

amc technical brief

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Why are we weighting?

When we calibrate an analytical system, we use a calibration set with concentrations $c_i, i = 1, \dots, n$ and measure r_i , the corresponding responses. If the values of c_i are essentially error-free, regression is usually appropriate to obtain the calibration function $r = f(c)$ that we use to estimate unknown concentrations. But should we use simple or weighted regression?

The question arises because simple regression is based on a statistical model in which the variance of an observed response is the same across the whole calibration range (Figure 1). However, this circumstance is unlikely to be strictly true in chemical analysis. In typical (but not all) analytical calibrations, the variance of the response is heteroscedastic, increasing steadily with the concentration. We can see this effect in the example data (Figure 2). (This example was chosen because, unusually, the variance in the response is large enough at higher concentrations to be visible on the scale of the figure.) In such instances, weighted regression, based on a heteroscedastic model (Figure 3), should give a more accurate answer. Differences between calibration functions estimated by the two methods are small.

towards $\sigma = SA_c$, that is, an almost constant relative standard deviation, and for this region weighted regression will be more accurate. But is the improvement in accuracy worthwhile? If so, where should we draw the line between our choice of methods? We can tackle this question by generalising Eq 1 across analytical methods. This is done by expressing concentration c and standard deviation σ in units of detection limit. This gives