

# Chemistry

## Modern Analytical Chemistry

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MODERN ANALYTICAL CHEMISTRY

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**error**

A measure of bias in a result or measurement.

**uncertainty**

The range of possible values for a measurement.

### 4B.3 Error and Uncertainty

Analytical chemists make a distinction between error and uncertainty.<sup>3</sup> **Error** is the difference between a single measurement or result and its true value. In other words, error is a measure of bias. As discussed earlier, error can be divided into determinate and indeterminate sources. Although we can correct for determinate error, the indeterminate portion of the error remains. Statistical significance testing which is discussed later in this chapter, provides a way to determine whether a bias resulting from determinate error might be present.

**Uncertainty** expresses the range of possible values that a measurement or result might reasonably be expected to have. Note that this definition of uncertainty is not the same as that for precision. The precision of an analysis, whether reported as a range or a standard deviation, is calculated from experimental data and provides an estimation of indeterminate error affecting measurements. Uncertainty accounts for all errors, both determinate and indeterminate, that might affect our result. Although we always try to correct determinate errors, the correction itself is subject to random effects or indeterminate errors.

To illustrate the difference between precision and uncertainty, consider the use of a class A 10-mL pipet for delivering solutions. A pipet's uncertainty is the range of volumes in which its true volume is expected to lie. Suppose you purchase a 10-mL class A pipet from a laboratory supply company and use it without calibration. The pipet's tolerance value of  $\pm 0.02$  mL (see Table 4.2) represents your uncertainty since your best estimate of its volume is  $10.00 \text{ mL} \pm 0.02 \text{ mL}$ . Precision is determined experimentally by using the pipet several times, measuring the volume of solution delivered each time. Table 4.8 shows results for ten such trials that have a mean of 9.992 mL and a standard deviation of 0.006. This standard deviation represents the precision with which we expect to be able to deliver a given solution using any class A 10-mL pipet. In this case the uncertainty in using a pipet is worse than its precision. Interestingly, the data in Table 4.8 allow

us to calibrate this specific pipet's delivery volume as 9.992 mL. If we use this volume as a better estimate of this pipet's true volume, then the uncertainty is  $\pm 0.006$ . As expected, calibrating the pipet allows us to lower its uncertainty.

**Table 4.8** Experimentally Determined Volumes Delivered by a 10-mL Class A Pipet

Trial	Volume Delivered (mL)	Trial	Volume Delivered (mL)
1	10.002	6	9.983
2	9.993	7	9.991
3	9.984	8	9.990
4	9.996	9	9.988
5	9.989	10	9.999

### 4C Propagation of Uncertainty

Suppose that you need to add a reagent to a flask by several successive transfers using a class A 10-mL pipet. By calibrating the pipet (see Table 4.8), you know that it delivers a volume of 9.992 mL with a standard deviation of 0.006 mL. Since the pipet is calibrated, we can use the standard deviation as a measure of uncertainty. This uncertainty tells us that when we use the pipet to repetitively deliver 10 mL of solution, the volumes actually delivered are randomly scattered around the mean of 9.992 mL.

If the uncertainty in using the pipet once is  $9.992 \pm 0.006$  mL, what is the uncertainty when the pipet is used twice? As a first guess, we might simply add the uncertainties for each delivery; thus

$$(9.992 \text{ mL} + 9.992 \text{ mL}) \pm (0.006 \text{ mL} + 0.006 \text{ mL}) = 19.984 \pm 0.012 \text{ mL}$$

It is easy to see that combining uncertainties in this way overestimates the total uncertainty. Adding the uncertainty for the first delivery to that of the second delivery assumes that both volumes are either greater than 9.992 mL or less than 9.992 mL. At the other extreme, we might assume that the two deliveries will always be on opposite sides of the pipet's mean volume. In this case we subtract the uncertainties for the two deliveries,

$$(9.992 \text{ mL} + 9.992 \text{ mL}) \pm (0.006 \text{ mL} - 0.006 \text{ mL}) = 19.984 \pm 0.000 \text{ mL}$$

underestimating the total uncertainty.

So what is the total uncertainty when using this pipet to deliver two successive volumes of solution? From the previous discussion we know that the total uncertainty is greater than  $\pm 0.000$  mL and less than  $\pm 0.012$  mL. To estimate the cumulative effect of multiple uncertainties, we use a mathematical technique known as the propagation of uncertainty. Our treatment of the propagation of uncertainty is based on a few simple rules that we will not derive. A more thorough treatment can be found elsewhere.<sup>4</sup>

#### 4C.1 A Few Symbols

Propagation of uncertainty allows us to estimate the uncertainty in a calculated result from the uncertainties of the measurements used to calculate the result. In the equations presented in this section the result is represented by the symbol  $R$  and the measurements by the symbols  $A$ ,  $B$ , and  $C$ . The corresponding uncertainties are  $s_R$ ,  $s_A$ ,  $s_B$ , and  $s_C$ . The uncertainties for  $A$ ,  $B$ , and  $C$  can be reported in several ways, including calculated standard deviations or estimated ranges, as long as the same form is used for all measurements.

#### 4C.2 Uncertainty When Adding or Subtracting

When measurements are added or subtracted, the absolute uncertainty in the result is the square root of the sum of the squares of the absolute uncertainties for the individual measurements. Thus, for the equations  $R = A + B + C$  or  $R = A + B - C$ , or any other combination of adding and subtracting  $A$ ,  $B$ , and  $C$ , the absolute uncertainty in  $R$  is

$$s_R = \sqrt{s_A^2 + s_B^2 + s_C^2} \quad 4.6$$

#### EXAMPLE 4.5

The class A 10-mL pipet characterized in Table 4.8 is used to deliver two successive volumes. Calculate the absolute and relative uncertainties for the total delivered volume.

#### SOLUTION

The total delivered volume is obtained by adding the volumes of each delivery; thus

$$V_{\text{tot}} = 9.992 \text{ mL} + 9.992 \text{ mL} = 19.984 \text{ mL}$$

Using the standard deviation as an estimate of uncertainty, the uncertainty in the total delivered volume is

$$s_R = \sqrt{(0.006)^2 + (0.006)^2} = 0.0085$$

Thus, we report the volume and its absolute uncertainty as  $19.984 \pm 0.008$  mL. The relative uncertainty in the total delivered volume is

$$\frac{0.0085}{19.984} \times 100 = 0.043\%$$

### 4C.3 Uncertainty When Multiplying or Dividing

When measurements are multiplied or divided, the relative uncertainty in the result is the square root of the sum of the squares of the relative uncertainties for the individual measurements. Thus, for the equations  $R = A \times B \times C$  or  $R = A \times B/C$ , or any other combination of multiplying and dividing  $A$ ,  $B$ , and  $C$ , the relative uncertainty in  $R$  is

$$\frac{s_R}{R} = \sqrt{\left(\frac{s_A}{A}\right)^2 + \left(\frac{s_B}{B}\right)^2 + \left(\frac{s_C}{C}\right)^2} \quad 4.7$$

### Example

#### EXAMPLE 4.6

The quantity of charge,  $Q$ , in coulombs passing through an electrical circuit is

$$Q = I \times t$$

where  $I$  is the current in amperes and  $t$  is the time in seconds. When a current of  $0.15 \pm 0.01$  A passes through the circuit for  $120 \pm 1$  s, the total charge is

$$Q = (0.15 \text{ A}) \times (120 \text{ s}) = 18 \text{ C}$$

Calculate the absolute and relative uncertainties for the total charge.

#### SOLUTION

Since charge is the product of current and time, its relative uncertainty is

$$\frac{s_R}{R} = \sqrt{\left(\frac{0.01}{0.15}\right)^2 + \left(\frac{1}{120}\right)^2} = \pm 0.0672$$

or  $\pm 6.7\%$ . The absolute uncertainty in the charge is

$$s_R = R \times 0.0672 = (18) \times (\pm 0.0672) = \pm 1.2$$

Thus, we report the total charge as  $18 \text{ C} \pm 1 \text{ C}$ .

### 4C.4 Uncertainty for Mixed Operations

Many chemical calculations involve a combination of adding and subtracting, and multiply and dividing. As shown in the following example, the propagation of uncertainty is easily calculated by treating each operation separately using equations 4.6 and 4.7 as needed.

**EXAMPLE 4.7**

For a concentration technique the relationship between the measured signal and an analyte's concentration is given by equation 4.5

$$S_{\text{meas}} = kC_A + S_{\text{reag}}$$

Calculate the absolute and relative uncertainties for the analyte's concentration if  $S_{\text{meas}}$  is  $24.37 \pm 0.02$ ,  $S_{\text{reag}}$  is  $0.96 \pm 0.02$ , and  $k$  is  $0.186 \pm 0.003 \text{ ppm}^{-1}$ .

**SOLUTION**

Rearranging equation 4.5 and solving for  $C_A$

$$C_A = \frac{S_{\text{meas}} - S_{\text{reag}}}{k} = \frac{24.37 - 0.96}{0.186 \text{ ppm}^{-1}} = 125.9 \text{ ppm}$$

gives the analyte's concentration as 126 ppm. To estimate the uncertainty in  $C_A$ , we first determine the uncertainty for the numerator,  $S_{\text{meas}} - S_{\text{reag}}$ , using equation 4.6

$$s_R = \sqrt{(0.02)^2 + (0.02)^2} = 0.028$$

The numerator, therefore, is  $23.41 \pm 0.028$  (note that we retain an extra significant figure since we will use this uncertainty in further calculations). To complete the calculation, we estimate the relative uncertainty in  $C_A$  using equation 4.7, giving

$$\frac{s_R}{R} = \sqrt{\left(\frac{0.028}{23.41}\right)^2 + \left(\frac{0.003}{0.186}\right)^2} = 0.0162$$

or a percent relative uncertainty of 1.6%. The absolute uncertainty in the analyte's concentration is

$$s_R = (125.9 \text{ ppm}) \times (0.0162) = \pm 2.0 \text{ ppm}$$

giving the analyte's concentration as  $126 \pm 2 \text{ ppm}$ .

**4C.5 Uncertainty for Other Mathematical Functions**

Many other mathematical operations are commonly used in analytical chemistry, including powers, roots, and logarithms. Equations for the propagation of uncertainty for some of these functions are shown in Table 4.9.

**EXAMPLE 4.8**

The pH of a solution is defined as

$$\text{pH} = -\log[\text{H}^+]$$

where  $[\text{H}^+]$  is the molar concentration of  $\text{H}^+$ . If the pH of a solution is 3.72 with an absolute uncertainty of  $\pm 0.03$ , what is the  $[\text{H}^+]$  and its absolute uncertainty?

**SOLUTION**

The molar concentration of  $H^+$  for this pH is

$$[H^+] = 10^{-\text{pH}} = 10^{-3.72} = 1.91 \times 10^{-4} \text{ M}$$

or  $1.9 \times 10^{-4} \text{ M}$  to two significant figures. From Table 4.9 the relative uncertainty in  $[H^+]$  is

$$\frac{s_R}{R} = 2.303 \times s_A = 2.303 \times 0.03 = 0.069$$

and the absolute uncertainty is

$$(1.91 \times 10^{-4} \text{ M}) \times (0.069) = 1.3 \times 10^{-5} \text{ M}$$

We report the  $[H^+]$  and its absolute uncertainty as  $1.9 (\pm 0.1) \times 10^{-4} \text{ M}$ .

**Table 4.9** Propagation of Uncertainty for Selected Functions<sup>a</sup>

Function	$s_R$
$R = kA$	$s_R = ks_A$
$R = A + B$	$s_R = \sqrt{s_A^2 + s_B^2}$
$R = A - B$	$s_R = \sqrt{s_A^2 + s_B^2}$
$R = A \times B$	$\frac{s_R}{R} = \sqrt{\left(\frac{s_A}{A}\right)^2 + \left(\frac{s_B}{B}\right)^2}$
$R = \frac{A}{B}$	$\frac{s_R}{R} = \sqrt{\left(\frac{s_A}{A}\right)^2 + \left(\frac{s_B}{B}\right)^2}$
$R = \ln(A)$	$s_R = \frac{s_A}{A}$
$R = \log(A)$	$s_R = 0.4343 \times \frac{s_A}{A}$
$R = e^A$	$\frac{s_R}{R} = s_A$
$R = 10^A$	$\frac{s_R}{R} = 2.303s_A$
$R = A^k$	$\frac{s_R}{R} = \left[ k \frac{s_A}{A} \right]$

<sup>a</sup>These equations assume that the measurements  $A$  and  $B$  are uncorrelated; that is,  $s_A$  is independent of  $s_B$ .

#### 4C.6 Is Calculating Uncertainty Actually Useful?

Given the complexity of determining a result's uncertainty when several measurements are involved, it is worth examining some of the reasons why such calculations are useful. A propagation of uncertainty allows us to estimate an ex-

pected uncertainty for an analysis. Comparing the expected uncertainty to that which is actually obtained can provide useful information. For example, in determining the mass of a penny, we estimated the uncertainty in measuring mass as  $\pm 0.002$  g based on the balance's tolerance. If we measure a single penny's mass several times and obtain a standard deviation of  $\pm 0.020$  g, we would have reason to believe that our measurement process is out of control. We would then try to identify and correct the problem.

A propagation of uncertainty also helps in deciding how to improve the uncertainty in an analysis. In Example 4.7, for instance, we calculated the concentration of an analyte, obtaining a value of 126 ppm with an absolute uncertainty of  $\pm 2$  ppm and a relative uncertainty of 1.6%. How might we improve the analysis so that the absolute uncertainty is only  $\pm 1$  ppm (a relative uncertainty of 0.8%)? Looking back on the calculation, we find that the relative uncertainty is determined by the relative uncertainty in the measured signal (corrected for the reagent blank)

$$\frac{0.028}{23.41} = \pm 0.0012, \text{ or } \pm 0.12\%$$

and the relative uncertainty in the method's sensitivity,  $k$ ,

$$\frac{0.003}{0.186} = \pm 0.016, \text{ or } \pm 1.6\%$$

Of these two terms, the sensitivity's uncertainty dominates the total uncertainty. Measuring the signal more carefully will not improve the overall uncertainty of the analysis. On the other hand, the desired improvement in uncertainty can be achieved if the sensitivity's absolute uncertainty can be decreased to  $\pm 0.0015$  ppm<sup>-1</sup>.

As a final example, a propagation of uncertainty can be used to decide which of several procedures provides the smallest overall uncertainty. Preparing a solution by diluting a stock solution can be done using several different combinations of volumetric glassware. For instance, we can dilute a solution by a factor of 10 using a 10-mL pipet and a 100-mL volumetric flask, or by using a 25-mL pipet and a 250-mL volumetric flask. The same dilution also can be accomplished in two steps using a 50-mL pipet and a 100-mL volumetric flask for the first dilution, and a 10-mL pipet and a 50-mL volumetric flask for the second dilution. The overall uncertainty, of course, depends on the uncertainty of the glassware used in the dilutions. As shown in the following example, we can use the tolerance values for volumetric glassware to determine the optimum dilution strategy.<sup>5</sup>

### Example

#### EXAMPLE 4.9

Which of the following methods for preparing a 0.0010 M solution from a 1.0 M stock solution provides the smallest overall uncertainty?

- A one-step dilution using a 1-mL pipet and a 1000-mL volumetric flask.
- A two-step dilution using a 20-mL pipet and a 1000-mL volumetric flask for the first dilution and a 25-mL pipet and a 500-mL volumetric flask for the second dilution.

**SOLUTION**

Letting  $M_a$  and  $M_b$  represent the molarity of the final solutions from method (a) and method (b), we can write the following equations

$$M_a = 0.0010 \text{ M} = \frac{(1.0 \text{ M})(1.000 \text{ mL})}{1000.0 \text{ mL}}$$

$$M_b = 0.0010 \text{ M} = \frac{(1.0 \text{ M})(20.00 \text{ mL})(25.00 \text{ mL})}{(1000.0 \text{ mL})(500.0 \text{ mL})}$$

Using the tolerance values for pipets and volumetric flasks given in Table 4.2, the overall uncertainties in  $M_a$  and  $M_b$  are

$$\left(\frac{s_R}{R}\right)_{M_a} = \sqrt{\left(\frac{0.006}{1.000}\right)^2 + \left(\frac{0.3}{1000.0}\right)^2} = 0.006$$

$$\left(\frac{s_R}{R}\right)_{M_b} = \sqrt{\left(\frac{0.03}{20.00}\right)^2 + \left(\frac{0.03}{25.00}\right)^2 + \left(\frac{0.2}{500.0}\right)^2 + \left(\frac{0.3}{1000.0}\right)^2} = 0.002$$

Since the relative uncertainty for  $M_b$  is less than that for  $M_a$ , we find that the two-step dilution provides the smaller overall uncertainty.

## 4D The Distribution of Measurements and Results

An analysis, particularly a quantitative analysis, is usually performed on several replicate samples. How do we report the result for such an experiment when results for the replicates are scattered around a central value? To complicate matters further, the analysis of each replicate usually requires multiple measurements that, themselves, are scattered around a central value.

Consider, for example, the data in Table 4.1 for the mass of a penny. Reporting only the mean is insufficient because it fails to indicate the uncertainty in measuring a penny's mass. Including the standard deviation, or other measure of spread, provides the necessary information about the uncertainty in measuring mass. Nevertheless, the central tendency and spread together do not provide a definitive statement about a penny's true mass. If you are not convinced that this is true, ask yourself how obtaining the mass of an additional penny will change the mean and standard deviation.

How we report the result of an experiment is further complicated by the need to compare the results of different experiments. For example, Table 4.10 shows results for a second, independent experiment to determine the mass of a U.S. penny in circulation. Although the results shown in Tables 4.1 and 4.10 are similar, they are not identical; thus, we are justified in asking whether the results are in agreement. Unfortunately, a definitive comparison between these two sets of data is not possible based solely on their respective means and standard deviations.

Developing a meaningful method for reporting an experiment's result requires the ability to predict the true central value and true spread of the population under investigation from a limited sampling of that population. In this section we will take a quantitative look at how individual measurements and results are distributed around a central value.