Electronic Appendix 3

On the equivalence of uncertainties obtained using the ratio-of-means and the mean-of-ratios approaches to the calculation of the count number ratio

There is a discussion in the literature of ICP and secondary ion mass spectrometry regarding the comparison of count number (intensity) ratio uncertainties obtained using the ratio-of-means and mean-of-ratio-definition of the isotope ratio\textsuperscript{1,3}. For a time-resolved signal made of \( n \) successive count number acquisitions, it is possible to define the count number ratio as a ratio of means:

\[
\frac{N^x}{N^y} = \frac{N^x_{\text{total}}}{N^y_{\text{total}}} / n = N^x_{\text{total}} / N^y_{\text{total}}
\]

or as a mean of ratios:

\[
\frac{N^x}{N^y} = \frac{\sum_{i=1}^{n} \left( \frac{N^x}{N^y} \right)_i}{n}
\]

It is instructive to prove that the ratio uncertainties obtained using the above definitions coincide:

\[
\text{Var} \left( \frac{\sum_{i=1}^{n} \left( \frac{N^x}{N^y} \right)_i}{n} \right) = \frac{1}{n^2} \text{Var} \left( \sum_{i=1}^{n} \left( \frac{N^x}{N^y} \right)_i \right) = \frac{1}{n} \text{Var} \left( \frac{N^x}{N^y} \right)_i
\]

\[
= \frac{1}{n} \left( \frac{1}{(N^y)^2} \text{Var}(N^x) + \frac{(N^y)^2}{(N^{y^2})^4} \text{Var}(N^y) - 2 \frac{1}{N^y} \frac{N^x}{(N^y)^2} \text{Cov}(N^x,N^y) \right)
\]

\[
= \frac{1}{(N^y)^2} \text{Var}(N^x) + \frac{(N^y)^2}{(N^{y^2})^4} \text{Var}(N^y) - 2 \frac{1}{N^y^2} \frac{N^x}{(N^y)^2} \text{Cov}(N^x,N^y)
\]

\[
= \frac{1}{(N^y)^2} \text{Var}(N^x) + \frac{(N^y)^2}{(N^{y^2})^4} \text{Var}(N^y) - 2 \frac{1}{N^y^2} \frac{N^x}{(N^y)^2} \text{Cov}(N^x,N^y)
\]

Published ICPMS data corroborate that ratio-of-means and mean-of-ratios uncertainties are approximately equal\textsuperscript{1,3}, provided \( N^x \) is not very low (to ensure an appropriate linearisation of the ratio function and applicability of the error propagation above).

References: