Supplementary Material (ESI) for Analyst

Standard additions: myth and reality

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Appendix – calculation of relative uncertainties of unknown concentrations

Single-point standard addition

For the single-point standard additions case, where

$$T = C\frac{r_T}{r_{T+C} - r_T}$$

we have, from error propagation

$$\mathrm{var}(T) = C^2\left\{\mathrm{var}(r_T)\left[\frac{1}{r_{T+C}-r_T} + \frac{r_T}{(r_{T+C}-r_T)^2}\right]^2 + \mathrm{var}(r_{T+C})\left[\frac{r_T}{(r_{T+C}-r_T)^2}\right]^2\right\} = \frac{C^2}{(r_{T+C}-r_T)^4}\left[\mathrm{var}(r_T)r_{T+C}{}^2 + \mathrm{var}(r_{T+C})r_T{}^2\right]$$

and

$$\mathrm{RSD}(T) = \frac{1}{T}\left\{\frac{C^2}{(r_{T+C}-r_T)^4}\left[\mathrm{var}(r_T)r_{T+C}{}^2 + \mathrm{var}(r_{T+C})r_T{}^2\right]\right\}^{1/2} = \frac{1}{r_T(r_{T+C}-r_T)}\left[\mathrm{var}(r_T)r_{T+C}{}^2 + \mathrm{var}(r_{T+C})r_T{}^2\right]^{1/2}.$$

Setting $Q = (C + T)/T = r_{T+C}/r_T$, $1/\kappa = c_L/T$, $\mathrm{var}(r_T) = A^2 + 1/4\kappa^2$, and $\mathrm{var}(r_{T+C}) = Q^2A^2 + 1/4\kappa^2$ we have:

$$\mathrm{RSD}(T) = \frac{1}{(Q-1)}\left[Q^2\left(A^2 + \frac{1}{4\kappa^2}\right) + Q^2A^2 + \frac{1}{4\kappa^2}\right]^{1/2} = \frac{Q}{(Q-1)}\left[2A^2 + \frac{1}{4\kappa^2}\left(1 + \frac{1}{Q^2}\right)\right]^{1/2}$$

Two-point calibration

For general two-point calibration,

$$T = C_0 + (C_1 - C_0)\frac{r_T - r_0}{r_C - r_0}$$

where, for generality, C_0 is taken as the lower and C_1 as the upper concentration corresponding to r_0 and r_1 respectively.

This gives, for the partial differentials

$$\frac{\partial T}{\partial r_0} = -(C_1 - C_0)\left[\frac{1}{r_1 - r_0} - \frac{r_T - r_0}{(r_1 - r_0)^2}\right] = -\frac{C_1 - C_0}{r_1 - r_0}\left[1 - \frac{r_T - r_0}{r_1 - r_0}\right] = -\frac{C_1 - C_0}{r_1 - r_0}\left[\frac{r_T - r_0}{r_1 - r_0}\right],$$

$$\frac{\partial T}{\partial r_1} = -\left(C_1 - C_0\right)\frac{r_T - r_0}{\left(r_1 - r_0\right)^2} = -\frac{C_1 - C_0}{r_1 - r_0}\frac{r_T - r_0}{r_1 - r_0}$$

and

$$\frac{\partial T}{\partial r_T} = \frac{C_1 - C_0}{r_1 - r_0}$$

from which

$$\mathrm{var}(T) = \left[\frac{C_1 - C_0}{r_1 - r_0}\right]^2 \left\{\mathrm{var}\left(r_T\right) + \mathrm{var}\left(r_0\right)\left[\frac{r_1 - r_T}{r_1 - r_0}\right]^2 + \mathrm{var}\left(r_1\right)\left[\frac{r_T - r_0}{r_1 - r_0}\right]^2\right\}.$$

Assuming zero for the lower concentration, and C for the upper, this becomes:

$$\mathrm{var}(T) = \left[\frac{C}{r_1 - r_0}\right]^2 \left\{\mathrm{var}\left(r_T\right) + \mathrm{var}\left(r_0\right)\left[\frac{r_1 - r_T}{r_1 - r_0}\right]^2 + \mathrm{var}\left(r_1\right)\left[\frac{r_T - r_0}{r_1 - r_0}\right]^2\right\}$$

The RSD is then:

$$\mathrm{RSD}(T) = \frac{C}{r_1 - r_0}\left\{\mathrm{var}\left(r_T\right) + \mathrm{var}\left(r_0\right)\left[\frac{r_1 - r_T}{r_1 - r_0}\right]^2 + \mathrm{var}\left(r_1\right)\left[\frac{r_T - r_0}{r_1 - r_0}\right]^2\right\}^{1/2} \Big/ C\frac{r_T - r_0}{r_1 - r_0} = \frac{1}{r_T - r_0}\left\{\mathrm{var}\left(r_T\right) + \mathrm{var}\left(r_0\right)\left[\frac{r_1 - r_T}{r_1 - r_0}\right]^2 + \mathrm{var}\left(r_1\right)\left[\frac{r_T - r_0}{r_1 - r_0}\right]^2\right\}^{1/2}$$

Setting $Q = C/T$, $1/\kappa = c_L/T$, $\mathrm{var}(r_0) = 1/4\kappa^2$, $\mathrm{var}(r_T) = A^2 + 1/4\kappa^2$, and $\mathrm{var}(r_1) = Q^2A^2 + 1/4\kappa^2$ gives:

$$\mathrm{RSD}(T) = \left\{A^2 + \frac{1}{4\kappa^2} + \frac{1}{4\kappa^2}\left[\frac{Q-1}{Q}\right]^2 + \left(Q^2A^2 + \frac{1}{4\kappa^2}\right)\left[\frac{1}{Q}\right]^2\right\}^{1/2} = \left\{2A^2 + \frac{1}{2\kappa^2}\left(1 - \frac{1}{Q} + \frac{1}{Q^2}\right)\right\}^{1/2}$$