

Table 4.9 Experimental Results for Volume Delivered by a 10-mL Class A Transfer Pipet

Number	Volume (mL)	Number	Volume (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

tion using a Class A 10-mL pipet. In this case the pipet's published uncertainty of ± 0.02 mL is worse than its experimentally determined precision of ± 0.006 mL. Interestingly, the data in Table 4.9 allows us to calibrate this specific pipet's delivery volume as 9.992 mL. If we use this volume as a better estimate of the pipet's expected volume, then its uncertainty is ± 0.006 mL. As expected, calibrating the pipet allows us to decrease its uncertainty.⁴

4C Propagation of Uncertainty

Suppose we dispense 20 mL of a reagent using the Class A 10-mL pipet whose calibration information is given in Table 4.9. If the volume and uncertainty for one use of the pipet is 9.992 ± 0.006 mL, what is the volume and uncertainty if we use the pipet twice?

As a first guess, we might simply add together the volume and the maximum uncertainty 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 appreciate 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 with each use the indeterminate error is in the same direction and is as large as possible. At the other extreme, we might assume that the uncertainty for one delivery is positive and the other is negative. If we subtract the maximum uncertainties for each delivery,

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

we clearly underestimate the total uncertainty.

So what is the total uncertainty? From the discussion above, we reasonably expect that the total uncertainty is greater than ± 0.000 mL and that it is less than ± 0.012 mL. To estimate the uncertainty 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.

Although we will not derive or further justify the rules presented in this section, you may consult this chapter's additional resources for references that discuss the propagation of uncertainty in more detail.

⁴ Kadis, R. *Talanta* **2004**, *64*, 167–173.

4C.1 A Few Symbols

A **PROPAGATION OF UNCERTAINTY** allows us to estimate the uncertainty in a result from the uncertainties in the measurements used to calculate that result. For the equations in this section we represent the result with the symbol R , and we represent the measurements with the symbols A , B , and C . The corresponding uncertainties are u_R , u_A , u_B , and u_C . We can define the uncertainties for A , B , and C using standard deviations, ranges, or tolerances (or any other measure of uncertainty), as long as we use the same form for all measurements.

The requirement that we express each uncertainty in the same way is a critically important point. Suppose you have a range for one measurement, such as a pipet's tolerance, and standard deviations for the other measurements. All is not lost. There are ways to convert a range to an estimate of the standard deviation. See [Appendix 2](#) for more details.

4C.2 Uncertainty When Adding or Subtracting

When we add or subtract measurements we propagate their absolute uncertainties. For example, if the result is given by the equation

$$R = A + B - C$$

then the absolute uncertainty in R is

$$u_R = \sqrt{u_A^2 + u_B^2 + u_C^2} \quad 4.6$$

Example 4.5

If we dispense 20 mL using a 10-mL Class A pipet, what is the total volume dispensed and what is the uncertainty in this volume? First, complete the calculation using the manufacturer's tolerance of $10.00 \text{ mL} \pm 0.02 \text{ mL}$, and then using the calibration data from [Table 4.9](#).

SOLUTION

To calculate the total volume we add the volumes for each use of the pipet. When using the manufacturer's values, the total volume is

$$V = 10.00 \text{ mL} + 10.00 \text{ mL} = 20.00 \text{ mL}$$

and when using the calibration data, the total volume is

$$V = 9.992 \text{ mL} + 9.992 \text{ mL} = 19.984 \text{ mL}$$

Using the pipet's tolerance as an estimate of its uncertainty gives the uncertainty in the total volume as

$$u_R = \sqrt{(0.02)^2 + (0.02)^2} = 0.028 \text{ mL}$$

and using the standard deviation for the data in [Table 4.9](#) gives an uncertainty of

$$u_R = \sqrt{(0.006)^2 + (0.006)^2} = 0.0085 \text{ mL}$$

Rounding the volumes to four significant figures gives $20.00 \text{ mL} \pm 0.03 \text{ mL}$ when we use the tolerance values, and $19.98 \pm 0.01 \text{ mL}$ when we use the calibration data.

4C.3 Uncertainty When Multiplying or Dividing

When we multiple or divide measurements we propagate their relative uncertainties. For example, if the result is given by the equation

$$R = \frac{A \times B}{C}$$

then the relative uncertainty in R is

$$\frac{u_R}{R} = \sqrt{\left(\frac{u_A}{A}\right)^2 + \left(\frac{u_B}{B}\right)^2 + \left(\frac{u_C}{C}\right)^2} \quad 4.7$$

Example 4.6

The quantity of charge, Q , in coulombs that passes 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 $0.15 \text{ A} \pm 0.01 \text{ A}$ passes through the circuit for $120 \text{ s} \pm 1 \text{ s}$, what is the total charge and its uncertainty?

SOLUTION

The total charge is

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

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

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

and the charge's absolute uncertainty is

$$u_R = R \times 0.0672 = (18 \text{ C}) \times (0.0672) = 1.2 \text{ C}$$

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 of multiply and dividing. As shown in the following example, we can calculate the uncertainty by separately treating each operation using equation 4.6 and equation 4.7 as needed.

Example 4.7

For a concentration technique, the relationship between the signal and the an analyte's concentration is

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

What is the analyte's concentration, C_A , and its uncertainty if S_{total} is 24.37 ± 0.02 , S_{mb} is 0.96 ± 0.02 , and k_A is $0.186 \pm 0.003 \text{ ppm}^{-1}$?

SOLUTION

Rearranging the equation and solving for C_A

$$C_A = \frac{S_{total} - S_{mb}}{k_A} = \frac{24.37 - 0.96}{0.186 \text{ ppm}^{-1}} = \frac{23.41}{0.186 \text{ ppm}^{-1}} = 125.9 \text{ ppm}$$

gives the analyte's concentration as 126 ppm. To estimate the uncertainty in C_A , we first use [equation 4.6](#) to determine the uncertainty for the numerator.

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

The numerator, therefore, is 23.41 ± 0.028 . To complete the calculation we use [equation 4.7](#) to estimate the relative uncertainty in C_A .

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

The absolute uncertainty in the analyte's concentration is

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

Thus, we report the analyte's concentration as $126 \text{ ppm} \pm 2 \text{ ppm}$.

4C.5 Uncertainty for Other Mathematical Functions

Many other mathematical operations are common in analytical chemistry, including the use of powers, roots, and logarithms. [Table 4.10](#) provides equations for propagating uncertainty for some of these function.

Example 4.8

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

SOLUTION

The concentration of H^+ is

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

Practice Exercise 4.2

To prepare a standard solution of Cu^{2+} you obtain a piece of copper from a spool of wire. The spool's initial weight is 74.2991 g and its final weight is 73.3216 g. You place the sample of wire in a 500 mL volumetric flask, dissolve it in 10 mL of HNO_3 , and dilute to volume. Next, you pipet a 1 mL portion to a 250-mL volumetric flask and dilute to volume. What is the final concentration of Cu^{2+} in mg/L, and its uncertainty? Assume that the uncertainty in the balance is $\pm 0.1 \text{ mg}$ and that you are using Class A glassware.

Click [here](#) when to review your answer to this exercise.

Table 4.10 Propagation of Uncertainty for Selected Mathematical Functions[†]

Function	u_R
$R = kA$	$u_R = ku_A$
$R = A + B$	$u_R = \sqrt{u_A^2 + u_B^2}$
$R = A - B$	$u_R = \sqrt{u_A^2 + u_B^2}$
$R = A \times B$	$\frac{u_R}{R} = \sqrt{\left(\frac{u_A}{A}\right)^2 + \left(\frac{u_B}{B}\right)^2}$
$R = \frac{A}{B}$	$\frac{u_R}{R} = \sqrt{\left(\frac{u_A}{A}\right)^2 + \left(\frac{u_B}{B}\right)^2}$
$R = \ln(A)$	$u_R = \frac{u_A}{A}$
$R = \log(A)$	$u_R = 0.4343 \times \frac{u_A}{A}$
$R = e^A$	$\frac{u_R}{R} = u_A$
$R = 10^A$	$\frac{u_R}{R} = 2.303 \times u_A$
$R = A^k$	$\frac{u_R}{R} = k \times \frac{u_A}{A}$

[†] Assumes that the measurements A and B are independent; k is a constant whose value has no uncertainty.

or 1.9×10^{-4} M to two significant figures. From Table 4.10 the relative uncertainty in $[\text{H}^+]$ is

$$\frac{u_R}{R} = 2.303 \times u_A = 2.303 \times 0.03 = 0.069$$

The uncertainty in the concentration, therefore, is

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

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

Writing this result as

$$1.9 (\pm 0.1) \times 10^{-4} \text{ M}$$

is equivalent to

$$1.9 \times 10^{-4} \text{ M} \pm 0.1 \times 10^{-4} \text{ M}$$

Practice Exercise 4.3

A solution of copper ions is blue because it absorbs yellow and orange light. Absorbance, A , is defined as

$$A = -\log\left(\frac{P}{P_0}\right)$$

where P_0 is the power of radiation as emitted from the light source and P is its power after it passes through the solution. What is the absorbance if P_0 is 3.80×10^2 and P is 1.50×10^2 ? If the uncertainty in measuring P_0 and P is 15, what is the uncertainty in the absorbance?

Click [here](#) to review your answer to this exercise.

4C.6 Is Calculating Uncertainty Actually Useful?

Given the effort it takes to calculate uncertainty, it is worth asking whether such calculations are useful. The short answer is, yes. Let's consider three examples of how we can use a propagation of uncertainty to help guide the development of an analytical method.

One reason to complete a propagation of uncertainty is that we can compare our estimate of the uncertainty to that obtained experimentally. For example, to determine the mass of a penny we measure its mass twice—once to tare the balance at 0.000 g and once to measure the penny's mass. If the uncertainty in each measurement of mass is ± 0.001 g, then we estimate the total uncertainty in the penny's mass as

$$u_R = \sqrt{(0.001)^2 + (0.001)^2} = 0.0014 \text{ g}$$

If we measure a single penny's mass several times and obtain a standard deviation of ± 0.050 g, then we have evidence that the measurement process is out of control. Knowing this, we can identify and correct the problem.

We also can use a propagation of uncertainty to help us decide how to improve an analytical method's uncertainty. In [Example 4.7](#), for instance, we calculated an analyte's concentration as $126 \text{ ppm} \pm 2 \text{ ppm}$, which is a percent uncertainty of 1.6%. Suppose we want to decrease the percent uncertainty to no more than 0.8%. How might we accomplish this? Looking back at the calculation, we see that the concentration's relative uncertainty is determined by the relative uncertainty in the measured signal (corrected for the reagent blank)

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

and the relative uncertainty in the method's sensitivity, k_A ,

$$\frac{0.003 \text{ ppm}^{-1}}{0.186 \text{ ppm}^{-1}} = 0.016 \text{ or } 1.6\%$$

Of these two terms, the uncertainty in the method's sensitivity dominates the overall uncertainty. Improving the signal's uncertainty will not improve the overall uncertainty of the analysis. To achieve an overall uncertainty of 0.8% we must improve the uncertainty in k_A to $\pm 0.0015 \text{ ppm}^{-1}$.

Practice Exercise 4.4

Verify that an uncertainty of $\pm 0.0015 \text{ ppm}^{-1}$ for k_A is the correct result.

Click [here](#) to review your answer to this exercise.

Finally, we can use a propagation of uncertainty to determine which of several procedures provides the smallest uncertainty. When we dilute a stock solution usually there are several combinations of volumetric glassware that will give the same final concentration. For instance, we can dilute a stock solution by a factor of 10 using a 10-mL pipet and a 100-mL volumetric

flask, or using a 25-mL pipet and a 250-mL volumetric flask. We also can accomplish the same dilution in two steps using a 50-mL pipet and 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 in the final concentration—and, therefore, the best option for the dilution—depends on the uncertainty of the volumetric pipets and volumetric flasks. As shown in the following example, we can use the tolerance values for volumetric glassware to determine the optimum dilution strategy.⁵

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) A one-step dilution that uses a 1-mL pipet and a 1000-mL volumetric flask.
- (b) A two-step dilution that uses 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

The dilution calculations for case (a) and case (b) are

$$\text{case (a): } 1.0 \text{ M} \times \frac{1.000 \text{ mL}}{1000.0 \text{ mL}} = 0.0010 \text{ M}$$

$$\text{case (b): } 1.0 \text{ M} \times \frac{20.00 \text{ mL}}{1000.0 \text{ mL}} \times \frac{25.00 \text{ mL}}{500.0 \text{ mL}} = 0.0010 \text{ M}$$

Using tolerance values from [Table 4.2](#), the relative uncertainty for case (a) is

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

and for case (b) the relative uncertainty is

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

Since the relative uncertainty for case (b) is less than that for case (a), the two-step dilution provides the smallest overall uncertainty.

Of course we must balance the smaller uncertainty for case (b) against the increased opportunity for introducing a determinate error when making two dilutions instead of just one dilution, as in case (a).

4D The Distribution of Measurements and Results

Earlier we reported results for a determination of the mass of a circulating United States penny, obtaining a mean of 3.117 g and a standard deviation of 0.051 g. [Table 4.11](#) shows results for a second, independent determination of a penny's mass, as well as the data from the first experiment. Although the means and standard deviations for the two experiments are similar, they are not identical. The difference between the two experiments

5 Lam, R. B.; Isenhour, T. L. *Anal. Chem.* **1980**, *52*, 1158–1161.