

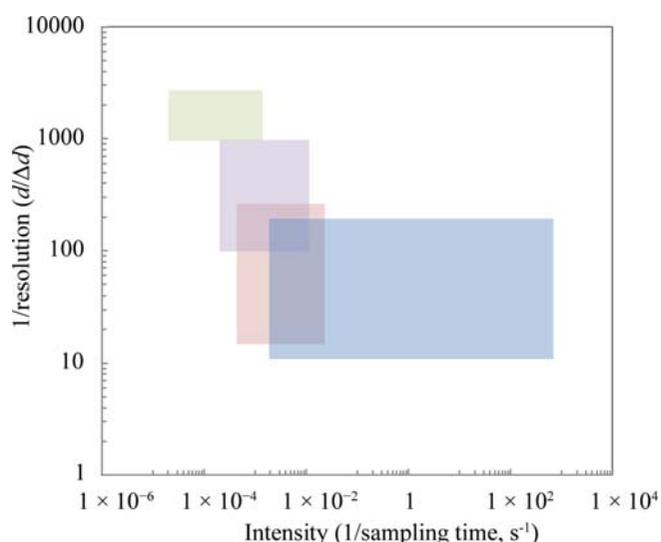
2. INSTRUMENTATION AND SAMPLE PREPARATION

Table 2.3.5

Advantages of CW and TOF instruments (modified from Kisi & Howard, 2008)

CW	TOF
(1) Incident beam may be essentially monochromatic, in which case the spectrum is well characterized	(1) The whole incident spectrum is utilized, but it needs to be carefully characterized if intensity data are to be used
(2) Large d -spacings are easily accessible for study of complex magnetic and large-unit-cell structures	(2) Data are collected to very large Q values (small d -spacings)
(3) Can fine tune the resolution during an experiment	(3) Few cold neutron instruments are available for study of complex magnetic and large-unit-cell structures
(4) More common	(4) Resolution is constant across the whole pattern
(5) Peak shapes are simpler to model	(5) Very high resolution is readily attained by using long flight paths
(6) Absorption and extinction corrections are relatively straightforward	(6) Complex sample environments are very readily used if 90° detector banks are available
(7) Data storage and reduction is simpler	(7) Simpler to intersect a large proportion of the Debye–Scherrer cones with large detector banks
(8) Extremely rapid data collection and stroboscopic measurements are feasible	(8) Very fast data collection is feasible
(9) Engineering diffractometers are very well suited for strain scanning in complex objects	(9) Engineering diffractometers use an extended diffraction pattern, ideal for <i>in situ</i> loading and/or heating
(10) Texture is straightforward to measure on engineering diffractometers	(10) Texture can be measured on universal instruments

facility (UK) or SuperHRPD at J-PARC confers a particular advantage. The CW equivalent high-resolution powder diffractometers such as D2B at ILL and ECHIDNA at ANSTO can almost match the absolute resolution of the TOF instruments, D2B achieving $\Delta d/d$ of 5.6×10^{-4} ; however, the resolution function for a CW diffractometer [equation (2.3.18)] has a strong minimum and so this resolution can only be achieved over a restricted range of d -spacing. The reflections appearing in the highest-resolution zone can be shifted by wavelength changes, which of necessity require re-recording of the pattern.

**Figure 2.3.25**

Schematic showing regions of intensity–resolution space in which different diffractometer types typically operate. High-resolution TOF diffractometers operate in the green area, engineering diffractometers (TOF or CW) in the purple area, multi-purpose TOF diffractometers such as POLARIS in the orange area and very high intensity CW diffractometers in the blue area.

The second extreme case is when rapid kinetic behaviours are to be studied. In this case, a small number of CW diffractometers (e.g. D20 at the Institut Laue–Langevin or WOMBAT at ANSTO) have a distinct advantage. Therefore at this time, processes that occur reproducibly and uniformly over a large sample on sub-1 s timescales are best suited to stroboscopic studies using one of the very rapid CW diffractometers available. There are nonetheless a great number of processes that can be studied on the timescales accessible using TOF, where near-constant resolution across the entire diffraction pattern lends considerable advantage.

If unaffected by extremes of resolution, intensity or highly specialized data types (stress, texture *etc.*), the choice between a CW or TOF instrument can be made based more casually on proximity to neutron sources and the access arrangements for national or regional neutron users.

2.3.5. Experimental considerations

2.3.5.1. Preliminary considerations

Neutron-diffraction studies are motivated by a desire to exploit the unique properties of neutrons as listed in Sections 2.3.1 and 2.3.2. As access to neutron diffraction is carefully regulated through an experiment proposal system, considerable planning is required in order to write a successful proposal. Owing to the expense of operating a neutron source and pressure on instrument time, there is an onus on the experimental team to make the best use of neutron beam time. Consideration should be given to the type of instrument required, the resolution that is needed, the d -spacing range of interest, how long each pattern will take to record, the requirement (or not) for standard samples and whether a special sample environment is needed.

2.3. NEUTRON POWDER DIFFRACTION

Table 2.3.6

Suitability of problems to high-resolution or high-intensity diffractometers

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Problem	High resolution	High intensity (medium resolution)
Solve a complex crystal or magnetic structure	Essential, especially in the presence of pseudo-symmetry	Not usually suitable†‡
Refine a complex crystal or magnetic structure	Essential. Will benefit from a high Q -range if available	Not usually suitable†‡
Solve or refine small inorganic structures	Beneficial, but not usually essential unless pseudosymmetry is present	Usually adequate
Quantitative phase analysis	Only required when peaks from the different phases are heavily overlapped	Usually adequate. Allows phase quantities to be tracked in fine environmental variable steps (T, P, E, H etc.) during <i>in situ</i> experiments
Phase transitions	Depends on the nature of the transition and complexity of the structures. Essential for transitions involving subtle unit-cell distortions and pseudosymmetry	Often adequate for small inorganic structure transitions and order–disorder transitions. Allows fine steps in an environmental variable (T, P, E, H etc.)
Line-broadening analysis	Essential for complex line broadening such as from a combination of strain and particle size, dislocations, stacking faults etc.	Adequate for tracking changes in severe line broadening as a function of an environmental variable (T, P etc.) especially if the pure instrumental peak shape is well characterized
Rapid kinetic studies	Not appropriate	Essential

† In some cases the symmetry and lattice parameters are such that the diffraction peaks are well spaced and not severely overlapped even at modest resolution. ‡ May be necessary to supplement high-resolution data to observe weak superlattice reflections in the presence of very subtle or incomplete order–disorder transitions.

Table 2.3.7

Guidance on choice of wavelength/detector bank

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Problem	Choice	Reasons
Solve complex or low-symmetry structures	Longer wavelength	Increase d -spacing resolution to allow correct symmetry and space group to be assigned
Refine a large or complex crystal structure	Shorter wavelength	Ensure that the number of peaks greatly exceeds the number of parameters. Improve determination of site occupancies and displacement parameters
Solve or refine magnetic structures	Longer wavelength	Ensure that large d -spacing peaks are observed. Spread the magnetic form factor over the entire diffraction pattern
Quantitative phase analysis	Usually shorter wavelength	Improve the accuracy of the determination. Longer wavelengths only required if peak overlap is severe
Phase transitions	Shorter wavelength	Ensures adequate data for order–disorder or other unit-cell-enlarging transitions
	Longer wavelength	Subtle unit-cell distortion or pseudosymmetric structures

In the general case, there is competition between the resolution and the intensity of diffractometers, although some of the modern TOF diffractometers (*e.g.* POLARIS, GEM, POWGEN, NOMAD and iMATERIA) simultaneously record patterns of moderate resolution and intensity, and high-intensity patterns at low resolution, in different detector banks. For the purposes of this chapter, high resolution is defined as a minimum diffraction peak width at half maximum height corresponding to $\Delta d/d \leq 10^{-3}$. This is the resolution typically required to observe lattice-parameter differences [*e.g.* $(a - b)/a$] of as little as 4×10^{-5} or so in the absence of sample-related peak broadening. Such a diffractometer is typically of the order of 10 to 1000 times slower than corresponding high-intensity diffractometers at the same neutron source. The decision to opt for a high-resolution diffractometer or a high-intensity diffractometer will depend critically on the nature of the problem under study. This situation

was considered in Kisi & Howard (2008) and their conclusions are reproduced in Table 2.3.6.

It might be expected that the total information content in a diffraction pattern correlates with the d -spacing range covered and therefore this should be maximized. However, this expectation overlooks the different purposes for which powder-diffraction patterns are used. A greater density of diffraction peaks (*e.g.* in a CW pattern recorded using a short neutron wavelength) makes the detailed refinement of complex crystal structures more precise; however, it makes the determination of unit cell and systematic absences *more* difficult as well as reducing access to information contained within the peak shapes concerning the sample microstructure. Table 2.3.7 summarizes these effects. It should be noted that in this context parallels exist between a short-wavelength CW diffraction pattern and a low-angle-detector-bank TOF pattern; and between a longer-

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wavelength CW pattern and a high-angle-detector-bank TOF pattern, subject to limitations imposed by the wavelength distribution in the incident spectrum.

A decision must be made on how long to spend recording each diffraction pattern, such that the greatest number of patterns (samples) may be studied without compromising the information content of each pattern. Since counting is governed by Poisson statistics, the statistical precision of N counts in a radiation detector (X-ray, electron or neutron) is represented by the standard deviation σ :

$$\sigma = N^{1/2}. \quad (2.3.23)$$

This is true regardless of whether a single count is made or multiple counts are summed to give an integrated intensity or a total count from several detectors. For a relatively constant arrival rate of neutrons, the precision of each data point will increase with counting time t in proportion to $t^{1/2}$, and this will be reflected in the agreement indices (*e.g.* R_{wp} ; Chapter 4.7) between the observed and calculated neutron intensities during structure refinements (*e.g.* Rietveld refinement) as well as in the estimated standard deviation (e.s.d.) of the refined crystal structure and other parameters. It has been shown by Hill & Madsen (1984) using CW X-ray powder-diffraction patterns that this is the case for small counting time; however, the agreement and e.s.d.'s quickly attain a plateau for counting times where 2000–5000 counts are recorded at the top of the largest diffraction peak. Beyond this, systematic errors in the models used for peak shapes, background *etc.* begin to dominate the fitting procedure. An important consequence is that since the expected values of the parameter e.s.d.'s fall in proportion to $t^{-0.5}$ whereas their actual values plateau, the statistical χ^2 increases for patterns recorded beyond the limit suggested by Hill & Madsen. A number of recommendations may be derived from these results:

- (i) It is of no benefit for routine crystal structure refinements to record data beyond the point where the strongest peak has 5000 or so counts at its apex and to do so may render parameter e.s.d.'s invalid.
- (ii) Counting for longer times *is* however recommended for problems that hinge upon weak superlattice or magnetic peaks. Similarly, it may be of benefit when minor phases are of interest, such as in complex engineering materials, in samples undergoing phase transitions or in multi-component geological materials.
- (iii) An equally important result from Hill & Madsen is that respectable refined parameter estimates could be obtained using powder-diffraction patterns with only 200–500 counts at the apex of the strongest peak. This is extremely useful when assessing counting times in rapid kinetic studies where the shortest acceptable counting time is preferred. Modern data-acquisition electronics are often configured to allow very short acquisition times or 'event-mode operation' (Section 2.3.4.2.2) with patterns subsequently added together to obtain the required statistical and/or time resolution. In this case, the shortest time step available should be used provided sufficient data storage capacity is at hand.

In CW measurements with a detector bank scanned in small angular steps, similar arguments to those above apply to the sampling interval. This too has been investigated by Hill & Madsen (1986) and again, improvements to the agreement between the calculated and observed patterns and indeed improvements to refined parameter e.s.d.'s were only observed

until systematic errors begin to dominate the fit. As a general rule of thumb, once the applicable counting *time* has been established, the counting interval should be adjusted to give at least 2 (but typically around 5) sampling points in the top half of the diffraction peak for routine crystal structure refinements. Finer sampling intervals are however beneficial in the case of:

- (i) subtle symmetry changes that manifest in the peak shape well before peak splitting is observable,
- (ii) following the evolution of a minor phase during an *in situ* experiment, or
- (iii) peak-shape analyses to explore the sample microstructure (crystallite size, strain distribution, dislocation density, stacking-fault probability *etc.*).

CW measurements using instruments with a fixed position-sensitive detector and TOF measurements both have their raw sampling interval fixed by the instrument architecture, which cannot be varied. The recorded patterns can be subsequently rebinned to a larger sampling interval, although this would usually only be considered to reduce serial correlations during profile refinement (Hill & Madsen, 1986).

2.3.5.2. Sample-related factors

Recording a neutron powder-diffraction pattern is in itself a simple operation. There are, however, a number of sample-related variables that can affect the accuracy or the precision of the resulting patterns, or the ability to analyse them. It is worth mentioning here that neutron-diffraction samples are often large, in the range 1–40 g, to compensate for the lower incident fluxes and scattering cross sections as compared with the X-ray case. Large sample size has a strong mitigating effect on many of the sample-induced problems to be discussed in Chapter 2.10 and below.

The absolute *accuracy* of the position, intensity and shape of neutron powder-diffraction peaks is primarily determined by:

- (i) *How representative the whole sample is of the whole system.* Known as disproportionation, this problem results from any non-random factor during sampling. For example, within rocks there is spatial variability in the mineral content (where to sample), hardness differences (different mineral particle sizes) and differing density (settling effects). Similar considerations apply to multiphase ceramic materials and metal alloys. With highly penetrating neutrons, this can be greatly reduced by using the polycrystalline solid sample provided that the crystallite size is relatively small [see (iii) below]. Disproportionation primarily influences quantitative phase analysis studies. Crystal-structure results are unaffected provided there is enough of each phase of interest to give a high-quality diffraction pattern.
- (ii) *How representative the irradiated part of the sample is of the whole system.* Although ideally the entire sample is bathed in the incident beam, for highly focused neutron beams on high-intensity and/or strain-scanning diffractometers, the beam-sample interaction volume is smaller than the whole sample. In such cases, if a gradient in an experimental variable such as temperature, pressure or composition is present, then the irradiated portion of the sample can be quite unrepresentative and this needs to be addressed in the overall experiment plan.
- (iii) *How representative the diffracting part of the sample is of the whole sample.* There are two circumstances in which the observed diffraction pattern may be unrepresentative of the irradiated portion of the sample. First, very large crystallite