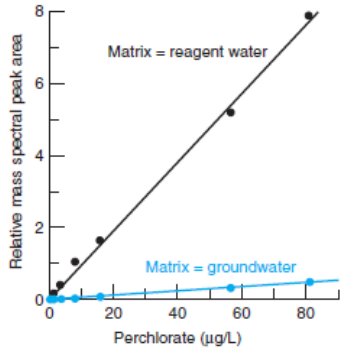



**FIGURE 5-4** Calibration curves for perchlorate in pure water and in groundwater. [Data from C. J. Koester, H. R. Beller, and R. U. Halden, "Analysis of Perchlorate in Groundwater by Electrospray Ionization Mass Spectrometry/Mass Spectrometry," *Environ. Sci. Technol.* **2000**, *34*, 1862.]

The matrix affects the magnitude of the analytical signal. In standard addition, all samples are in the same matrix.

## 5-3 Standard Addition[9]

In **standard addition**, known quantities of analyte are added to the unknown. From the increase in signal, we deduce how much analyte was in the original unknown. This method requires a linear response to analyte. As in titrations, higher precision can be achieved when standards are added by mass instead of volume.[10]

Standard addition is especially appropriate when the sample composition is unknown or complex and affects the analytical signal. The *matrix* is everything in the unknown, other than analyte. A **matrix effect** is a change in the analytical signal caused by anything in the sample other than analyte.

Figure 5-4 shows a strong matrix effect in the analysis of perchlorate ($ClO_4^-$) by mass spectrometry. Perchlorate at a level above 18 μg/L in drinking water is of concern because it can reduce thyroid hormone production. Standard solutions of $ClO_4^-$ in pure water gave the upper calibration curve in Figure 5-4. The slope in the lower curve for standard solutions in groundwater was 15 times less. Reduction of the $ClO_4^-$ signal is a *matrix effect* attributed to other anions present in the groundwater.

Different groundwaters have different concentrations of many anions, so there is no way to construct a calibration curve for this analysis that would apply to more than one specific groundwater. Hence, the method of standard addition is required. When we add a small volume of concentrated standard to an existing unknown, we do not change the concentration of the matrix very much.

Consider a standard addition in which a sample with unknown initial concentration of analyte $[X]_i$ gives a signal intensity $I_X$. Then a known concentration of standard, S, is added to an aliquot of the sample and a signal $I_{S+X}$ is observed for this second solution. Addition of standard to the unknown changes the concentration of the original analyte because of dilution. Let's call the diluted concentration of analyte $[X]_f$, where "f" stands for "final." We designate the concentration of standard in the final solution as $[S]_f$. (Bear in mind that the chemical species X and S are the same.)

Signal is directly proportional to analyte concentration, so

$$\frac{\text{Concentration of analyte in initial solution}}{\text{Concentration of analyte plus standard in final solution}} = \frac{\text{signal from initial solution}}{\text{signal from final solution}}$$

*Standard addition equation:*

$$\frac{[X]_i}{[S]_f + [X]_f} = \frac{I_X}{I_{S+X}} \qquad (5\text{-}7)$$

Derivation of Equation 5-7:

$I_X = k[X]_i$, where $k$ is a constant of proportionality

$I_{S+X} = k([S]_f + [X]_f)$, where $k$ is the same constant

Dividing one equation by the other gives

$$\frac{I_X}{I_{S+X}} = \frac{k[X]_i}{k([S]_f + [X]_f)} = \frac{[X]_i}{[S]_f + [X]_f}$$

For an initial volume $V_o$ of unknown and added volume $V_S$ of standard with concentration $[S]_i$, the total volume is $V = V_o + V_S$ and the concentrations in Equation 5-7 are

$$[X]_f = [X]_i\left(\frac{V_o}{V}\right) \qquad [S]_f = [S]_i\left(\frac{V_S}{V}\right) \qquad (5\text{-}8)$$

↑ The quotient (initial volume/final volume), which relates final concentration to initial concentration, is called the **dilution factor.** It comes directly from Equation 1-3.

By expressing the diluted concentration of analyte, $[X]_f$, in terms of the initial concentration of analyte, $[X]_i$, we can solve for $[X]_i$, because everything else in Equation 5-7 is known.

### EXAMPLE Standard Addition

Serum containing $Na^+$ gave a signal of 4.27 mV in an atomic emission analysis. Then 5.00 mL of 2.08 M NaCl were added to 95.0 mL of serum. This spiked serum gave a signal of 7.98 mV. Find the original concentration of $Na^+$ in the serum.

**Solution** From Equation 5-8, the final concentration of $Na^+$ after dilution with the standard is $[X]_f = [X]_i(V_o/V) = [X]_i(95.0\text{ mL}/100.0\text{ mL})$. The final concentration of added standard is $[S]_f = [S]_i(V_S/V) = (2.08\text{ M})(5.00\text{ mL}/100.0\text{ mL}) = 0.104\text{ M}$. Equation 5-7 becomes

$$\frac{[Na^+]_i}{[0.104\text{ M}] + 0.950[Na^+]_i} = \frac{4.27\text{ mV}}{7.98\text{ mV}} \Rightarrow [Na^+]_i = 0.113\text{ M}$$

***Test Yourself*** If spiked serum gave a signal of 6.50 mV, what was the original concentration of $Na^+$? (*Answer:* 0.182 M)

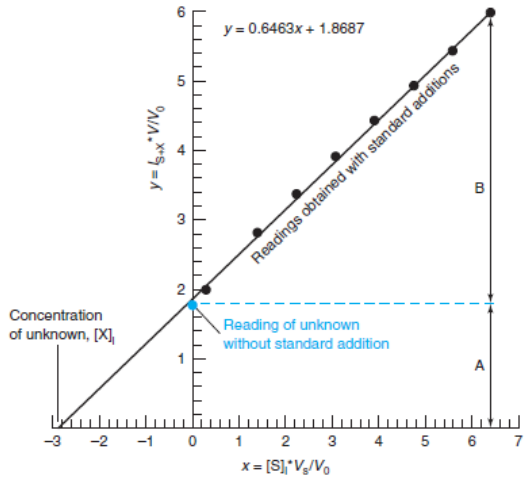
## Graphical Procedure for Standard Addition to a Single Solution

There are two common methods to perform standard addition. If the analysis does not consume solution, we begin with an unknown solution and measure the analytical signal. Then we add a small volume of concentrated standard and measure the signal again. We add several more small volumes of standard and measure the signal after each addition. Standard should be concentrated so that only small volumes are added and the sample matrix is not appreciably altered. Added standards should increase the analytical signal by a factor of 1.5 to 3. The other common procedure is described in the next section.

| | A | B | C | D | E |
|---|---|---|---|---|---|
| 1 | Vitamin C standard addition experiment | | | | |
| 2 | Add 0.279 M ascorbic acid to 50.0 mL orange juice | | | | |
| 3 | | | | | |
| 4 | | Vs = | | | |
| 5 | Vo (mL) = | mL ascorbic | I(s+x) = | x-axis function | y-axis function |
| 6 | 50 | acid added | signal ($\mu$A) | Si*Vs/Vo | I(s+x)*V/Vo |
| 7 | [S]i (mM) = | 0.000 | 1.78 | 0.000 | 1.780 |
| 8 | 279 | 0.050 | 2.00 | 0.279 | 2.002 |
| 9 | | 0.250 | 2.81 | 1.395 | 2.824 |
| 10 | | 0.400 | 3.35 | 2.232 | 3.377 |
| 11 | | 0.550 | 3.88 | 3.069 | 3.923 |
| 12 | | 0.700 | 4.37 | 3.906 | 4.431 |
| 13 | | 0.850 | 4.86 | 4.743 | 4.943 |
| 14 | | 1.000 | 5.33 | 5.580 | 5.437 |
| 15 | | 1.150 | 5.82 | 6.417 | 5.954 |
| 16 | | | | | |
| 17 | D7 = $A$8*B7/$A$6 | | E7 = C7*($A$6+B7)/$A$6 | | |

**FIGURE 5-5** Data for standard addition experiment with *variable total volume.*

Figure 5-5 shows data for an experiment in which ascorbic acid (vitamin C) was measured in orange juice by an electrochemical method. The current between a pair of electrodes immersed in the juice is proportional to the concentration of ascorbic acid. Eight standard additions increased current from 1.78 to 5.82 μA (column C), which is at the upper end of the desired range of 1.5- to 3-fold increase in analytical signal.




The equation of a line is $y = mx + b$. The $x$-intercept is obtained by setting $y = 0$:

$0 = mx + b$

$x = -b/m$

**FIGURE 5-6** Graphical treatment of standard additions to a single solution *with variable total volume*. Data from Figure 5-5. Standard additions should increase the analytical signal to between 1.5 and 3 times its original value (that is, B = 0.5A to 2A).

Figure 5-6 allows us to find the original concentration of unknown. The theoretical response is derived by substituting expressions for $[X]_f$ and $[S]_f$ from Equations 5-8 into Equation 5-7. Following a little rearrangement, we find

*For successive standard additions to one solution:*

$$\underbrace{I_{S+X}\left(\frac{V}{V_o}\right)}_{\text{Function to plot on y-axis}} = I_X + \frac{I_X}{[X]_i}\underbrace{[S]_i\left(\frac{V_s}{V_o}\right)}_{\text{Function to plot on x-axis}} \qquad (5\text{-}9)$$

Successive standard additions to one solution:

Plot $I_{S+X}\left(\frac{V}{V_o}\right)$ versus $[S]_i\left(\frac{V_s}{V_o}\right)$

$x$-intercept is $[X]_i$

A graph of $I_{S+X}(V/V_o)$ (the *corrected response*) on the $y$-axis versus $[S]_i(V_S/V_o)$ on the $x$-axis should be a straight line. The data plotted in Figure 5-6 are computed in columns D and E of Figure 5-5. The right side of Equation 5-9 is 0 when $[S]_i(V_S/V_o) = -[X]_i$. The magnitude of the intercept on the $x$-axis is the *original* concentration of unknown, $[X]_i = 2.89$ mM in Figure 5-6.

The uncertainty in the $x$-intercept is[11]

$$\text{Standard deviation of } x\text{-intercept} = \frac{s_y}{|m|}\sqrt{\frac{1}{n} + \frac{\bar{y}^2}{m^2 \sum (x_i - \bar{x})^2}} \qquad (5\text{-}10)$$

where $s_y$ is the standard deviation of $y$ (Equation 4-20), $|m|$ is the absolute value of the slope of the least-squares line (Equation 4-16), $n$ is the number of data points (nine in Figure 5-6), $\bar{y}$ is the mean value of $y$ for the nine points, $x_i$ are the individual values of $x$ for the nine points, and $\bar{x}$ is the mean value of $x$ for the nine points. For the points in Figure 5-6, the uncertainty in the $x$-intercept is $0.09_8$ mM.

The confidence interval is $\pm t \times$ (standard deviation of $x$-intercept) where $t$ is Student's $t$ (Table 4-2) for $n - 2$ degrees of freedom. The 95% confidence interval for the intercept in Figure 5-6 is $\pm(2.365)(0.09_8 \text{ mM}) = \pm 0.23$ mM. The value $t = 2.365$ was taken from Table 4-2 for $9 - 2 = 7$ degrees of freedom.

## Graphical Procedure for Multiple Solutions with Constant Volume

The second common standard addition procedure is shown in Figure 5-7. Equal volumes of unknown are pipetted into several volumetric flasks. Increasing volumes of standard are added to each flask and each is diluted to the *same final volume*. Every flask contains the same concentration of unknown and differing concentrations of standard. For each flask, a measurement of analytical signal, $I_{S+X}$, is then made. The method in Figure 5-7 is necessary when the analysis consumes some of the solution.

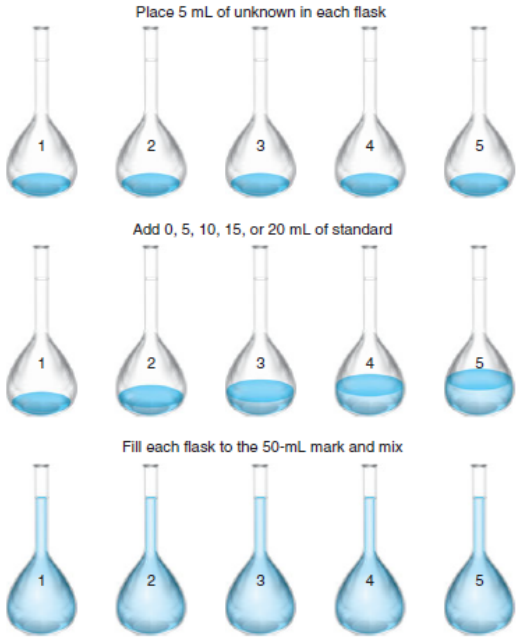



**FIGURE 5-7** Standard addition experiment with *constant total volume*.

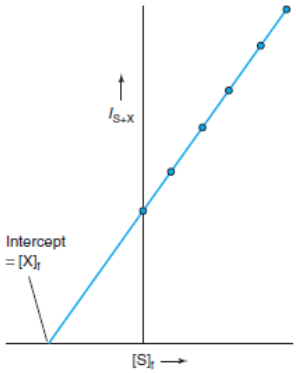



**FIGURE 5-8** Graphical treatment of standard addition with *constant total volume*. Plot $I_{S+X}$ versus $[S]_f$, and the $x$-intercept is $[X]_f$. The lines in Figures 5-6 and 5-8 are both derived from Equation 5-9.

If all standard additions are made to a constant final volume, plot the signal $I_{S+X}$ versus the concentration of diluted standard, $[S]_f$ (Figure 5-8). In this case, the $x$-intercept is the *final* concentration of unknown, $[X]_f$, after dilution to the final sample volume. Equation 5-10 still applies to the uncertainty. The initial concentration of unknown, $[X]_i$, is calculated from the dilution that was applied to make the final sample.