Types of Experimental Error

Systematic Error (aka; Determinant Error)

Bias

Random Error (aka; Indeterminant Error)

Precision

Approaches to Estimate Systematic Errors

1. Analysis of SRM/CRM

2. Analysis by alternate reliable method or independent laboratory

3. Analysis of 'spiked' samples – known amount of analyte is intentionally added to sample. Percent recovery expresses amount of analyte increase relative to the amount added. Spikes can be done in the field to check for losses in due to sampling, storage, transport etc. or in the lab to check for losses handling, preparation steps or instrumental analysis. Recoveries often based on deuterated analyte spikes.

4. Analysis of Blanks – to reveal interferences and/or contaminations
Field blanks, transport blanks, bottle blanks, reagent blanks, sample blanks

5. Variation of Sample size

Bias is the degree of agreement between a measured value and the accepted or 'true' value. Bias can be expressed in absolute or relative terms.

Approaches to Estimate Random Errors

Analysis of replicates

Precision is defined as level of agreement amoung individual measuremnts of the same property. Precision can be expressed as standard deviation, relative standard deviation or variance.

Sample standard deviation

→ variance

True standard deviation

→ variance

RSD (or CV = coefficient of variation)

More on Standard Deviations

Gaussian distribution of random errors can be characterized by;

1.

2.

3.

When N (the number of replicates) is greater than 20, the true standard deviation, σ is given by;

σ =

In analytical chemistry, the **standard deviation** is a measure of the breadth of the distribution of data and consequently the preision of the analysis.

i.e., 68% of the data lie within one standard deviation of the mean value ($\pm 1\sigma$)
95% of the data lie within two standard deviations of the mean value ($\pm 2\sigma$)

Most analytical chemists will preform less than 20 replicate measurements and use the '**sample standard deviation**' ***s*** (or σ_{n-1}).

s =

Check once manually and then use calculators or spreadsheets to preform this calculation.

Pooling data to improve the reliability of ***s***

Assuming the same sources of random error, the data from a series of similar analysis can be accumulated to give a better estimate of the standard deviation.

s_{pooled} =