QA/QC in-class exercise.

J. Renée Brooks, ([Brooks.ReneeJ@epa.gov](mailto:Brooks.ReneeJ@epa.gov))

Goals:

* Learn the difference between sample precision and analytical precision of the IRMS.
* Learn about accuracy and bias in measurements.
* Learn about propagating error including that of the primary standard.
* Learn to calculate the sample precision and accuracy from all the QA/QC data from your study for reporting in your paper.

The Spreadsheet “QAQC Exercise 2019” contains QC data that I have compiled from multiple IRMS spreadsheets containing some samples collected from the 2013 National Rivers and Streams Assessment. You are going calculate sample precision on duplicate samples collected on the same day in the field (sample precision). You will also calculate accuracy and precision for the laboratory QC standards. In your manuscripts, you should report precision (σ) based on *n* duplicates, and accuracy (µ ± σ) based on *n* QC standards. **For every study, you should compile a similar QA/QC page**.

1. *Sample Precision*: In columns A-C, I have compiled the data from 10 sample replicates. Precision is the closeness of repeated measures to each other, and is usually expressed as the *standard deviation*. Since you have more than one repeated sample (and they have different values from each other), the standard deviation is calculated using the following equation:



where s2 is the variance between replicates and n-1 is the degrees of freedom for a set of replicates. This equation weights your variance by sample size, and then calculates the standard deviation.

For Excel =var(values) gives s2

=sum(values) gives ∑

=sqrt(value) gives square root

=count(values) gives n

* 1. Calculate *d-excess* in Column D (*d-excess* = D – 8\*18O)
  2. In column E put the degrees of freedom (n-1, Note: since we only have two replicates per sample df=1, this also means that s2(n-1) = s2, so we don’t have to multiply s2 and (n-1) those for pairs).
  3. In columns F-H, calculate the variance for each pair of samples for D, 18O and *d-excess*.
  4. Sum the variances and the degrees of freedom, putting the results in the yellow cells in row 24.
  5. In the yellow cells in Row 26, take the square root of the sum of the variance divided by the sum of the degrees of freedom (equation above). Check your answers against mine.

1. *Accuracy and Precision of the QC standards.* In Columns K-M are the results from the QC standards (one per run). These standards have not been used to correct the data in anyway, so they are your quality assurance that your results are good. Since we have known values for these, we can calculate accuracy.
   1. Calculate *d-excess* in Column N (*d-excess* = D – 8\*18O)
   2. *Accuracy*: for each isotope, calculate the difference between measured (Col L-N) and actual (Col O-Q) (measured – actual) in Columns R-T.
   3. Calculate the *average* difference (=average(diff values)) in the yellow boxes (Row 20). This is the overall accuracy during your study period and should be near zero.
   4. Calculate the standard deviation of the differences (=stdev(diff values)) in yellow boxes (Row 21). This describes the variation in accuracy over your study period, and should be larger than the average. *Standard deviation should be larger than the average.*
   5. *Precision:* Calculate precision as described for sample replicates (steps 1.2-1.5), **EXCEPT** *note that degrees of freedom will be greater than 1*! Thus, you must multiply s2 and (n-1) for each standard, and put results in Columns U-AA. Put the answers in the yellow boxes (Row 20 and 22).

Questions:

1. How well is the machine running? Is there a significant machine bias?
2. How variable are my samples (variation within a sample)?
3. Have my samples been unintentionally fractionated since collection?
4. Does the uncertainty around the IAEA standard affect my reporting error?
5. How different are my populations going to have to be to detect a difference?