X-ray Powder Diffractometry of Small (20mg to 1μg) Samples Using Standard Equipment

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Calculations of the diffraction intensities from a small specimen on a counter diffractometer show that, with a 10–20 mg specimen, the intensities should be 50% or more of those obtained from a normal specimen. Observed values are in reasonable agreement with the calculations. With small quantities the strategy is to disperse the sample evenly as a fine powder over the whole irradiated area. This is especially important at the lower diffraction angles. A glass support is usually suitable. With specimens < 1 mg in weight dispersion difficulties can be eased by mixing with diamond powder, and background scattering can be considerably reduced by using a single crystal as a support. The lower limit of detection of quartz by this method has been shown to be probably <1 μg. Quantitative estimates of 10% quartz in a few milligrams of sample and crystallite size measurements on 50 μg of nickel oxide are examples of work with these experimental arrangements.

Introduction

Small quantities of materials are usually examined by photographic techniques. Debye–Scherrer cameras can examine ~5 μg quantities while improvements in the recorded patterns can be obtained by using either Guinier focusing cameras or the higher X-ray flux densities obtained with fine-focus X-ray sources or X-ray focusing devices such as the toroidal mirror. Although times can be reasonably short with the high-flux methods the signal/noise ratio recorded on the film is often simply not great enough for quantitative work via a microdensitometer.

The purpose of this paper is to show the important parameters involved in counter-diffractometry work on small specimens and to describe the experimental techniques adopted.

Calculation of diffracted intensity

Consider an incident beam of intensity $I_0$ falling on to a diffractometer powder specimen at an angle $\theta$. The intensity of incident radiation, $I_1$, on a specimen element, thickness $dt$, situated at a depth $t$ below the surface will be given by:

$$I = I_0 \exp \left( -\frac{\mu t(1-v)}{\sin \theta} \right)$$

where

$\mu =$ linear absorption coefficient;

$v =$ fraction voidage of material in specimen.

A fraction $1/m$ of this radiation will be diffracted by the specimen element and the emergent intensity of the beam from the surface of the specimen will be:

$$I = \frac{1}{m} I_0 \exp \left( -\frac{2\mu t(1-v)}{\sin \theta} \right).$$

The total diffracted intensity for a specimen of thickness $t$ will thus be:

$$I = \int_{0}^{t} \frac{1}{m} I_0 \exp \left( -\frac{2\mu t(1-v)}{\sin \theta} \right) dt$$

where

$$\int_{0}^{t} \frac{1}{m} I_0 \exp \left( -\frac{2\mu t(1-v)}{\sin \theta} \right) dt$$

For an infinitely thick specimen $I_\infty = \frac{1}{n} I_0$.

It is more convenient to express this in terms of specimen weight. If $L'$ is the specimen length and $B$ the breadth, then the weight, $W$, is given by:

$$W = L' B t (1-v)$$

i.e.

$$I_t = \frac{1}{n} I_0 \left[ 1 - \exp \left( -\frac{2\mu W}{L' B \sin \theta} \right) \right]$$

where

$\mu =$ mass absorption coefficient, $\frac{\mu}{\rho}$.

Comparing this with an infinitely long and thick specimen, the percentage relative intensities are:

$$\frac{I_t}{I_\infty} = 100 \left[ 1 - \exp \left( -\frac{2\mu W}{L' B \sin \theta} \right) \right].$$

Errors could arise in practice when using this expression with very low-absorption specimens: the defocusing and specimen holder cut-off effects at low angles would be important in these cases.

The length of the intercept of the specimen plane with the X-ray beam is given by:

$$L = \frac{R \Delta}{\sin \theta},$$

where $R$ is the diffractometer radius and $\Delta$ is the beam divergence.

The length from which diffraction will occur will depend on the relative values of $L$, the beam intercept,
$L'$, the small specimen length, and $L''$, the normal 'infinite' specimen length (greater than $L'$, usually about 2 cm). Assuming that $B$ is constant, the total incident X-ray flux will depend upon these relative lengths and three cases arise:

(i) at low angles $L > L'' > L'$;
(ii) at medium angles $L'' > L > L'$;
(iii) at higher angles $L'' > L' > L$.

Equation (1) must thus be modified since the intensities $I_t$ and $I_\infty$ [case (i)] or $I_t$ [case (ii)] would be reduced, giving:

\[
\frac{I_t}{I_\infty} = \frac{100L'}{\text{Mid}|L'',L',L|} \left[1 - \exp\left(-\frac{2\mu^*W}{LB \sin \theta}\right)\right] (2)
\]

where \(\text{Mid}|L'',L',L|\) represents the middle value of the three lengths.

Curves from equation (2) for silicon, calcite and urea are shown in Figs. 1–3. In these figures $I_\infty$ represents the intensity from the normal diffractometer specimen 2 cm long; $R$ is taken as 17.2 cm and a 1° divergence slit has been assumed. The curves show that reasonable diffraction intensities should be obtained from 10–20 mg specimens and that the order of intensities to be expected from specimens of 0.1 mg weight are a few percent of the normally observed intensity. Also, they show that when specimen quantities are small the important point is to fill the whole area of the incident X-ray beam. This criterion is important at low angles and must be satisfied in preference to Alexander & Klug's (1948) criterion of minimum thickness if maximum diffraction intensity is to be achieved.

When considering how to disperse a small quantity of material over a surface, thought must be given to specimen preparation. The ideal dispersion can be considered as being a monolayer of close-packed spheres. The weight (in mg) of such a monolayer to cover 1 cm$^2$ is given by:

\[
W = 0.121 \rho q
\]

where \(r = \text{sphere radius in } \mu m\)

and \(\rho = \text{density of sphere in } g \text{ cm}^{-3}\).

Examples of the necessary sphere radii are:

- silicon: $\rho = 2.33$, $W = 1 \text{ mg}$, $r = 3.5 \mu m$;
- urea: $\rho = 1.33$, $W = 1 \text{ mg}$, $r = 6.2 \mu m$.

Hence for specimens < 1 mg the particle diameters must be <10 $\mu m$ for complete coverage and must be <1.0 $\mu m$ for complete coverage at 100 $\mu g$. Above 1 mg the crystallites, although not necessarily the particles, would

![Fig. 1. Diffraction intensities from thin silicon specimens ($\mu^* = 60$ for Cu K$\alpha$). — Calculated values. ⋄ Observed values for 9 mg specimen, 2 cm long. ⋄ Observed values for 10.5 mg specimen, 2 cm long.](image-url)
be less than 5 μm to ensure reproducible diffraction intensities.

**Experimental**

The work was carried out with a Philips PW 1050 goniometer using Cu K radiation, a proportional counter and pulse-height discrimination.

For relatively large amounts of specimen, say 10 mg, a stainless steel specimen holder with a recess of about 2 × 1 cm, similar to that of the standard Philips specimen holder but with an integral floor, was used. The recess depth was ~1 mm. This could be reduced by the insertion of glass sheets of various thicknesses to give a choice of specimen thicknesses.

For quantities less than about 1 mg the background count from the glass becomes serious and it was found to be better to disperse the specimen over a crystal surface. Single crystals of natural fluorite, cut parallel to (100) and (410) planes, the latter so that no X-ray reflexions occurred, were used. The background count was reduced to 5–10 c.p.s. with the (410) crystal although there were a few sharp weak peaks due to inclusions over the range 25–85° 2θ. Subsequently, polished synthetic crystals of fluorite, previously used as infrared windows, were found better because of the absence of impurities and the fact that the polished surface helped specimen dispersion and removal.

With microgram quantities of material, dispersion difficulties were eased by mixing the finely divided specimens with a few milligrams of powdered diluent. Diamond is very satisfactory since it has a low mass absorption coefficient, gives a low background and only a few diffraction lines. Diamond grinding paste is readily available in standard particle size ranges. For comparisons with the calculated intensities the specimen on the single-crystal face was weighed, then the diamond powder on the crystal on top of the specimen was weighed and dispersed to give a uniform coating over the crystal.

In all cases, when non-standard specimen mounts are used, care must be taken to ensure that the diffraction geometry is preserved, this being checked and corrected if necessary by the use of an internal standard.

**Results**

1. **Comparison of calculated and observed intensities**

Four different specimens were used, all being supported on glass slides. The diffraction intensities from these small specimens were compared with those from

![Fig.2. Diffraction intensities from thin calcite specimens (μ* = 71 for Cu Kα). — Calculated values. ⊙ Observed values for 23 mg specimen, 2 cm long.](image-url)
standard 2 cm long specimens. Peak heights were used except in the case of urea where the low absorption resulted in the diffraction lines from the thick specimen being much broader than those from the thin specimen and the product of the peak height and half-breadth was used instead. The specimens were as follows.

(a) Silicon
Carefully sieved to \( \leq 15\mu m \) particle size. 9 mg weight, 2 cm long, 40\( \mu m \) thick.

(b) Silicon
Particle size 5–20\( \mu m \), 10.5 mg weight, 2 cm long, 60\( \mu m \) thick.

The results for these two samples are shown in Fig. 1.

(c) Calcite
Particle size 5–10\( \mu m \), 23 mg weight, 2 cm long, 60\( \mu m \) thick. The results are shown in Fig. 2.

(d) Urea
Particle size \( \leq 37\mu m \), 19 mg weight, 2 cm long, 60\( \mu m \) thick. The results are shown in Fig. 3.

The accuracy of the measurements shown in Figs. 1–3 is estimated as about 5–10%.

2. Lower limit of detection

5.6\( \mu g \) of quartz (\( \leq 15\mu m \)) and 72\( \mu g \) of diamond (extracted from 14\( \mu m \) paste) were weighed on to a (100) face of a natural fluorite crystal, mixed and dispersed over a 1 cm square with ethylene glycol. After drying, the 10\( 10 \) quartz line was step-scanned using Cu K\( \alpha \) radiation and counting for 1000 sec at steps of 0.01° 2\( \theta \). A typical profile is shown in Fig. 4. With these con-
Table 1. Quantitative quartz determinations (8.8 wt. %)

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Background (c.p.s.)</th>
<th>Peak heights above background (c.p.s.)</th>
<th>Estimated wt. % quartz</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Total weight = 2.6 mg</td>
<td>123</td>
<td>3.34 Å quartz 491</td>
<td>10.0</td>
</tr>
<tr>
<td>Weight of quartz = 0.23 mg</td>
<td>112</td>
<td>3.14 Å silicon 408</td>
<td></td>
</tr>
<tr>
<td>Cu Kα radiation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Total weight = 0.35 mg</td>
<td>166</td>
<td>3.34 Å quartz 70</td>
<td>10.0</td>
</tr>
<tr>
<td>Weight of quartz = 0.03 mg</td>
<td>151</td>
<td>3.14 Å silicon 57</td>
<td></td>
</tr>
<tr>
<td>Cu Kα radiation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. Total weight = 0.35 mg</td>
<td>470</td>
<td>3.34 Å quartz 147</td>
<td>8.8</td>
</tr>
<tr>
<td>Weight quartz = 0.03 mg</td>
<td>416</td>
<td>3.14 Å silicon 136</td>
<td></td>
</tr>
<tr>
<td>Cu Kα radiation</td>
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</table>

Table 2. Crystallite size measurements on 50 μg specimen of nickel oxide

<table>
<thead>
<tr>
<th>hkl</th>
<th>Background (c.p.s.)</th>
<th>Peak height above background (c.p.s.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>37</td>
<td>19</td>
</tr>
<tr>
<td>220</td>
<td>41</td>
<td>8</td>
</tr>
</tbody>
</table>

Conclusions

1. Expressions derived for the diffracted intensities from thin specimens show that powdered silicon specimens of about 10 mg weight can give, on a diffractometer, 50% or more of the diffracted intensity that would be expected from a normal 'thick' specimen. Also, similar samples of about 1 mg would give 10-30% of the normal intensity. Observed values for a 9 mg silicon specimen agree reasonably with the calculated values. Observed values from materials of different absorption coefficients are also in reasonable agreement with the calculated values.

2. For maximum diffraction intensity at any angle it is important to ensure that the whole of the available incident-beam area is filled. This becomes important at low diffraction angles when thickness must be sacrificed in order to obtain area coverage.

3. For samples of 1 mg weight or less a suitable experimental arrangement has been found to be to dilute the sample with diamond powder extracted from diamond grinding paste and disperse it over a single crystal face such as a fluorite (410) face. This gives a very low background and should enable sub-microgram quantities to be examined.

4. Quantitative measurements of the amount of quartz in a few milligrams of sample are satisfactory at a quartz level of ~10%.

5. Crystallite size measurements are satisfactory on NiO samples of weight ~50 μg.

Reference