**Appendix F: Calculation of Standard Uncertainty**

While it is necessary to report all of the relevant information discussed in the text, for the sake of convenience, here we present a single metric for summarizing analytical uncertainty that incorporates both accuracy (a good indicator of measurement bias or systematic error) and precision (a good indicator of random error in measurement). Through proper calibration, systematic errors leading to inaccurate results should be minimized, but it is likely that some small amount (<0.1 ‰ deviation from the ‘true’ value as evaluated by analysis of check standards) will remain (Skrzypek, 2013). This metric is informed by the procedures for combining standard uncertainties outlined by the Guide to the Expression of Uncertainty in Measurement (GUM) (Joint Committee for Guides in Metrology, 2008) and the Nordtest Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories (Magnusson et al., 2012). The latter of these two presents a more accessible and reasonable means of assessing uncertainty than the component-by-component procedure outlined by the GUM, particularly for those not involved in instrument operation and primary data acquisition. The overall analytical uncertainty consists of a number of different components and as a standard practice, when these components are combined, this process involves taking the root-sum-square of those components (Joint Committee for Guides in Metrology, 2008).

The standard uncertainty of a sample (*uc*) is defined by Equation 1:

Equation 1

$$u\_{c}= \sqrt{u\left(R\_{w}\right)^{2} + \left(u(bias)\right)^{2} }$$

The first term of Equation 1, *u(Rw)*, is associated with random errors within the laboratory and is equated, in terms of performance characteristics, with measurements of precision (Menditto et al., 2007) or repeatability as described in the text (following Carter and Fry, 2013). The second term in Equation 1, *u(bias)*, is associated with systematic measurement errors and can be equated, in terms of performance characteristics, with measurements of ‘trueness’ (Menditto et al., 2007) or accuracy as described in the text (following Carter and Fry, 2013) . With respect to IRMS measurements, the random error term (*u(Rw)*) is the summed standard deviations of all repeated measurements during the relevant analytical sessions, which includes: check and calibration standards (*ssrm*) and any unknown samples analyzed multiple times (*srep*). The random error term (*u(Rw)*) is the root-sum-square of these two uncertainty components, as defined by Equation 2:

Equation 2

$$u\left(R\_{w}\right)= \sqrt{\left(s\_{srm}\right)^{2} + \left(s\_{rep}\right)^{2} }$$

Both *ssrm* and *srep* are defined as the pooled standard deviation of each component (*sx*), following Equation 3:

**Equation 3**

$$s\_{x}= \sqrt{\frac{\left(n\_{1}-1\right)s\_{1}^{2}+ \left(n\_{2}-1\right)s\_{2}^{2}+ . . . + \left(n\_{k}-1\right)s\_{k}^{2}}{n\_{1}+ n\_{2}+ . . . + n\_{k}-k}}$$

Where *k* is the number of different samples analyzed repeatedly such that in the case of calculating *ssrm k* would be equal to the number of different standard reference materials that were analyzed and in the case of calculating *srep* *k* would equal the number of samples that were analyzed in duplicate or triplicate and so on. The term *nk* represents the number of measurements made for a specific standard or sample and *sk* represents within standard reference material or sample standard deviation. For *ssrm* each *sk* term represents one standard reference material measured in one analytical session, not the average of one standard reference material measured across all analytical sessions.The pooled standard deviation is a weighted average of multiple standard deviations. It is advantageous to simply computing an average standard deviation because it provides more ‘weight’ to those samples or standards that have been analyzed more times (i.e., more weight to samples analyzed in triplicate relative to samples analyzed in duplicate). The second term in Equation 1 (*u(bias)*) is defined by Equation 4:

**Equation 4**

$$u(bias)= \sqrt{\left(RMS\_{bias}\right)^{2} + u(Cref)^{2} }$$

*RMSbias* represents the root-mean-square of the difference (*biasi*) between the observed mean (*Clabi*) and known (*Crefi*) values of the standard reference materials that are treated as unknowns during analysis (check standards). *RMSbias* is therefore defined by Equation 5 and *biasi* is defined by Equation 6:

**Equation 5**

$$RMS\_{bias}= \sqrt{\frac{\sum\_{}^{}\left(bias\_{i}\right)^{2}}{n}}$$

**Equation 6**

$$bias\_{i}= Clab\_{i}- Cref\_{i}$$

The second term in Equation 4 (*u(Cref)*) is simply the root-mean-square of the known standard deviations of the reference materials used as check standards, either determined through long-term monitoring (for in-house standards) or provided upon purchase (for certified reference materials) as defined in Equation 7:

**Equation 7**

$$u\left(Cref\right)= \sqrt{\frac{\sum\_{}^{}u\left(Cref\_{i}\right)^{2}}{n}}$$

These calculations can be performed easily in a simple spreadsheet, such as in Appendix F. The sample calculations in this spreadsheet are associated with the data presented in Appendix D. Note that if data are included across multiple analytical sessions, a new column should be added for each check standard analyzed in each session. The calculated standard uncertainty represents a coverage factor (*k*) of 1, corresponding to one standard deviation.

**References**

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