Recommended Uncertainty Propagation for U-Pb geochronology by LA-ICPMS.

These guidelines are compiled from discussions of a breakout group at the Data Handling Workshop in San Francisco 2010. Guideline authors are Noah McLean, Norman Pearson, Chad Paton & Blair Schoene. It is proposed that these guidelines form the basis for a recommended uncertainty propagation protocol for LA-ICP-MS U-Th-Pb data.

The breakout group began by enumerating all sources that may contribute to the uncertainty of a LA-ICPMS U-Pb date. Aspects identified include:

a. Counting statistics while measuring each peak
b. Beam instability/drift
c. Elemental fractionation (between U and Pb), during ablation and ionization
d. Mass fractionation (between isotopes of the same element), during ablation and ionization
e. Matrix-induced bias
f. Detector calibration (linearity and relative gain)
g. Spatial variability, in the cell and on the mount
h. Hg correction (magnitude of correction and Hg IC, or isotopic composition)
i. Common Pb correction (both magnitude and IC)
j. Background correction, for gas blank and tracer blank
k. Ratio determinations for the primary standard
l. Standard age uncertainty
m. Decay constant uncertainties

The group, along with the rest of the workshop participants, also agreed on a general scheme for data reduction and uncertainty propagation, which was compiled into a flow chart.

Prior to measurement, estimate the common Pb and mercury ICs and their uncertainties. For ion counters, estimate the deadtime and its uncertainty.

1) Measure the baseline/gas blank before the analysis. Calculate the average count rate of each baseline peak. For low count rates, Poisson statistics are appropriate to determine the uncertainty of baseline intensities.
2) Ablate, ionize, and measure intensities under peaks.
    a. Subtract the baseline directly from the measured intensities.
    b. If performing a common Pb correction, subtract the Hg interference from time-resolved 204 data.
    c. If performing a common Pb correction, use the remaining 204 to subtract common Pb from the time-resolved signal.
3) Calculate an isotope ratio for each standard and unknown that has not been corrected for session-scale drift in elemental or mass fractionation. Four methods are currently used:

   a. Calculate the ratio of the mean intensities during each analysis. The uncertainty calculated is predominantly due to the drift in these intensities during each analysis.
   b. Calculate a ratio for each intensity measurement during the analysis, and then take the mean of the ratios. The uncertainty calculated is predominantly due to drift in these ratios during each analysis.
   c. Fit a curve (line, polynomial, exponential, etc.) to the trend in isotope ratios with time. Extrapolate back to time zero, when the laser began ablating. The uncertainty in the ratio is the uncertainty in this intercept from the parametric fit.
   d. Follow (b) for each of the standard measurements. Stack these measurements and fit a curve (exponential, polynomial, smoothing spline, etc.) to the ratios to model the *change* in down-hole fractionation with time. Apply this time-resolved correction to each of the standards and unknowns, and then calculate the mean and standard error of each (Paton et al 2010, G3).

4) Use the standard measurements to correct the unknowns for elemental and mass fractionation.
   a. Find the normalization factor (standard true value / standard measured value) as a function of time for the session. If the standard ratios do not change during a session, take their mean and apply this correction to each of the unknowns. If the ratios drift, fit a curve (line, polynomial, smoothing spline) to the means of the standard measurements for the session, then interpolate between the standards to the unknowns. Standard data can be screened by an outlier detection algorithm to avoid biasing neighboring unknown measurements.
   b. Determine the excess scatter, ε^2, in the standard measurements. This is the variance that must be added to each point on top of the variance measured in (3) to explain the scatter in the data. The squared distance of each standard mean from the best-fit line in 4a is divided by its variance; these terms are added and divided by the degrees of freedom (one for a mean in 4a, two for a line, etc.) to determine the MSWD. Solve for the ε^2 that makes the MSWD unity.
   c. Add ε^2 to the variance for each standard and use this total uncertainty—from (3) and (4b)—to determine the uncertainty of the interpolated normalization factor.
   d. Additionally, add ε^2 to the variance for each unknown from (3) to correct for their "excess scatter," which is assumed to be the same as that of the standard.
5) If the IC of common Pb and/or Hg is assumed to vary from analysis to analysis, propagate the uncertainty in this variability.
6) It is now appropriate to screen for outliers in the unknown isotope ratios, and calculate population statistics as appropriate. If the data represent repeated measurements of a single date, calculate mean statistics. If the data represent an age spectrum, estimate the population's probability density function. *Guidelines for the quantification of detrital zircon data will form the focus of a future workshop.*

7) There are three important external sources of uncertainty: the age of the primary normalization standard, the long-term scatter observed in secondary standard measurements, and the U decay constants. These are included after calculating the relevant statistics in (6). A parallel may be made to the ID-TIMS community, and uncertainties reported in three levels:
    a. Analytical uncertainties alone, as calculated in (6).
    b. Analytical uncertainties plus the uncertainty contributed by the age of the primary normalization standard, usually as determined by ID-TIMS. This will be a small contribution, but it's necessary for comparison of data measured with different standards.
    c. Analytical, standard age, and decay constant uncertainties

Instead of adding in systematic uncertainties after (6), they may be propagated with the algorithm of McLean et al (in prep), which determines the sensitivity of each analysis to the systematic uncertainty and then treats these as uncertainty correlations between the unknowns. Another important and unexplored source of correlation between unknowns is incurred when each is corrected by an uncertain normalization factor that is calculated from the same set of standard measurements.