26 - STANDARD ADDITIONS

SDSU CHEM 251

STANDARD ADDITION

- The standard addition process is a way of getting around complications due to the sample matrix negatively impacting results.
- The sample (e.g. Pb^{2+}) is prepare (it may be diluted) and then a known amount of standard (Pb^{2+}) is added to the sample.
- Measurements are compared for the sample with and without the added standard to determine the concentration of the analyte in the sample.
- As long as the amount of standard solution added to the sample is relatively small the sample does not need to be prepared in a comparable matrix, as the dilution should be minimal.

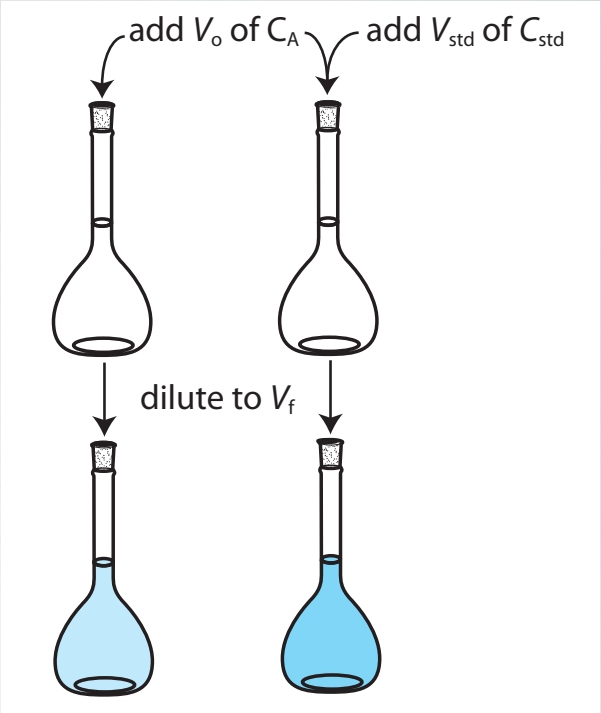
STANDARD ADDITIONS

- **Standard addition** - the addition of a known amount of standard to the sample - can minimize the matrix effects.
- **Single standard addition** can be performed in two ways:
  - Two solutions with equal amounts of sample, one with a known amount of standard.
  - One solution of sample, measured before and after the addition of a known amount of standard.
- The signals from each solution can be used to extrapolate the concentration of the sample in the solution.

SINGLE ADDITION - TWO FLASKS

A 1.00 mL sample of blood is diluted to volume in a 5.00 mL volumetric flask. When measured for it's Pb^{2+} content the signal (S_{samp}) was 0.193.

A second 1.00 mL blood sample was prepared and spiked with 1.00 µL of 1560 ppb Pb^{2+} before being diluted to 5.00 mL. When the spiked sample was measured the signal (S_{spike}) was determined to be 0.419. What is the concentration of Pb^{2+} in the blood sample?



V_O : volume of sample

V_{spike}: volume of spike solution

V_F : final solution volume

$$S_{samp} = k_A C_A \frac{V_O}{V_F} \qquad S_{spike} = k_A \left(C_A \frac{V_O}{V_F} + C_{spike} \frac{V_{spike}}{V_F} \right)$$

$$\frac{S_{samp}}{C_A \frac{V_O}{V_F}} = \frac{S_{spike}}{C_A \frac{V_O}{V_F} + C_{spike} \frac{V_{spike}}{V_F}}$$

$$V_O = 1.00 mL$$

$$V_{spike} = 1.00 \mu L = 1.00 \times 10^{-3} mL$$

$$V_F = 5.00 mL$$

$$C_{spike} = 1560 ppb$$

$$S_{samp} = 0.193$$

$$S_{spike} = 0.419$$

$$C_A = ?$$

$$\frac{S_{samp}}{C_A \frac{V_O}{V_F}} = \frac{S_{spike}}{C_A \frac{V_O}{V_F} + C_{spike} \frac{V_{spike}}{V_F}}$$

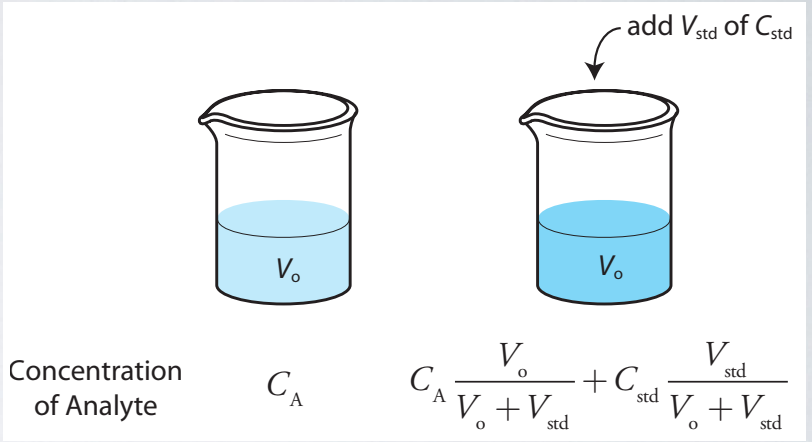
$$\frac{0.193}{C_A \frac{1.00 mL}{5.00 mL}} = \frac{0.419}{C_A \frac{1.00 mL}{5.00 mL} + 1560 \frac{1.00 \times 10^{-3} mL}{5.00 mL}}$$

$$\frac{0.193}{0.200 C_A} = \frac{0.419}{0.200 C_A + 0.3120 ppb} \qquad C_A = 1.33 ppb$$

STANDARD ADDITION - ONE FLASK

A 5.00 mL blood sample is measured for it's concentration of Pb^{2+}, the resulting signal (S_{samp}) is found to be 0.712.

To the 5.00 mL blood sample, 5.00 µL of a Pb^{2+} standard (1560 ppb)is added. When the blood sample is remeasured the signal (S_{spike}) is now 1.546. What is the concentration of Pb^{2+} in the blood sample?



$$S_{samp} = k_A C_A$$

$$S_{spike} = k_A \left(C_A \frac{V_O}{V_O + V_{spike}} + C_{spike} \frac{V_{spike}}{V_O + V_{spike}} \right)$$

$$\frac{S_{samp}}{C_A} = \frac{S_{spike}}{C_A \frac{V_O}{V_O + V_{spike}} + C_{spike} \frac{V_{spike}}{V_O + V_{spike}}}$$

$$V_O = 5.00 mL$$

$$V_{spike} = 5.00 \mu L = 5.00 \times 10^{-3} mL$$

$$V_F = 5.005 mL$$

$$C_{spike} = 1560 ppb$$

$$S_{samp} = 0.712$$

$$S_{spike} = 1.546$$

$$C_A = ?$$

$$\frac{0.712}{C_A} = \frac{1.546}{C_A \frac{5.00 mL}{5.005 mL} + 1560 ppb \left(\frac{5.00 \times 10^{-3} mL}{5.005 mL} \right)}$$

$$\frac{0.712}{C_A} = \frac{1.546}{0.9990 C_A + 1.558 ppb} \qquad C_A = 1.33 ppb$$

STANDARD ADDITION

- **Multiple standard additions:** where a known amount of sample is added to multiple flasks, with varied amounts of standard (e.g. iron UV analysis lab).

- Though a very effective means of doing a calibration it is often not used due to the fact that each new sample must be analyzed with it's own set of standard additions.