ISSN 1757- 5958

amc technical briefs

Editor: Michael Thompson Analytical Methods Committee AMCTB No 37 March 2009

Standard additions: myth and reality

'Standard additions' is a generally applicable calibration technique, devised to overcome a particular type of matrix effect that would otherwise give rise to a biased result. This 'rotational effect' is manifested as a change in the slope of the calibration function. But the standard additions paradigm found in many textbooks does not tell the whole story. We must recognise that the method cannot overcome other types of matrix effect, which must be eliminated by additional measures before standard additions can be effective. Properly implemented, however, standard additions eliminates rotational effects with a negligible effect on precision.

Rotational and translational matrix effects

Matrix effects come in two main styles (Figure 1). Matrix A is the matrix of the analyte for calibration purposes. A rotational effect (Matrix B) arises when the size of the signal derived from the analyte is affected by non-analyte constituents of the test solution. The size of the effect for a given matrix is usually proportional to the signal and is therefore sometimes called a 'proportional' effect. It changes the slope of the calibration function, but not in its intercept. A 'translational effect' (Matrix C) arises from a signal produced by concomitant substances present in the test solution but not by the analyte. It is therefore independent of the concentration of the analyte. It is often referred to as a 'background' or 'baselin

unusual for both effects to be present simultaneously, but the method of standard additions can correct rotational effects only. Translational effects (if present) have to bs

ly have the same outcome.

The method of standard additions

The method is usually presented as the separate addition of several different equally-spaced amounts of analyte to separate aliquots of test solution (Figure 2). Measurement is followed by extrapolation of the calibration line to zero response.

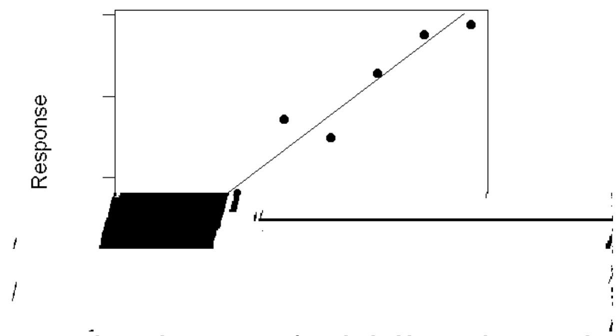

Figure 2. The usual presentation of standard additions. The estimated calibration function (solid line) is extrapolated to zero response, and the magnitude of the corresponding negative reading (*c*) is the concentration estimate.

The use of several spiking concentrations is justified in the standard paradigm by the idea that it helps to check that the calibration is truly linear. However, this rationale is not compelling in a routine, quality-assured laboratory, because:

Does standard additions degrade precision?

It is often assumed that the extrapolation involved in standard additions causes the precision of the result to be degraded in comparison with ‘normal’ external