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Technical note

Comparison of quantification strategies for one-point standard addition calibration: The heteroscedastic case

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ABSTRACT

Two quantification strategies for one-point standard addition calibration have been compared mathematically. One strategy involved the extrapolation of measurement points to their intercept with the *x*-axis to determine the analyte content in the unknown sample, and the other strategy is based upon direct calculation of the analyte content in the unknown sample using the instrumental responses obtained during measurement. The cases of both conventional standard addition calibration (C-SAC) and sequential standard addition calibration (S-SAC) have been considered. The heteroscedastic situation has been considered, where the relative precision of instrumental responses is constant.

1. Introduction

Comparison against calibration standards of known analyte content allows the unknown analyte content in a sample to be calculated [1]. When the matrix of the samples requiring measurement affects the sensitivity of the measuring instrument, standard addition calibration is employed. In this regime the calibration standards are added directly to the sample prior to analysis. Previously two distinct types of standard addition calibration have been described [2]: (a) conventional standard addition calibration (C-SAC) compares the instrumental responses (defined here as the numerical value produced by the measuring instrument resulting from the measurement of a sample) of several solutions in separate vessels containing the same quantity of sample, but different quantities of calibration standard and blank, such that the volume in each vessel is fixed, and (b) sequential standard addition calibration (S-SAC) compares the instrumental response from a quantity of sample in a single vessel to the instrumental response following the addition of portions of calibration solution into this same vessel, such that the volume considered in each measurement is not fixed. Quantification in both cases is performed by extrapolation of the calibration relationship produced to the intercept with the *x*-axis at zero analyte content, giving the content of the unknown directly (in the case of C-SAC) or indirectly (in the case of S-SAC) [3,4]. The mathematics and theory underpinning these techniques has been previously described [2,5,6].

It has been shown that, if the linearity of the measuring instrument has been proved, then extrapolations of equal or, in some cases, better precision may be achieved by the use of just one standard addition – yielding just two measurement points: the measurement of the sample and the measurement of the sample plus the standard [7]. In such a simple situation it is also possible to perform quantification by simple equations that compare the instrumental responses obtained at the two measurements points, rather than using extrapolation – this is referred to in this paper as 'quantification using only instrumental responses'. A comparison of the precision of these two modes of quantification for one point standard addition calibra-

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tion has been performed for the homoscedastic case where the ***absolute*** precision of instrumental responses is constant [8]. This paper now presents the analogous case for the heteroscedastic case where the ***relative*** precision of instrumental responses is constant.

2. Results and discussion

It is assumed throughout that measurement points are significantly in excess of the detection limit of the measuring instrument, only uncertainties in y-axis measurements (i.e. instrumental responses) are significant, the sensitivity of the measuring instrument is unity, and that the measurement regime is heteroscedastic such that the relative precision of the instrumental responses is constant regardless of their magnitude. The mathematics underpinning these calculations has been discussed at length previously [8], so here we present just the essentials of the new case under consideration.

2.1. Quantification by extrapolation

For quantification by extrapolation we consider two measurement points: P_0, which represents measurement of the unknown sample, and; P_1, which represents measurement of the unknown sample plus one standard addition. For C-SAC [2]:

$$P_0 = \left(0, \frac{m_s x_s}{m_s + m_a}\right); \tag{1}$$

$$P_1 = \left(\frac{m_a x_a}{m_a + m_s}, \frac{m_a x_a + m_s x_s}{m_a + m_s}\right); \tag{2}$$

For S-SAC [2]:

$$P_0 = \left(0, \frac{m_s x_s}{m_s}\right); \tag{3}$$

$$P_1 = \left(\frac{m_a x_a}{m_a + m_s}, \frac{m_a x_a + m_s x_s}{m_a + m_s}\right); \tag{4}$$

where: m_s is the mass of the unknown sample; m_a is the mass of the standard solution added; x_s is the fractional content of target analyte in the unknown sample; x_a is the fractional content of target analyte in the standard solution.

2.2. Quantification using only instrumental responses

For quantification by comparison of the instrumental responses (I) we consider, in effect, just the y-components of the measurement points in Eqs. (1)–(4), such that for C-SAC:

$$I_0 = m_s x_s / (m_s + m_a) \tag{5}$$

$$I_1 = (m_s x_s + m_a x_a)/(m_s + m_a) \tag{6}$$

and for S-SAC:

$$I_0 = m_s x_s / m_s \tag{7}$$

$$I_1 = (m_s x_s + m_a x_a)/(m_s + m_a) \tag{8}$$

2.3. Generalised solution

Having defined the two quantification strategies, we may now examine the generalised condition assuming heteroscedastic conditions in order to obtain directly the precision ratio produced using each method. As in our previous work [8] let us consider observables I_0 and I_1 whose dependence on x_s may be generalised for S-SAC and C-SAC such that:

$$I_0 = \alpha x_s \tag{9}$$

$$I_1 = \beta x_s + \gamma \tag{10}$$

where α, β and γ are constants given by Eqs. (5)–(8). These observables correspond to measurements made at $x = 0$ and $x = \gamma$ respectively. Combining Eqs. (9) and (10) yields:

$$x_s = \frac{\gamma I_0}{\alpha I_1 - \beta I_0} \tag{11}$$

Considering that the uncertainty of the instrumental responses in the heteroscedastic case is proportional to their value thus: $u(I_0) = \psi I_0$ and $u(I_1) = \psi I_1$, the uncertainty on x_s can be computed using the GUM method [9] to be:

$$u(x_s) = \sqrt{\left(\frac{\partial x_s}{\partial I_0}\right)^2 u(I_0)^2 + \left(\frac{\partial x_s}{\partial I_1}\right)^2 u(I_1)^2} \tag{12}$$

The partial derivatives can be computed directly from the expression for x_s in Eq. (11), yielding

$$\frac{\partial x_s}{\partial I_0} = \frac{\alpha\gamma I_1}{(\alpha I_1 - \beta I_0)^2} \tag{13}$$

$$\frac{\partial x_s}{\partial I_1} = \frac{-\alpha\gamma I_0}{(\alpha I_1 - \beta I_0)^2} \tag{14}$$

Defining $\varsigma_{ai} = u(x_s)/\psi$, we obtain:

$$\varsigma_{ai} = \frac{\alpha k \gamma \sqrt{2} I_0 I_1}{(\alpha I_1 - \beta I_0)^2} \tag{15}$$

Following from the earlier discussion, we can also determine x_s using an extrapolation procedure. The uncertainty for this procedure has been previously defined for a two-point situation as [8]:

$$\varsigma_{en} = \sigma/\sigma_0 = \frac{1}{\dot{V}\sqrt{2}}\sqrt{1 + \frac{\bar{y}^2}{\dot{V}^2 \bar{x}^2}} \tag{16}$$

where σ is the precision of the extrapolation of the calibration relationship to its intercept with the x-axis and σ_0 is the precision of measurement points in the y-direction. In the heteroscedastic case we replace σ_0 with the average of the precision of the two measurement points in the y-direction: $[u(I_0) + u(I_1)]/2$. The normalised uncertainty with respect to ψ (i.e. $\varsigma_{en} = \sigma/\psi$) is then:

$$\varsigma_{en} = \frac{1}{2}(I_0 + I_1)\frac{1}{\sqrt{2}\dot{V}}\sqrt{1 + \frac{\bar{y}^2}{\dot{V}^2 \bar{x}^2}} \tag{17}$$

We may then calculate the ratio $\varsigma_{ai}/\varsigma_{en}$. Noting, as previously [8], the simplifications: $\bar{y} = \frac{1}{2}(I_0 + I_1)$,