3.9. QUANTITATIVE PHASE ANALYSIS

Table 3.9.5
Calculated values of μD (where μ is the linear absorption coefficient and D is the particle diameter) for Cu $K\alpha$ X-rays for corundum, magnetite and zircon with a range of particle sizes

Diameter (μm)	μD		
	Corundum, Al_2O_3 ($\mu = 125$ cm^{-1})	Magnetite, Fe_3O_4 ($\mu = 1167$ cm^{-1})	Zircon, $ZrSiO_4$ ($\mu = 380$ cm^{-1})
0.1	0.001	0.012	0.004
0.2	0.003	0.023	0.008
0.5	0.006	0.058	0.019
1	0.013	0.117	0.038
2	0.025	0.233	0.076
5	0.063	0.584	0.190
10	0.125	1.167	0.380
20	0.251	2.334	0.759

(ii) $0.01 < \mu D < 0.1$ – medium powder. Microabsorption is likely to be present and the normal Brindley correction model can be applied.

(iii) $0.1 < \mu D < 1.0$ – coarse powder. A large microabsorption effect is present. The Brindley model can only be used to provide an approximate correction provided that μD is closer to the lower limit of the range.

(iv) $\mu D > 1.0$ – very coarse powder. This indicates that severe microabsorption is likely to be present and that any correction is well beyond the limits of the model.

It is difficult for the analyst encountering a new sample to determine whether a correction for microabsorption is required without first obtaining additional information. A minimum requirement should be to calculate μD for each phase present. However, this requires knowledge of the particle size which, in a multiphase sample, can be very difficult to obtain unambiguously. Even when the particle size is measured by, for example, dynamic light scattering or optical or SEM image analysis, the applicability of the correction can still be unclear. In addition, the correction factor embodied in equations (3.9.48) and (3.9.49) makes the assumption that the particles of the phase of interest are spherical and of uniform size. This assumption is unrealistic in almost all samples; in reality, each phase is likely to be present at a wide
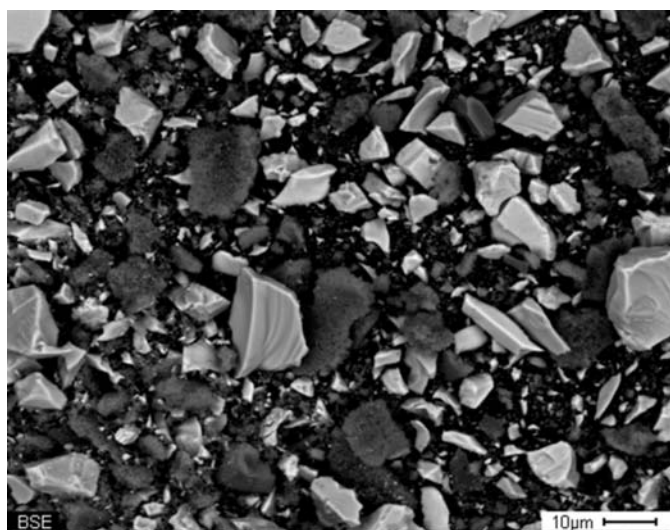
Figure 3.9.19
Backscattered-electron SEM image of a mixture of approximately equal amounts of corundum (dark grey), magnetite and zircon (lighter grey). Note the wide range of particle sizes present for each of the three phases.

range of particle sizes and the particles are highly unlikely to be spherical.

Table 3.9.5 shows the calculated values of μD for Cu $K\alpha$ radiation for some commonly encountered phases in mineralogical analysis. For the least absorbing phase (corundum), the upper range of applicability of the Brindley model (medium powder) is reached at about 5 μm; by 8 μm, the coarse powder criterion has been reached and the correction model is no longer applicable. For magnetite, these limits are reached an order of magnitude earlier at about 0.5 and 0.9 μm, respectively.

Fig. 3.9.19 shows an SEM image of a mixture of approximately equal amounts of corundum, magnetite and zircon. The individual components of the sample were weighed and the mixture ground in ethanol in a McCrone micronizing mill (McCrone Research Associates, London) for 10 min g^{-1}. This approach to sample preparation is generally accepted as best practice for powder XRD because it minimizes structural damage during grinding (Hill & Madsen, 2002). After decanting and drying, the sample was back-packed into a cavity sample holder for XRD data collection; the same sample was then used to obtain the SEM image in Fig. 3.9.19. Visual observation shows a wide range of particle sizes (from submicron to greater than 10 μm) and shapes that do not even approximate spheres. Even if this information is obtained, selection of a particle size that best represents each individual phase is a difficult task. In addition, in many sample suites, the component phases exhibit a range of hardness resulting in different rates of grinding and hence difference size ranges. Regrettably, what happens too often in practice is that analysts will micronize the sample and then select an arbitrary particle size in order to derive a 'preferred' value for the final analysis. Therefore, caution is advised in the application of these correction models. The IUCr CPD round robin on QPA (Madsen *et al.*, 2001; Scarlett *et al.*, 2002) showed that many participants severely degraded their results by applying a correction when none was necessary.

Equation (3.9.48) shows that there two ways to minimize microabsorption. The first is to reduce the absorption contrast by, for example, changing the X-ray wavelength. While corundum and magnetite have very different linear absorption coefficients for Cu $K\alpha$ radiation (126 and 1123 cm^{-1}, respectively), the difference is reduced to 196 and 231 cm^{-1}, respectively, for Co $K\alpha$ radiation. The second approach is to reduce the particle size in order to meet Brindley's fine- or medium-powder criteria.

However, even these steps may not be sufficient to eliminate the microabsorption effect. Slightly different absorption coefficients, or different particle sizes for phases with the same absorption coefficients, may still introduce a bias between expected and analysed concentrations. In this situation, it may be better to use a calibrated hkl_phase or peaks_phase (Section 3.9.6) instead of a Rietveld, structure-based phase. The calibration step involved in the generation of such a phase incorporates the microabsorption problem into the calibration constant.

Fig. 3.9.20 shows the bias between known concentrations (derived from chemical analysis) and QPA-determined concentrations for a series of salt samples. The samples contain halite (NaCl), sylvite (KCl) and kieserite ($MgSO_4 \cdot H_2O$) as major phases and small amounts of anhydrite ($CaSO_4$), langbeinite [$K_2Mg_2(SO_4)_3$] and carnallite [$KMgCl_3 \cdot 6(H_2O)$]. The linear absorption coefficient of sylvite (254 cm^{-1}) is much higher than halite (165 cm^{-1}). Using crystal-structure-based analysis, there is a systematic deviation of up to 3% with an overestimation of the low absorber (halite) and an underestimation of the high absorber (sylvite). After replacing sylvite by a calibrated

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