

where C_{n-1} and C_n are the corrected concentrations obtained in the $(n-1)$ th and n th iterations respectively, and \bar{C}_{n-1} and \bar{C}_n are the concentrations substituted in the correction formulae in the same iterations. Two cycles in simple iteration are carried out before starting to use (16.1).

— This method is significantly better than simple iteration for analyses with large corrections (Reed and Mason, 1967; Beaman and Isasi, 1970). Non-convergence is practically eliminated, and usually the number of iterations required is reduced, though this advantage is offset by the greater complexity of the calculations. Non-convergence occurs only with very severe absorption, which should be avoided by using a sufficiently low accelerating voltage and having a reasonably high take-off angle.

16.5 Hyperbolic iteration

Criss and Birks (1966) proposed an iteration procedure based on the 'alpha coefficient approximation' (§16.6), whereby the calibration curve of C' versus C for a binary compound is represented by the hyperbola:

$$(1 - C')/C' = \alpha(1 - C)/C. \quad (16.2)$$

This formula is used only as an aid to convergence, and no constraint is placed on the procedures used to calculate the relationship between X-ray intensity and composition.

For each element the value of C' that would be obtained for a given assumed composition is calculated from first principles, and α is deduced from (16.2), which is then used to calculate C from the observed value of C' . This procedure is repeated using a new assumed composition derived from the latest C values, and in this way progressively improved values of α are obtained.

For binary compounds convergence is very rapid, since α is almost constant. Ternary and higher systems are treated as pseudo-binaries, but the relative proportions of the residual elements may change from one cycle to the next, causing α to change, possibly substantially. Therefore it is not obvious that hyperbolic iteration will perform well for multi-element analyses with large corrections. However, Heinrich (1972) used hyperbolic iteration with normalisation before each α calculation, and obtained convergence in not more than four iterations in all cases

tested, though this probably did not include large absorption corrections.

16.6 Alpha coefficients

The approximation:
$$C'_A = \frac{\alpha_A C_A}{\alpha_A C_A + \alpha_B C_B}, \quad (16.3)$$

for binary A - B compounds was first proposed by Castaing (1951) for atomic number corrections (combined stopping power and backscattering), and was further developed by Poole and Thomas (1963, 1966) for this purpose. Ziebold and Ogilvie (1966) showed that the same expression may also be used to approximate the Philibert absorption formula (14.5) when the correction is not too large.

Ziebold and Ogilvie (1964) proposed using (16.3) for quantitative analysis with empirical α coefficients for systems in which a standard of known composition is available, and in other cases using simplified models of absorption, fluorescence, and atomic number effects to calculate α . Equation (16.3) is not strictly suitable for fluorescence corrections, since the correction factor is a nonlinear function of concentration (fig. 15.5), but the absolute concentration error resulting from this approximation is usually small.

By substituting $\sum \alpha_i C_i$ for $\alpha_A C_A + \alpha_B C_B$, (16.3) may be extended to ternary and higher systems. For binaries the equation may be solved directly by substituting $C_B = 1 - C_A$, giving (16.2), with $\alpha = \alpha_A/\alpha_B$. However, for ternary and higher systems a set of linear simultaneous equations is obtained, and these require solution by matrix inversion or an iterative procedure.

Bence and Albee (1968) applied the alpha coefficient approximation to silicates and oxides, with the composition expressed in terms of weight per cent oxides (e.g. MgO, SiO₂, FeO) rather than elements. Each oxide is assigned an alpha coefficient and treated as an element. Oxide alpha coefficients were derived by Bence and Albee partly empirically and partly by calculation. These are valid only for an accelerating voltage of 15 kV and an X-ray take-off angle of 52°30'.