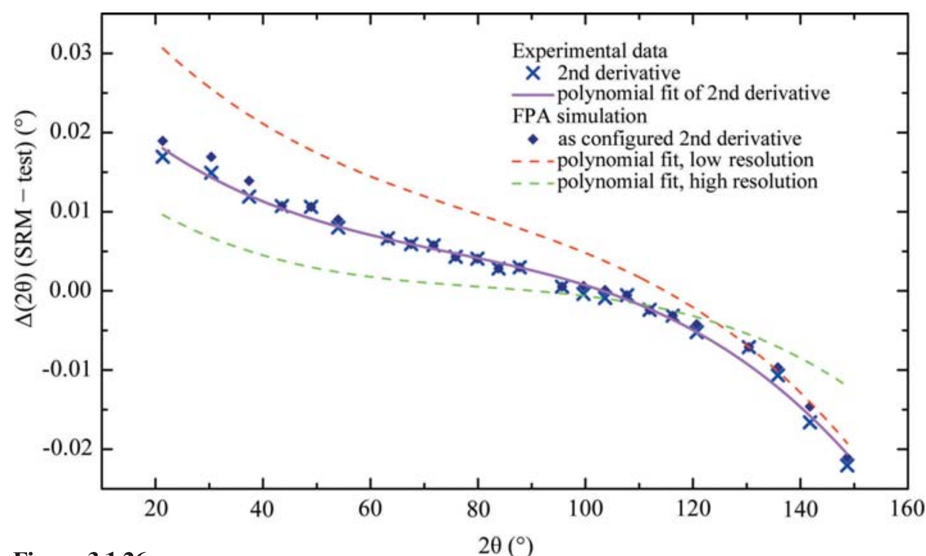

Figure 3.1.26
$\Delta(2\theta)$ curve using SRM 660b illustrating the peak-position shifts as function of 2θ. The peak positions were determined *via* a second-derivative algorithm, and $\Delta(2\theta)$ values (SRM − test) were fitted with a third-order polynomial. Simulated data are from *FPAPC* and were analysed *via* the second-derivative algorithm and polynomial fits as per the experimental data.

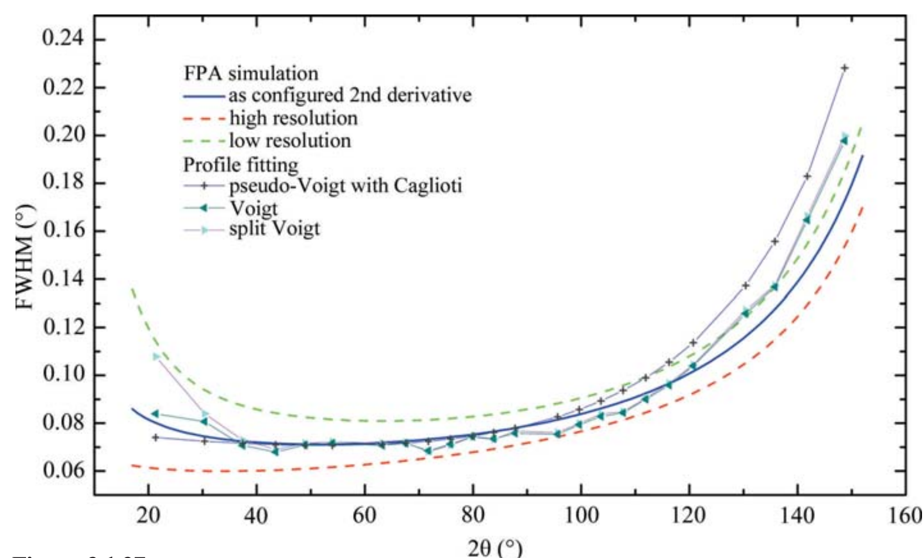

Figure 3.1.27
Simulated and actual FWHM data from SRM 660b using the two Voigt PSFs with (‘with Caglioti’) and without constraints.

sity, in addition to parameters describing profile shape and breadth. The discussion of the IPF in Section 3.1.1, as well as a quick look at Figs. 3.1.26–3.1.28, shows the complexity in the line profile shape from a Bragg–Brentano instrument. The profiles are symmetric only in a limited region of 2θ; in other regions, the degree and direction of profile asymmetry also vary as a function of 2θ. To a first approximation, the optics of an instrument contribute to the Gaussian nature of the profiles; this Gaussian nature will be constant with respect to 2θ. The Lorentzian contribution is primarily from the emission spectrum; given the dominance of angular-dispersion effects at high angle, one can expect to see an increase in the Lorentzian character of the profiles with increasing 2θ. While it can be argued that it is physically valid to model specific contributions to the IPF with Gaussian and Lorentzian PSFs, either of these two analytical functions alone cannot be expected to fit the complexities of the IPF and yield useful results. Combinations of these two functions, however, using shape parameters that vary as a function of 2θ, have given credible results for fitting of data from the Bragg–Brentano diffractometer and have been widely incorporated into Rietveld structure-refinement software. The Voigt function is a convolution of a Gaussian with a Lorentzian, while the pseudo-Voigt is the sum of the two. The parameters that are refined consist of an FWHM and shape parameter that indicates the ratio of the Gaussian to Lorentzian character. The Voigt, being a true convolution, is the more desirable PSF as it is more physically realistic; the pseudo-Voigt tends to be favoured as it is less computationally intensive and the differences between the two PSFs have been demonstrated to be minimal (Hastings *et al.*, 1984), although there is not universal agreement about this.

can be plotted *versus* 2θ to describe the instrument and evaluate its performance.

The least computationally intensive methods for the analysis of XRPD data, which have been available since the onset of automated powder diffraction, are based on first- or second-derivative algorithms. These methods report peak positions as the 2θ value at which a local maximum in diffraction intensity is detected in the raw data. Typical software provides ‘tuning’ parameters so that the operation of these algorithms can be optimized for the noise level, step width and profile width of the raw data. These methods are highly mature and offer a quick and reliable means of analysing data in a manner suitable for qualitative analysis and lattice-parameter refinement. However, they only give information about the position of the top of the peak. Calibration of the diffractometer *via* this method is useful only for subsequent analyses that also use such peak-location methods.

Profile fitting with an analytical profile-shape function offers the potential for greater accuracy, because the entire profile is used in the analysis. As with the derivative-based methods, profile fitting also reports the observed 2θ position of maximum inten-

Refining the profile shapes independently invariably leads to errors when analysing patterns with peak overlap, as correlations

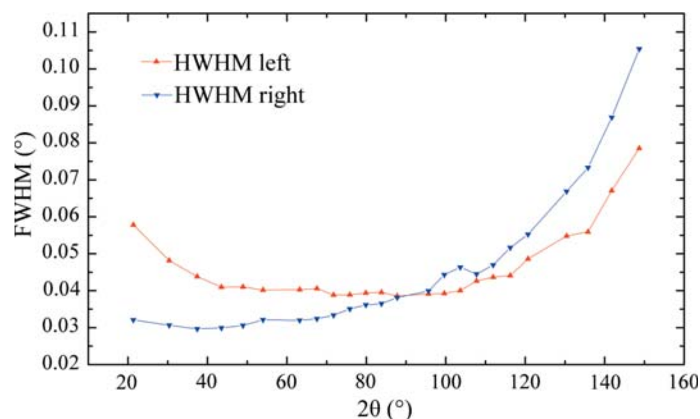

Figure 3.1.28
Left and right HWHM data from SRM 660b using the split pseudo-Voigt PSF fitted with uniform weighting.

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