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

\[ T = \frac{C}{r_{T+c} - r_T} \]

we have, from error propagation

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

and

\[ \text{RSD}(T) = \frac{1}{T} \left\{ \frac{C^2}{(r_{T+c} - r_T)} \left[ \text{var}(r_T) r_{T+c}^2 + \text{var}(r_{T+c}) r_T^2 \right] \right\}^{1/2} = \frac{1}{r_T} \left( \frac{1}{r_{T+c} - r_T} \right) \left[ \text{var}(r_T) r_{T+c}^2 + \text{var}(r_{T+c}) r_T^2 \right]^{1/2} \]

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

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

Two-point calibration

For general two-point calibration,

\[ T = C_0 + \left( C_1 - C_0 \right) \frac{r_T - r_0}{r_T - r_0} \]

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

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

\[ = -\frac{C_1 - C_0}{r_T - r_0} \left[ 1 - \frac{r_T - r_0}{r_T - r_0} \right] = -\frac{C_1 - C_0}{r_T - r_0} \left[ r_T - r_0 \right] \]

\[ = -\frac{C_1 - C_0}{r_T - r_0} \left[ r_T - r_0 \right] \]
\[
\frac{\partial T}{\partial \tau_1} = -(C_i - C_o) \frac{\tau_1 - \tau_0}{\tau_1 - \tau_0} = -\frac{C_i - C_o}{\tau_1 - \tau_0} \frac{\tau_1 - \tau_0}{\tau_1 - \tau_0}
\]

and

\[
\frac{\partial T}{\partial \tau_T} = \frac{C_i - C_o}{\tau_1 - \tau_0}
\]

from which

\[
\text{var}(T) = \left[ \frac{C_i - C_o}{\tau_1 - \tau_0} \right]^2 \left\{ \text{var}(\tau_1) + \text{var}(\tau_T) \left[ \frac{\tau_1 - \tau_0}{\tau_1 - \tau_0} \right]^2 + \text{var}(\tau_T) \left[ \frac{\tau_T - \tau_0}{\tau_T - \tau_0} \right]^2 \right\},
\]

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

\[
\text{var}(T) = \left[ \frac{C}{\tau_1 - \tau_0} \right]^2 \left\{ \text{var}(\tau_1) + \text{var}(\tau_T) \left[ \frac{\tau_1 - \tau_0}{\tau_1 - \tau_0} \right]^2 + \text{var}(\tau_T) \left[ \frac{\tau_T - \tau_0}{\tau_T - \tau_0} \right]^2 \right\}
\]

The RSD is then:

\[
\text{RSD}(T) = \frac{C}{\tau_1 - \tau_0} \left\{ \text{var}(\tau_1) + \text{var}(\tau_T) \left[ \frac{\tau_1 - \tau_0}{\tau_1 - \tau_0} \right]^2 + \text{var}(\tau_T) \left[ \frac{\tau_T - \tau_0}{\tau_T - \tau_0} \right]^2 \right\}^{1/2}
\]

Setting \( Q = C/T \), \( 1/\kappa = c_0/T \), \( \text{var}(\tau_0) = 1/4\kappa^2 \), \( \text{var}(\tau_1) = A^2 + 1/4\kappa^2 \), and \( \text{var}(\tau_T) = Q^2A^2 + 1/4\kappa^2 \) gives:

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