as the internal standard. The intensities (Table 3.9.2) and known concentrations (Table 3.9.1) of these phases can then be used to derive $C_{\alpha s}^{ij}$ from equation (3.9.8) to eliminate the need to know or measure μ_m^* for the sample.

$$\frac{I_{\rm fluorite}}{I_{\rm zincite}}\frac{W_{\rm zincite}}{W_{\rm fluorite}} = C_{\alpha s}^{ij} = \frac{5132.0}{5996.8}\times\frac{0.3019}{0.3469} = 0.7448. \qquad (3.9.29)$$

Analysis of the unknowns (Fig. 3.9.2) then proceeds *via* equation (3.9.9) and is demonstrated here using sample 1D:

$$W_{\rm fluorite} = \frac{W_{\rm zincite}}{C_{\alpha s}^{ij}}\frac{I_{\rm fluorite}}{I_{\rm zincite}} = \frac{0.3289}{0.7448}\frac{6559.6}{5468.5} = 0.5297, \qquad (3.9.30)$$

compared with a value of 0.5358 added to the sample by weight.

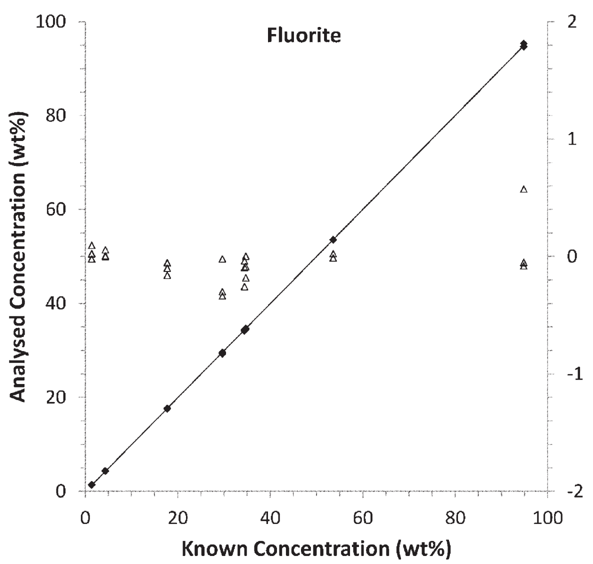

Figure 3.9.1
Plot of the analysed concentration (black diamonds – left axis) and the bias (open triangles – right axis) expressed as wt% for fluorite using the absorption–diffraction method. The analysis was calibrated using sample 1D, which has a fluorite concentration of 53.58 wt%.

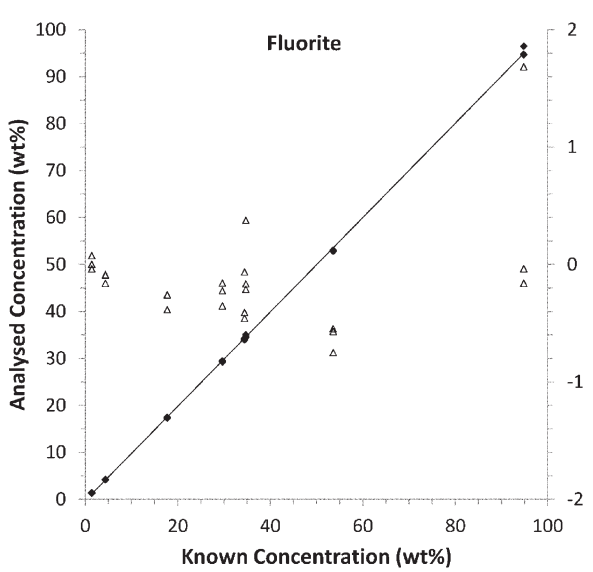

Figure 3.9.2
Plot of the analysed concentration (black diamonds – left axis) and the bias (open triangles – right axis) expressed as wt% for fluorite using the internal standard method with zincite designated as the internal standard. The analysis was calibrated using sample 1H where the fluorite and zincite concentrations are 34.69 and 30.19 wt%, respectively.

3.9.4.3. *Reference intensity ratio*

For this exercise, the peak intensities and phase concentrations in Tables 3.9.1 and 3.9.2 for sample 1H can be used to determine the RIRs for fluorite and zincite.

$${\rm RIR}_{\rm fluorite} = \frac{5132.0}{1436.5}\times\frac{0.3512}{0.3469} = 3.617, \qquad (3.9.31)$$

$${\rm RIR}_{\rm zincite} = \frac{5996.8}{1436.5}\times\frac{0.3512}{0.3019} = 4.856. \qquad (3.9.32)$$

These RIRs should be compared with reported values for fluorite in the ICDD database (ICDD, 2015) which have an average of 3.83 (n = 33) but range from 2.40 to 4.21. For zincite the reported RIR values have an average of 5.24 (n = 50) and range from 4.50 to 5.87. The discrepancies in the various reported values of the RIRs highlight the need to determine them under the same conditions as the samples being analysed if the highest accuracy is to be achieved.

Fig. 3.9.3 shows the RIR values calculated from all 24 (eight samples, three replicates each) measurements for fluorite and zincite plotted as a function of corundum concentration. At intermediate concentrations there is quite good agreement between the determined values. However, there are significant deviations at low corundum concentration, resulting in insufficient measured intensity in the corundum peak to ensure sufficient accuracy in the RIR. Hence, care should be taken to ensure that there are sufficient counts in the peaks used to determine the RIR. In addition, a low concentration automatically means that there are fewer grains contributing to the diffraction process; hence particle statistics may also present a significant problem.

The presence of other sample-related aberrations that affect the measured intensities also needs to be considered. For example, microabsorption may affect measured RIR values differently in different concentration ranges. The impact of such effects on the analysis is reduced by their inclusion in the measured RIR provided that variation induced by, for example, sample preparation can be kept to a minimum.

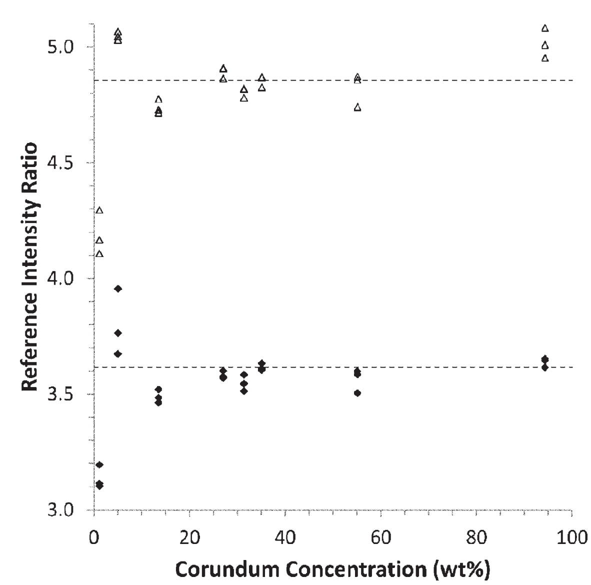

Figure 3.9.3
Plot of the 24 determined RIR values for fluorite (black diamonds) and zincite (open triangles) as a function of corundum concentration. The dashed lines represent the average RIR values for fluorite (lower) and zincite (upper) determined from the three replicates of sample 1H where all phases have approximately equal concentration.