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 prepared (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 ($S_{\text{samp}}$) 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 ($S_{\text{spike}}$) was determined to be 0.419. What is the concentration of Pb$^{2+}$ in the blood sample?

\[ V_O = 1.00 \text{mL} \]
\[ V_{\text{spike}} = 1.00 \mu\text{L} = 1.00 \times 10^{-3} \text{mL} \]
\[ V_F = 5.00 \text{mL} \]
\[ C_{\text{spike}} = 1560 \text{ppb} \]

\[ S_{\text{samp}} = 0.193 \]
\[ S_{\text{spike}} = 0.419 \]

\[ \frac{S_{\text{samp}}}{C_A \frac{V_O}{V_F}} = \frac{S_{\text{spike}}}{C_A \frac{V_O}{V_F} + C_{\text{spike}} \frac{V_{\text{spike}}}{V_F}} \]

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

\[ 0.193 \]
\[ 0.200C_A \]

\[ C_A = 1.33 \text{ppb} \]
A 5.00 mL blood sample is measured for its concentration of Pb\(^{2+}\), the resulting signal \((S_{\text{samp}})\) 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 \((S_{\text{spike}})\) is now 1.546. What is the concentration of Pb\(^{2+}\) in the blood sample?

\[ S_{\text{samp}} = k_A C_A \]
\[ S_{\text{spike}} = k_A \left( \frac{C_A V_O}{V_O + V_{\text{spike}}} + C_{\text{spike}} \frac{V_{\text{spike}}}{V_O + V_{\text{spike}}} \right) \]
\[ \frac{S_{\text{samp}}}{C_A} = \frac{S_{\text{spike}}}{C_A} = \frac{V_O}{V_O + V_{\text{spike}}} + C_{\text{spike}} \frac{V_{\text{spike}}}{V_O + V_{\text{spike}}} \]

\[ S_{\text{samp}} = 0.712 \]
\[ S_{\text{spike}} = 1.546 \]

\[ V_O = 5.00 mL \]
\[ V_{\text{spike}} = 5.00 \mu L = 5.00 \times 10^{-3} mL \]
\[ V_F = 5.005 mL \]
\[ C_{\text{spike}} = 1560 \text{ ppb} \]

\[ \frac{0.712}{C_A} = \frac{1.546}{C_A} \]

\[ C_A = 1.33 \text{ ppb} \]
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 its own set of standard additions.