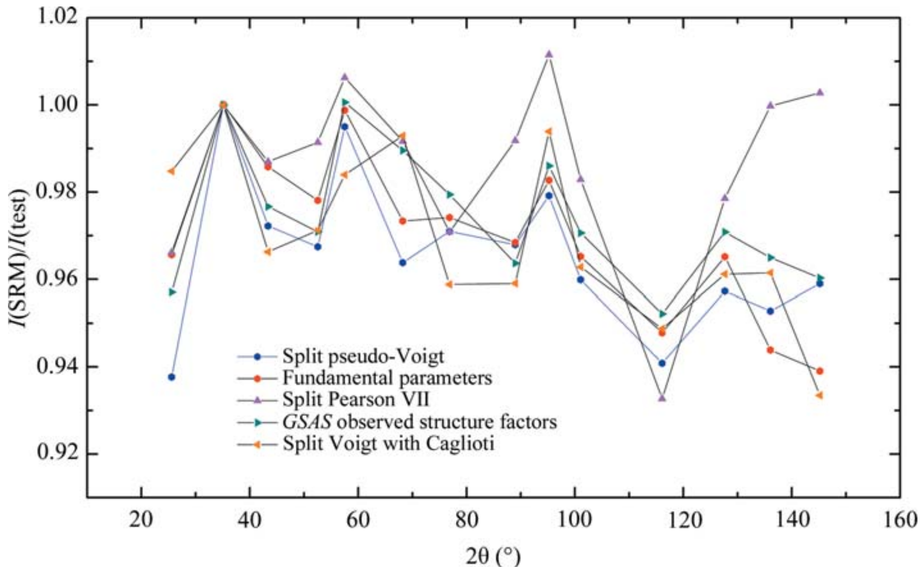

Figure 3.1.43
Qualification of a machine using SRM 1976b. The data were analysed using several PSFs.

The structure common to all the data sets of Fig. 3.1.43 is as yet unexplained. With any of these methods, modelling the background is of critical concern. The intensity scale of the fitted pattern must be expanded to allow for inspection of the background fit alone. The weak amorphous peak at approximately 25° 2θ, which is associated with the anorthite glass matrix phase, complicates the matter. Certain refinement programs allow for the insertion of a broad peak to account for this. Alternatively an 11- to 13-term Chebyshev polynomial could be used. Keeping the number of these terms to a minimum is consistent with preventing the background function from interfering with the modelling of the profiles. Lastly, the use of $K\beta$ filters in conjunction with a PSD can be problematic for the calibration of instrument response using SRM 1976b. Such filters typically impart an absorption edge in the background on the low-energy side of the profiles. With the use of a high-count-rate PSD, this effect can be quite pronounced and can cause difficulties in fitting the background and, therefore, erroneous determination of the profile intensity.

3.1.7. Conclusions

In this chapter, we reviewed the theoretical background behind the well known complexity of X-ray powder diffraction line profiles. A divergent-beam laboratory X-ray diffractometer with a conventional layout was used to rigorously examine the full range of procedures that have been developed for the analysis of the instrument profile function. The machine featured superlative accuracy in angle measurement, and attention was paid to the precision and stability of the optical components and sample positioning. The instrument was aligned in accordance with first-principles methods and was shown to exhibit an optical performance that conformed with the expectations of established theories for powder-diffraction optics.

Data-analysis methods can be divided into two categories that require fundamentally different approaches to instrument calibration. Empirical profile-analysis methods, either based on second-derivative algorithms or profile fitting using analytical profile-shape functions, seek to characterize the instrument performance in terms of shape and position parameters that are used in subsequent analysis for determining the character of the specimen. These methods, however, provide no information about the origins of the peak shift or profile shape that they describe. Model-based methods seek to link the observation directly to the character of the entire experiment. The calibration procedure for the first category can be regarded as a 'classical' calibration where a correction curve is developed through the use of an SRM and applied to subsequent unknowns. With model-based methods, it is the user's responsibility to calibrate the instrument in a manner that ensures that the models that are being used correctly correspond to the experiment. This is best accomplished through the analysis of results from empirical methods, particularly $\Delta(2\theta)$ curves, as well as the analysis of data from an SRM followed by a critical examination of the refined parameters.

Second-derivative-based algorithms for determining peak locations are able to provide the 2θ positions (the positions of the maxima in the observed profile intensity) to within $\pm 0.0025^\circ$ 2θ. Profile fitting using analytical profile-shape functions to determine the peak position was shown to be problematic; errors of up to 0.015° 2θ were noted. The use of uniform weighting in the refinements resulted in improved accuracy in the reported peak positions and FWHM values. Using a Johansson incident-beam monochromator led to high-quality fits of diffraction data using analytical profile shape functions. The Caglioti function can be used to improve the reliability of FWHM values.

The fundamental-parameters approach was found to be effective in modelling the performance of the Bragg–Brentano divergent-beam X-ray diffractometer. The form of the $\Delta(2\theta)$ curve, determined *via* a second-derivative algorithm, can be explained quantitatively through an examination of FPA models. Furthermore, FPA simulations of diffraction data, computed from the instrument configuration using both commercial and NIST FPA codes, and analysed using the same second-derivative algorithm, reproduced the $\Delta(2\theta)$ results from the experimental data. This self-consistency verified the correct operation of both the instrument and the FPA models. Using the FPA for modelling the diffraction profiles provided the best fits to the observations and the most accurate results for the 'true' reported peak positions. The TCH/Finger models for profile shape yielded credible results for refinement of lattice parameters *via* the Rietveld method.

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