

2. INSTRUMENTATION AND SAMPLE PREPARATION

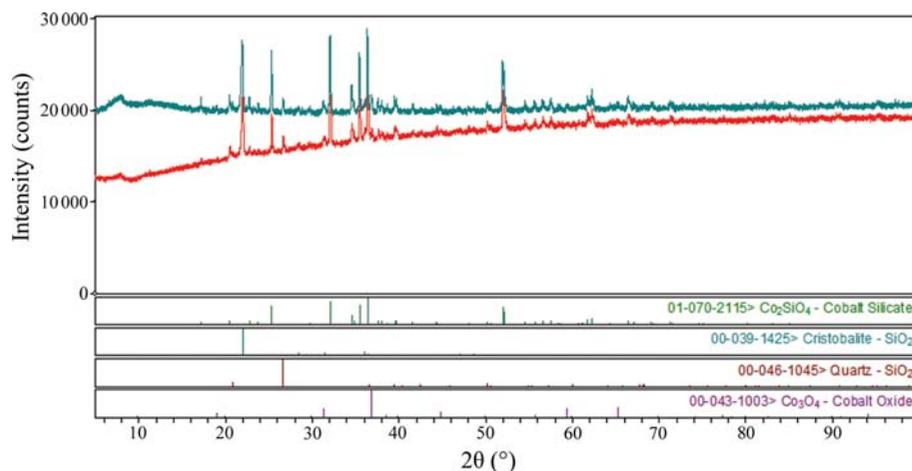


Figure 2.10.30

Powder patterns of a commercial cobalt silicate sample, measured from a (rough) slurry-mounted specimen (red) and from a (flat) conventional front-packed specimen (green). The surface roughness decreases the intensities of the low-angle peaks and background.

peak and background intensities at low angles than a conventionally front-packed specimen. Refinement using the 'rough' data yielded unreasonably negative displacement coefficients. Including a surface-roughness model in the refinement resulted in reasonable displacement coefficients, identical to those obtained using the 'flat' data.

Models by Suortti (1972) and Pitschke *et al.* (1993) exist in most analysis software. They both yield similar results, but the Suortti correction is generally regarded as slightly more stable at 2θ angles below 20° .

2.10.1.3.2. Microabsorption

Microabsorption is widely regarded as the greatest impediment to the application of quantitative phase analysis with powder X-ray diffraction data. Misapplication of a microabsorption correction can degrade accuracy (Scarlett *et al.*, 2002). The infamous sample 4 in the Commission for Powder Diffraction quantitative phase analysis round robin (Scarlett *et al.*, 2002) was deliberately designed to be difficult to analyse accurately using any wavelengths available to a laboratory X-ray diffractometer because of microabsorption effects.

Brindley (1945) published a theoretical correction (model) for microabsorption, but the range for an appropriate application can be easily exceeded. In the absence of such a correction, relative concentration errors can commonly be 20–30%. The extent of microabsorption for a phase was described by Brindley in terms of μD , where μ is the linear absorption coefficient and D is the particle (not crystallite) diameter. While a crystallite size can be estimated from the profile widths, determining the particle size requires additional information, such as laser light-scattering measurements. Where $\mu D > 0.1$ the Brindley correction may not be accurate, and ideally μD for every phase present should be less than 0.01, where microabsorption can safely be ignored. Brindley also suggested a rule-of-thumb for the maximum acceptable particle size for quantitative phase analysis, where $D_{\max} = 1/(100\mu)$.

The terms μ and D show that microabsorption can be affected by X-ray wavelength and particle size. The easiest approach for the analyst with a troublesome sample is to reduce the particle size by micronizing the sample. Some in-house laboratories may have multiple systems or the flexibility to change wavelengths. As a rule the linear absorption coefficient decreases with increasing

energy, but users should beware of absorption edges that can create a serious discontinuity in this trend. Synchrotron beamlines have more flexibility for avoiding absorption edges and can achieve higher energies that are not practical in laboratory systems. Even when using this high-energy 'sledgehammer' approach there is still a benefit to reducing the crystallite size to avoid some of the other effects mentioned in this chapter.

Microabsorption results from differences in linear absorption coefficients and particle sizes, and can sometimes arise in unexpected situations. Adding a NIST SRM 640b silicon internal standard to a micronized mullite sample (Kaduk, 2009) in order to quantify the amorphous content resulted in a significant microabsorption effect, the result of differences in both particle size and absorption coefficients. The microabsorption could be

overcome by micronizing the mullite/Si blend.

Even in cases where the absorption contrast is small, large differences in particle size can result in significant microabsorption effects. For anatase/rutile mixtures ($\mu = 489.4$ and 534.2 cm^{-1} , respectively) in which the anatase and rutile particle sizes were 3 and $150 \mu\text{m}$, respectively, concentration errors of 20% relative were observed. The errors were corrected by micronizing the mixtures (Kaduk, 2013). Similarly, mixtures of large-particle ($23 \mu\text{m}$) MFI zeolite ($\mu = 65.66 \text{ cm}^{-1}$) and a quartz internal standard ($\mu = 96.39 \text{ cm}^{-1}$, $10 \mu\text{m}$) resulted in relative concentration errors of 5%; these errors were corrected by micronizing the mixtures.

Neutrons are absorbed much less than X-rays, which means that microabsorption is practically nonexistent in neutron diffraction data. The lack of microabsorption is why neutron diffraction is often regarded as the 'gold standard' for quantitative phase analysis, although the beamline proposal process tends to make its application in conventional quantitative phase analysis uncommon. The application of quantitative phase analysis using neutron diffraction data is most often seen when studying phase evolution in an *in situ* experiment. Microabsorption is an issue specific to quantitative phase analysis and a more detailed discussion of the problem is given in Chapter 3.9.

2.10.1.3.3. Extinction

Extinction effects are not common in X-ray powder diffraction but may be significant when using neutrons. Extinction is dependent on the size/shape of the coherently diffracting domains, and is a multiple-scattering phenomenon. Primary extinction occurs when a second diffracting event occurs within a single crystallite. Secondary extinction occurs in mosaic crystals and is not seen in powders. When primary extinction occurs, the re-diffracted beam will continue in the same direction as the incident beam but interfere destructively with it. Re-diffraction within a crystallite is not likely to occur where imperfections disrupt the ordering of a crystallite. Consequently, primary extinction is usually only seen in powders of highly ordered and crystalline materials. A classic example is powdered single-crystal silicon as used in studies on extinction such as that by Cline & Snyder (1987). The most commonly encountered phase that can exhibit primary extinction is high-quality natural quartz.