3-3 Types of Error

Every measurement has some uncertainty, which is called *experimental error*. Conclusions can be expressed with a high or a low degree of confidence, but never with complete certainty. Experimental error is classified as either *systematic* or *random*.

Systematic Error

Systematic error, also called **determinate error**, arises from a flaw in equipment or the design of an experiment. If you conduct the experiment again in exactly the same manner, the error is reproducible. In principle, systematic error can be discovered and corrected, although this may not be easy.

For example, a pH meter that has been standardized incorrectly produces a systematic error. Suppose you think that the pH of the buffer used to standardize the meter is 7.00, but it is really 7.08. Then all your pH readings will be 0.08 pH unit too low. When you read a pH of 5.60, the actual pH of the sample is 5.68. This systematic error could be discovered by using a second buffer of known pH to test the meter.

Systematic error is a consistent error that can be detected and corrected. Box 3-1 provides an example from environmental analysis.

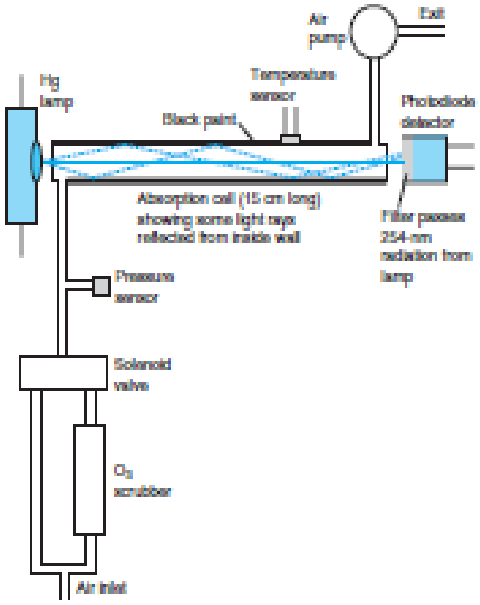
BOX 3-1 Case Study in Ethics: Systematic Error in Ozone Measurement

Ozone (O_3) is an oxidizing, corrosive gas that harms your lungs and all forms of life. It is formed near the surface of the Earth by the action of sunlight on air pollutants largely derived from automobile exhaust. The U.S. Environmental Protection Agency sets an 8-h average O_3 limit of 80 ppb (80 nL/L by volume) in air. Regions that fail to meet this standard can be required to reduce sources of pollution that contribute to O_3 formation. Error in ozone measurement can have serious consequences for the health and economy of a region.

To monitor compliance, a variety of instruments are used. The instrument in the diagram pumps air through a cell with a pathlength of 15 cm. Ultraviolet radiation from a mercury lamp is partially absorbed by O_3. The more O_3 in the air, the less radiation reaches the detector. From the measured absorbance, the instrument computes O_3 concentration. In routine use, the operator only adjusts the zero control, which sets the meter to read zero when O_3-free air is drawn through the instrument. Periodically, the instrument is recalibrated with a source of known O_3.

A study of commercial O_3 monitors found that controlled changes in humidity led to *systematic errors in the apparent O_3 concentration of tens to hundreds of ppb* (errors several times greater than the O_3 being measured). Increasing humidity produced systematic *positive* errors in some types of instruments and systematic *negative* errors in other instruments.

Water does not absorb the ultraviolet wavelength measured by the detector, so humidity is not interfering by absorbing radiation. A perceptive analysis of the problem led to the hypothesis that *adsorption* of moisture on the inside surface of the measurement cell changed the reflectivity of that surface. In one type of instrument, water adsorbed inside a quartz cell reflects less light than dry quartz and thus increases the amount of light lost by absorption in black paint on the outside of the cell. This instrument produces a false, *high* O_3 reading. Another instrument has a highly reflective aluminum cell coated on the inside with polyvinylidene fluoride. Adsorption of moisture on polyvinylidene fluoride reduces total internal reflection within the coating and increases the radiant energy reaching the detector, giving a false, *low* O_3 reading. These effects need not be large. A 0.03% change in light intensity reaching the detector corresponds to an O_3 change of 100 ppb. The solution to the problem was to install a length of water-permeable tubing just before the absorption cell to equalize the humidity in air being measured and that used to zero the instrument.



Optical path of 2B Technologies Model 202 Ozone Monitor. The solenoid alternately admits ambient air or air that has been scrubbed free of O_3. Absorbance of ultraviolet radiation from the Hg lamp is proportional to O_3 concentration. [Diagram from www.2btech.com/manuals/model_202_new.pdf. Story from K. L. Wilson and J. W. Birks, "Mechanism and Elimination of a Water Vapor Interference in the Measurement of Ozone by UV Absorbance," *Environ. Sci. Technol.* **2006**, *40*, 6361.]

Prior to understanding the effect of humidity on O_3 measurement, it was known that O_3 monitors often exhibit erratic behavior on hot, humid days. It was conjectured by some people that half of the regions deemed to be out of compliance with the O_3 standard might actually have been under the legal limit. This error could force expensive remediation measures when none were required. Conversely, there were rumors that some unscrupulous operators of O_3 monitors were aware that zeroing their instrument at night when the humidity is higher produced lower O_3 readings the next day, thereby reducing the number of days when a region is deemed out of compliance.

Ways to detect systematic error:

1. Analyze a known sample, such as a certified reference material. Your method should reproduce the known answer. (See Box 14-1 for an example.)
2. Analyze blank samples containing no analyte being sought. If you observe a nonzero result, your method responds to more than you intend. Section 5-1 discusses different kinds of blanks.
3. Use different analytical methods to measure the same quantity. If results do not agree, there is error in one (or more) of the methods.
4. *Round robin* experiment: Different people in several laboratories analyze identical samples by the same or different methods. Disagreement beyond the estimated random error is systematic error.

Another systematic error arises from an uncalibrated buret. The manufacturer's tolerance for a Class A 50-mL buret is ±0.05 mL. When you think you have delivered 29.43 mL, the real volume could be anywhere from 29.38 to 29.48 mL and still be within tolerance. One way to correct for an error of this type is to construct a calibration curve, such as that in Figure 3-3, by the procedure on page 49. To do this, deliver distilled water from the buret into a flask and weigh it. Determine the volume of water from its mass by using Table 2-7. Figure 3-3 tells us to apply a correction factor of −0.03 mL to the measured value of 29.43 mL. The actual volume delivered is 29.43 − 0.03 = 29.40 mL.

A key feature of systematic error is that it is reproducible. For the buret just discussed, the error is always −0.03 mL when the buret reading is 29.43 mL. Systematic error may always be positive in some regions and always negative in others. With care and cleverness, you can detect and correct a systematic error.

Random Error

Random error, also called **indeterminate error,** arises from uncontrolled (and maybe uncontrollable) variables in the measurement. Random error has an equal chance of being positive or negative. It is always present and cannot be corrected. There is random error associated with reading a scale. Different people reading the scale in Figure 3-1 report a range of values representing their subjective interpolation between the markings. One person reading the same instrument several times might report several different readings. Another random error results from electrical noise in an instrument. Positive and negative fluctuations occur with approximately equal frequency and cannot be completely eliminated.

Random error cannot be eliminated, but it might be reduced by a better experiment.

Precision and Accuracy

Precision: reproducibility

Accuracy: nearness to the "truth"

Precision describes the reproducibility of a result. If you measure a quantity several times and the values agree closely with one another, your measurement is precise. If the values vary widely, your measurement is not precise. **Accuracy** describes how close a measured value is to the "true" value. If a known standard is available, accuracy is how close your value is to the known value.

The U.S. National Institute of Standards and Technology and national standards laboratories in other countries sell **certified reference materials** (called *Standard Reference Materials* in the U.S.), such as clinical and environmental standards and engineering materials that you can use to test the accuracy of your analytical procedures.[1] The quantity of analyte in a reference material is certified—with painstaking care—to lie in a stated range.

A measurement might be reproducible, but wrong. If you made a mistake preparing a solution for a titration, you might do a series of reproducible titrations but report an incorrect result because the concentration of the titrating solution was not what you intended. In this case, precision is good but accuracy is poor. Conversely, it is possible to make poorly reproducible measurements clustered around the correct value. For this case, precision is poor but accuracy is good. An ideal procedure is both precise and accurate.

Accuracy is defined as nearness to the "true" value. *True* is in quotes because somebody must *measure* the "true" value, and there is error associated with *every* measurement. The "true" value is best obtained by an experienced person using a well-tested procedure. It is desirable to test the result by using different procedures, because systematic error could lead to poor agreement between methods. Good agreement among several methods affords us confidence, but never proof, that results are accurate.

Absolute and Relative Uncertainty

An uncertainty of ±0.02 mL means that, when the reading is 13.33 mL, the true value could be anywhere in the range 13.31 to 13.35 mL.

Absolute uncertainty expresses the margin of uncertainty associated with a measurement. If the estimated uncertainty in reading a calibrated buret is ±0.02 mL, we say that ±0.02 mL is the absolute uncertainty associated with the reading.

Relative uncertainty compares the size of the absolute uncertainty with the size of its associated measurement. The relative uncertainty of a buret reading of 12.35 ± 0.02 mL is a dimensionless quotient:

Relative uncertainty:

$$\text{Relative uncertainty} = \frac{\text{absolute uncertainty}}{\text{magnitude of measurement}} \qquad (3\text{-}2)$$

$$= \frac{0.02\ \text{mL}}{12.35\ \text{mL}} = 0.002$$

The percent relative uncertainty is simply

Percent relative uncertainty:

$$\text{Percent relative uncertainty} = 100 \times \text{relative uncertainty} \tag{3-3}$$

$$= 100 \times 0.002 = 0.2\%$$

If you use a 50-mL buret, design your titration to require 20–40 mL of reagent to produce a small relative uncertainty of 0.1–0.05%.

If the absolute uncertainty in reading a buret is constant at ±0.02 mL, the percent relative uncertainty is 0.2% for a volume of 10 mL and 0.1% for a volume of 20 mL.

In a gravimetric analysis, plan to have enough precipitate for a low relative uncertainty. If weighing precision is ±0.3 mg, a 100-mg precipitate has a relative weighing error of 0.3% and a 300-mg precipitate has an uncertainty of 0.1%.

3-4 Propagation of Uncertainty from Random Error[2]

We can usually estimate or measure the random error associated with a measurement, such as the length of an object or the temperature of a solution. Uncertainty might be based on how well we can read an instrument or on our experience with a particular method. If possible, uncertainty will be expressed as the *standard deviation of the mean* or a *confidence interval*, which we discuss in Chapter 4. This section applies only to random error. We assume that systematic error has been detected and corrected.

Most propagation of uncertainty computations that you will encounter deal with random error, not systematic error. Our goal is always to eliminate systematic error.

For most experiments, we need to perform arithmetic operations on several numbers, each of which has a random error. The most likely uncertainty in the result is not the sum of individual errors, because some of them are likely to be positive and some negative. We expect some cancellation of errors.

Addition and Subtraction

Suppose you wish to perform the following arithmetic, in which the experimental uncertainties, designated e_1, e_2, and e_3, are given in parentheses.

$$\begin{aligned} &1.76\ (\pm 0.03) \leftarrow e_1 \\ &+\ 1.89\ (\pm 0.02) \leftarrow e_2 \\ &-\ 0.59\ (\pm 0.02) \leftarrow e_3 \\ &\overline{\qquad\qquad\qquad} \\ &3.06\ (\pm e_4) \end{aligned} \tag{3-4}$$

The arithmetic answer is 3.06. But what is the uncertainty associated with this result?

For addition and subtraction, the uncertainty in the answer is obtained from the *absolute uncertainties* of the individual terms as follows:

Uncertainty in addition and subtraction:

$$e_4 = \sqrt{e_1^2 + e_2^2 + e_3^2} \tag{3-5}$$

For addition and subtraction, use absolute uncertainty.

For the sum in Equation 3-4, we can write

$$e_4 = \sqrt{(0.03)^2 + (0.02)^2 + (0.02)^2} = 0.04_1$$

The absolute uncertainty e_4 is ±0.04, and we express the answer as 3.06 ± 0.04. Although there is only one significant figure in the uncertainty, we wrote it initially as 0.04_1, with the first insignificant figure subscripted. We retain one or more insignificant figures to avoid introducing round-off errors into later calculations through the number 0.04_1. The insignificant figure was subscripted to remind us where the last significant figure should be when we conclude the calculations.

To find the percent relative uncertainty in the sum of Equation 3-4, we write

$$\text{Percent relative uncertainty} = \frac{0.04_1}{3.06} \times 100 = 1_3\%$$

The uncertainty, 0.04_1, is 1_3% of the result, 3.06. The subscript 3 in 1_3% is not significant. It is sensible to drop the insignificant figures now and express the final result as

$$\begin{aligned} &3.06\ (\pm 0.04) \qquad \text{(absolute uncertainty)} \\ &3.06\ (\pm 1\%) \qquad \text{(relative uncertainty)} \end{aligned}$$

For addition and subtraction, use absolute uncertainty. Relative uncertainty can be found at the end of the calculation.

EXAMPLE **Uncertainty in a Buret Reading**

The volume delivered by a buret is the difference between final and initial readings. If the uncertainty in each reading is ±0.02 mL, what is the uncertainty in the volume delivered?

Solution Suppose that the initial reading is 0.05 (±0.02) mL and the final reading is 17.88 (±0.02) mL. The volume delivered is the difference:

$$\begin{array}{l} 17.88\ (\pm 0.02) \\ -\ 0.05\ (\pm 0.02) \\ \hline 17.83\ (\pm e) \end{array} \qquad e = \sqrt{0.02^2 + 0.02^2} = 0.02_8 \approx 0.03$$

Regardless of the initial and final readings, if the uncertainty in each one is ±0.02 mL, the uncertainty in volume delivered is ±0.03 mL.

Test Yourself What would be the uncertainty in volume delivered if the uncertainty in each reading were 0.03 mL? (*Answer:* ±0.04 mL.)

Multiplication and Division

For multiplication and division, first convert all uncertainties into percent relative uncertainties. Then calculate the error of the product or quotient as follows:

or multiplication and division, use percent lative uncertainty.

Uncertainty in multiplication and division:

$$\%e_4 = \sqrt{(\%e_1)^2 + (\%e_2)^2 + (\%e_3)^2} \tag{3-6}$$

For example, consider the following operations:

$$\frac{1.76\ (\pm 0.03) \times 1.89\ (\pm 0.02)}{0.59\ (\pm 0.02)} = 5.64 \pm e_4$$

First convert absolute uncertainties into percent relative uncertainties.

dvice Retain one or more extra insignificant gures until you have finished your entire alculation. Then round to the correct number f digits. When storing intermediate results in calculator, keep all digits without rounding.

$$\frac{1.76\ (\pm 1._7\%) \times 1.89\ (\pm 1._1\%)}{0.59\ (\pm 3._4\%)} = 5.64 \pm e_4$$

Then find the percent relative uncertainty of the answer by using Equation 3-6.

$$\%e_4 = \sqrt{(1._7)^2 + (1._1)^2 + (3._4)^2} = 4._0\%$$

The answer is 5.6_4 (±$4._0$%).

To convert relative uncertainty into absolute uncertainty, find $4._0$% of the answer.

$$4._0\% \times 5.6_4 = 0.04_0 \times 5.6_4 = 0.2_3$$

The answer is 5.6_4 (±0.2_3). Finally, drop the insignificant digits.

or multiplication and division, use percent lative uncertainty. Absolute uncertainty can e found at the end of the calculation.

$$\begin{array}{ll} 5.6\ (\pm 0.2) & \text{(absolute uncertainty)} \\ 5.6\ (\pm 4\%) & \text{(relative uncertainty)} \end{array}$$

The denominator of the original problem, 0.59, limits the answer to two digits.

Mixed Operations

Now consider a compulation containing subtraction and division:

$$\frac{[1.76\ (\pm 0.03) - 0.59\ (\pm 0.02)]}{1.89\ (\pm 0.02)} = 0.61_9 \pm\ ?$$

First work out the difference in the numerator, using absolute uncertainties. Thus,

$$1.76\ (\pm 0.03) - 0.59\ (\pm 0.02) = 1.17\ (\pm 0.03_6)$$

because $\sqrt{(0.03)^2 + (0.02)^2} = 0.03_6$.

Then convert into percent relative uncertainties. Thus,

$$\frac{1.17\ (\pm 0.03_6)}{1.89\ (\pm 0.02)} = \frac{1.17\ (\pm 3._1\%)}{1.89\ (\pm 1._1\%)} = 0.61_9\ (\pm 3._5\%)$$

because $\sqrt{(3._1\%)^2 + (1._1\%)^2} = 3._5\%$.