EXPERIMENTAL ERRORS ACCURACY

CHEM 251 SDSU

ERRORS IN MEASUREMENTS

- When we conduct a set of measurements, such as in the table to the the right, two significant questions arise:

  - Does the mean (or other central tendency) agree with the expected (or "true") value?

  - Why is there variability in the measurements of the sample?

- The first question deals with **accuracy** while the second deals with **precision**.

Trial	Value
1	2.785
2	2.746
3	2.756
4	2.762
5	2.777
6	2.751
7	2.773
Mean	2.764
Sted. Dev.	0.014

ACCURACY

- The **accuracy** of a set of measurements is <u>how close</u> the measure of central tendency is to the expected value (μ).

- The accuracy can be described in two ways:

  - The absolute error (e)

  - The percent relative error (%e$_r$)

Absolute Error

$$e = x - \mu$$

Percent Relative Error

$$\%e_r = \frac{|\bar{x} - \mu|}{\mu} \times 100$$

DETERMINATE ERRORS

- Errors that influence the accuracy of a measurement are termed **determinate errors**.

- There are several different sources for determinate errors, all of which combine to influence the accuracy of a measurement.

- Each source of error in a given measurement will have its own magnitude and sign, which will be replicable.

- Indeterminate errors, which will be discussed later are random and will change from positive to negative errors in replicate measurements.

SAMPLING ERRORS

- **Sampling errors** occur when the sample does not properly represent the system.

- For example, samples from the left and right banks of the river in the photo will have very different levels of sediment present.

- In the lab this can easily occur if you do not *invert and mix volumetric flasks before taking aliquots.*

The Rio Negro meets the Amazon River
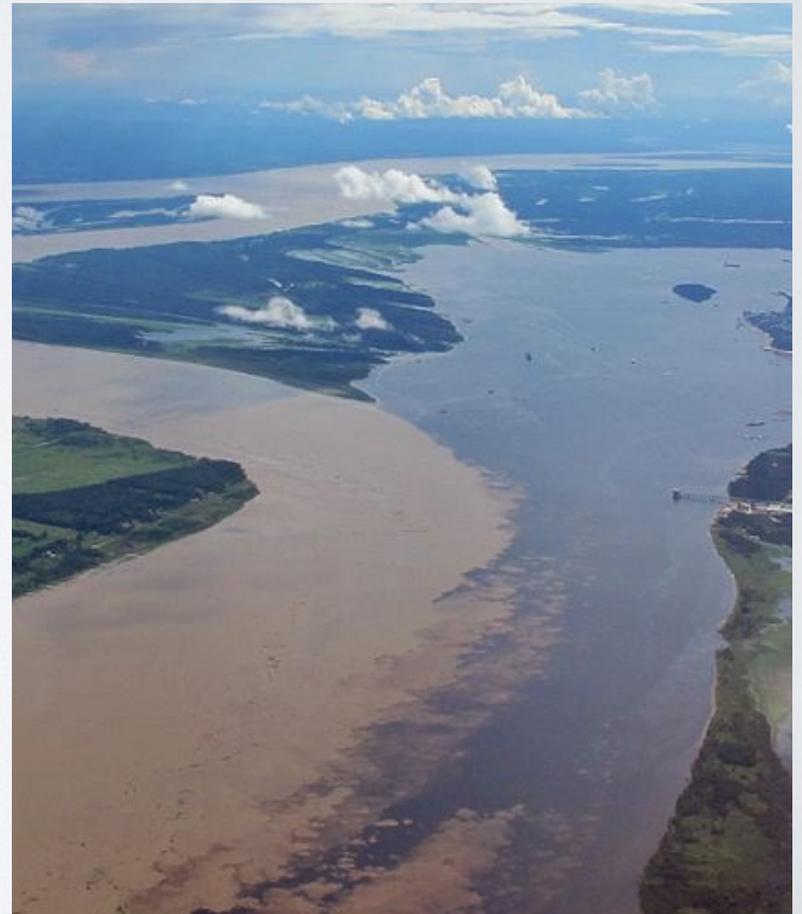
METHOD ERRORS

- For all analyses there is a relationship between the signal that we measure (S_{total}) and either the absolute amount of the analyte (n_A) or the concentration of the analyte (C_A).

$$S_{total}=k_A n_A+S_{mb}$$

$$S_{total}=k_A C_A+S_{mb}$$

- The sensitivity of the method (k_A) and the method blank (S_{mb}) must both be valid in order to avoid a **method error**.

MEASUREMENT ERRORS

- **Measurement errors** are inherent on all manufactured instruments and equipment. The maximum **measurement error** or **tolerance** is typically reported on the instrument (i.e. 25±0.030 mL).

- A delivery from this pipette could be anywhere between 25.030 mL and 24.970 mL.

- Each pipette will have its own error, some will be positive, some will be negative, but they will be consistent.

- The determinate error in the delivery can be reduced drastically by proper calibration of the pipette (e.g. the pipette may be determined to deliver 25.018 mL)

PERSONAL ERRORS

- **Personal errors** are the "human factor" in any analysis.

- These can include:

  - Sensitivity to seeing a color change endpoint.

  - Biases: over- or underestimating readings.

  - Failures to calibrate.

  - Misinterpretations of procedural directions.

IDENTIFYING DETERMINATE ERRORS

- It can be difficult to identify determinate errors, but when identified they can be corrected.

- Determinate errors can fall into two categories: **constant** and **proportional**.

- Constant determinant errors provide the same magnitude or error regardless of the amount of analyte. Can be detected by analyzing different amounts of the same sample.

- Proportional determinant errors provide differing magnitudes of error with different amounts of analyte. These are much more difficult to detect, likely need a reference standard or alternate method.