

Considerations on Calibration and Prediction in Quantitative X-ray Fluorescence Analysis

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X-ray fluorescence analysis cannot be considered as an “absolute” method and uses calibration standards to relate measured x-ray intensities to amounts in the sample. Over the years a variety of successful calibration procedures have been developed, mainly concentrating on the problem of matrix correction. However relatively little attention has been paid to the mathematical – statistical aspect of calibration and prediction. Even the application of the most simple calibration relation, the straight line $y = \alpha_0 + \alpha_1 x + \varepsilon$, implies a number of assumptions that are not always met in practice.

We have investigated the effect of violating various assumptions such as deviation from normality and heteroscedasticity in so called “classical” and “inverse” calibration. It will be shown that the prediction itself is little affected, but the uncertainty estimate on the prediction can become very unreliable.

The presence of outliers is a more serious problem, especially in complex calibration schemes involving many standards and elements simultaneously. The concepts of robust calibration will be introduced and the merits and disadvantages will be discussed.

Finally, nowadays so called multi-variate calibration techniques are popular in analytical chemistry. Although potentially appealing as they require little knowledge of the physical process behind the data, we will emphasize on the dangers of using such methods.