Acta Cryst.* **22**, 755.  
 WEISS, R. J. (1966). *X-Ray Determination of Electron Distribution*. Amsterdam: North-Holland Publishing Co.  
 WOLFF, P. M. DE (1956). *Acta Cryst.* **9**, 682.

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**Simplified method of computing centroids of X-ray profiles.** By JOHN S. THOMSEN, *Department of Physics, The Johns Hopkins University, Baltimore, Maryland 21218, U.S.A.* and F. Y. YAP, *Department of Physics, Wilson College, Chambersburg, Pennsylvania 17201, U.S.A.*

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One definition employed by crystallographers in fixing the centroid of an X-ray diffraction profile has previously involved in its application the use of successive approximations. A simplified method, sufficiently accurate to eliminate such iterations in most cases, is given, based on the Thomsen & Yap analysis of statistical errors in centroid, median, and peak. Certain differences between the above error analysis and Wilson's recent work are discussed briefly.

Crystallographers have frequently employed the centroid of experimentally observed diffraction profiles in the determination of crystal grating constants (Pike & Wilson, 1959; Taylor, Mack & Parrish, 1964). From a mathematical standpoint it would be desirable to deal with the centroid of the entire profile, *i.e.* with integration limits  $\pm\infty$ ; in this case, the convolution theorem for the addition of centroids would be rigorously applicable. In practice, of course, the use of some finite truncation limits is unavoidable.

Taylor, Mack & Parrish considered several possible conventions for defining such limits and recommended the following: An angular range which is large compared with the width of the aberration functions is selected and located symmetrically about the centroid of the observed curve to establish the truncation range. Since this centroid position is obviously not known *a priori*, they suggest the use of successive approximations.

In the present note we describe a simplified procedure which usually eliminates the need for any iterations. We have recently completed a comprehensive analysis of statistical errors in various possible wavelength criteria – centroid, median, and peak (Thomsen, 1965; Wilson, Thomsen, & Yap, 1965; Thomsen & Yap, 1968). The simplified technique for locating the centroid constituted a relatively minor part of the rather lengthy Thomsen & Yap paper. Hence it seems useful to give a slightly modified derivation here.

Let us denote the abscissa variable (wavelength, energy, or angle) by  $v$  and the ordinate (counts or intensity) by  $f(v)$ . We will take the initial guess (zeroth approximation) for the centroid of the truncated profile as the origin of  $v$ . Let the result of the first iteration (first approximation) be  $c_1$  and the true centroid position be  $c$ . The specified truncation range will be taken as  $2V$ ; initially this range is simply  $-V \leq v \leq V$ . Thus the first approximation  $c_1$  is given by

$$c_1 = \frac{\int_{-V}^V vf(v)dv}{\int_{-V}^V f(v)dv} \quad (1)$$

The true centroid is defined in terms of the range  $c - V \leq v \leq c + V$ , which involves the as yet unknown position  $c$ . The integrand in the denominator of equation (1) is always positive and is relatively small for large  $v$ ; hence the denominator will be only slightly affected if the range of integration is translated by the small displacement  $c$ . On the other hand, the numerator will be quite sensitive to such a shift; in fact it will differ from zero only because  $c \neq 0$ , *i.e.* only because of the inaccuracy of the initial guess. Thus, with a slight approximation, we may rewrite equation (1) as

$$c_1 \approx \frac{\int_{c-V}^{c+V} vf(v)dv}{\int_{c-V}^{c+V} f(v)dv} - \frac{\int_V^{c+V} vf(v)dv - \int_{-V}^{c-V} vf(v)dv}{\int_{-V}^V f(v)dv} \quad (2)$$

The first term on the right hand side is, by definition, the true centroid  $c$ . Thus, with an obvious additional approximation, we may rewrite the above expression as

$$c_1 \approx c - rc, \quad (3)$$

where

$$r \equiv \frac{V[f(V) + f(-V)]}{\int_{-V}^V f(v)dv} \quad (4)$$