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[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:

$$\left(\frac{N^x}{N^y}\right)_{mean} = \frac{\overline{N}_i^x}{\overline{N}_i^y} = \frac{N^x_{total}/n}{N^y_{total}/n} = \frac{N^x_{total}}{N^y_{total}}$$

or as a mean of ratios:

$$\left(\frac{N^x}{N^y}\right)_{mean} = \overline{\left(\frac{N^x}{N^y}\right)_i} = \frac{\sum_{i=1}^{n}\left(\frac{N^x}{N^y}\right)_i}{n}$$

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

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

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

$$= \frac{1}{(\overline{N}^y)^2}\frac{Var(N^x)}{n} + \frac{(\overline{N}^x)^2}{(\overline{N}^y)^4}\frac{Var(N^y)}{n} - 2\frac{1}{\overline{N}^y}\frac{\overline{N}^x}{(\overline{N}^y)^2}\frac{Cov(N^x,N^y)}{n}$$

$$= \frac{1}{(\overline{N}^y)^2}Var(\overline{N}^x) + \frac{(\overline{N}^x)^2}{(\overline{N}^y)^4}Var(\overline{N}^y) - 2\frac{1}{\overline{N}^y}\frac{\overline{N}^x}{(\overline{N}^y)^2}Cov(\overline{N}^x,\overline{N}^y)$$

$$= Var\left(\frac{\overline{N}^x}{\overline{N}^y}\right) = Var\left(\frac{N^x_{total}/n}{N^y_{total}/n}\right) = Var\left(\frac{N^x_{total}}{N^y_{total}}\right)$$

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

References:

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