

2. INSTRUMENTATION AND SAMPLE PREPARATION

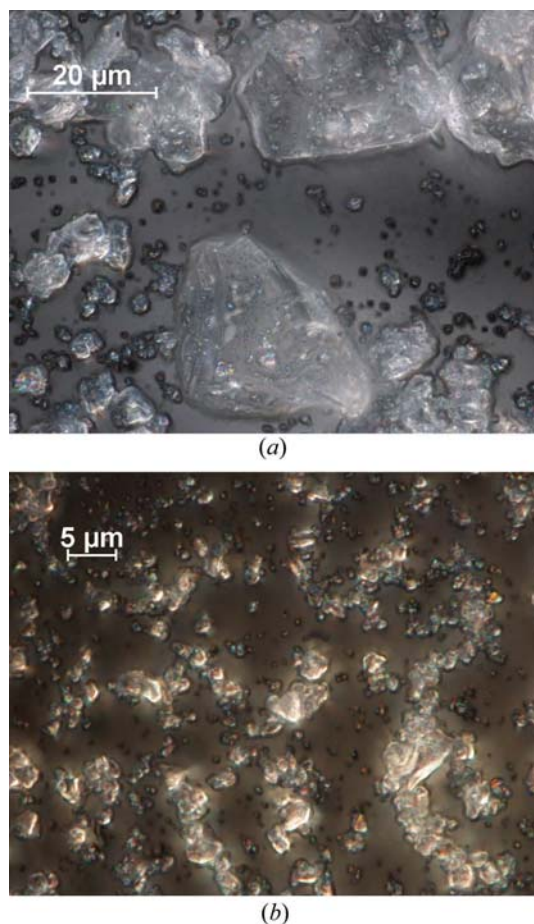


Figure 2.10.14
Optical micrographs of (a) -400 mesh quartz at 100 \times magnification and (b) quartz milled in a McCrone micronizer for 15 min in isopropyl alcohol at 150 \times magnification.

elements (corundum or agate in the micronizing mill; possibly iron, WC, SiC *etc.* in other types of mill).

Obviously, a reduction of the crystallite size to the μm -sized region will produce size broadening if the instrument has sufficient resolution to detect it. It is worth bearing in mind that micronizing does not guarantee a problem-free sample. Micronized specimens almost always exhibit some microstrain broadening. In principle, this could be decreased by an annealing treatment, but this step is rarely practiced. When a mixture contains both very hard and very soft phases, the hard phases may not mill properly. This has been observed in mixtures containing organics and a minor quartz fraction. Despite milling

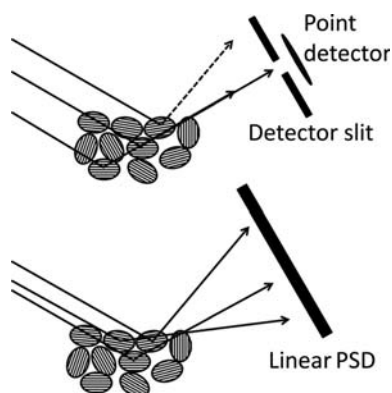


Figure 2.10.15
Diagram showing the source of improved particle statistics in reflection geometry using a 1D position sensitive detector (PSD) *versus* a point detector.

for 30 min or more, the classical split 101 quartz reflection (such as seen in Fig. 2.10.11) was still visible in some data sets, an indication of the ‘rocks in dust’ phenomenon. Although the McCrone mill is designed to minimize microstructural damage to samples, damage can still occur with very soft materials, and ductile materials may weld as opposed to mill. With very soft and pliable materials a possible alternative could be to cryo-mill the samples, taking advantage of the increased brittleness of materials at low temperature.

2.10.1.2. Preferred orientation

Preferred orientation is usually undesirable in a powder diffraction pattern, although sometimes it *is* the information required, as in texture studies. One of the exceptions is the analysis of clays, where orientation is deliberately induced to identify related reflections. Preferred orientation manifests itself as continuous but non-uniform intensity in the Debye rings, and so is easily characterized with 2D detectors. Preferred orientation does not change the total diffracted intensity, but renormalizes some classes of reflections with respect to others.

Reference is commonly made to a preferred-orientation ‘correction’. Strictly speaking, what is done is ‘modelling’ of the preferred orientation. The proper way to correct preferred orientation is through better specimen preparation.

Models for preferred orientation exist in many analysis packages, specifically the March–Dollase (Dollase, 1986) and spherical-harmonics (Järvinen, 1993) formalisms. Apparent severe preferred orientation may be a sign of large crystallites, which may result in one or more of the other problems outlined in this section.

Additional care must be taken where software corrections are used during quantitative phase analysis, where overlapping reflections can cause serious correlations and erroneous results. The March–Dollase correction is less prone to this, as an orientation direction must be supplied by the analyst. The spherical-harmonics correction has no such constraint. It behaves properly where peak overlap is not extensive, but negative peak intensities are not uncommon (especially when too high an order is used) when applying it without thought in complex mixtures. Negative peak intensities are obviously impossible, so the results of such an analysis must be viewed with great suspicion.

The presence of preferred orientation can be most easily discerned by comparing the observed pattern to a calculated pattern (random) of the same phase from the Powder Diffraction File or other source. The likelihood of preferred orientation can be assessed by calculating the Bravais–Friedel–Donnay–Harker (Bravais, 1866; Friedel, 1907; Donnay & Harker, 1937) morphology from the crystal structure using *Mercury* (Sykes *et al.*, 2011) or other tools.

Orientation tends to occur in materials where the crystallites have either a needle or plate-like morphology. Plates are common in the analysis of mineral samples, such as the commercial phlogopite mica used here as an example. Conventional top-loading of such samples can result in very few reflections being visible because of almost perfect orientation of the plates during pressing, as seen in Fig. 2.10.16. Where the aspect ratio of the crystallites is large, micronizing the sample does not reduce the preferred orientation significantly (Fig. 2.10.17).

The most common approach to decrease preferred orientation of troublesome samples such as this mica is a technique known as back-loading. [Others are discussed in Buhre *et al.* (1998).] The concept is that the surface of the sample is not subjected to