How Good Is Your Number?
Part 1: Measurement Variability

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The quality of a chemical measurement can be described by the bias and variability of the measurement. Bias is the systematic error in a measurement and results in measurements that differ from the true value in the same direction. Variability is the random error in a measurement and results in measurements randomly distributed around the true value. For most chemical measurement methods, a normal distribution of random errors is observed. For this presentation, a normal distribution of random error and zero bias are assumed.

Variability is characterized by the repeated application of the measurement method under the same conditions. In other words, variability is characterized by the measurement of “replicates.” Replicates are two or more samples collected such that they are considered essentially identical. Variability typically is expressed as a standard deviation and statistical confidence limits can be calculated to describe the limits to random error for a single measurement. With measurement variability defined, one can determine if two measurements are significantly different. An example calculation of confidence limits will be presented.

Two errors are common in the characterization of the variability of chemical measurements. The first error is the failure to recognize that variability is a function of concentration—as concentration increases, standard deviation increases. Estimates of variability at one concentration may not be appropriate at a different concentration. The second error is that individual estimates of standard deviation should not be averaged to obtain an overall estimate of standard deviation. Averaging standard deviations will produce a biased-low estimate of the population standard deviation. Rather, individual estimates of variance (standard deviation squared) should be averaged and the square root taken to produce an unbiased estimate of the population standard deviation. Examples of both types of errors will be presented.