18.4.3.3 Evaluation function

The *evaluation function* is the inverse of the calibration function. It is generated by applying the *evaluation operator G* to the calibration function. For a single analyte, this is *G(F(x)),* which is equal to *G(E(y))*. If the presumed calibration function is the actual calibration function (correct model), then *G* will be the inverse of *F*, and the operation *G(F(x))* will return the actual concentration *x*. Application of *G* to the observed response *y* together with the estimated parameters, leads to $\hat{x} = G(y)$ for the estimated concentration. Thus, for the simplest (straight line) calibration function we obtain

$$\hat{x} = (y - \hat{B}) / \hat{A} \tag{18.4.5}$$

The process is not quite so simple, of course, in terms of possible interference and losses and chemical matrix corrections. Error propagation, particularly if e_y is non-normal, and for the non-linear parts of the transformation [denominator of Eq. 5], also is not always trivial.

In the more general, multicomponent analytical process, the *evaluation function* is the inverse of the multicomponent calibration function, given by $G(F(\boldsymbol{x}))$, where, if the presumed multicomponent calibration model is correct, *G* is now the generalized inverse of *F*. The estimated concentration vector $\hat{x}$ is obtained by operating on the observed signal vector $\boldsymbol{y}$. Thus,

$$\hat{x} = G(y) \tag{18.4.6}$$

Under the best of circumstances, *G* will be a linear operator derived from the calibration function, as in linear least squares estimation. Uncertainties in the numbers, identities, and spectra of the component analytes -- as well as multicollinearity (spectrum similarities) -- can lead to severe difficulties in the inversion of Eq. 18.4.4. That is, the identity

$$G\,F = I \tag{18.4.7}$$

may not obtain, or the solution may not be numerically stable due to near singularity. For multicomponent analysis, therefore, the Evaluation Function plays a major role in determining the precision and accuracy of the CMP.