Elementary Quantitative Analysis

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CHEM 234

Chapter 3
Experimental Error

Overview

3-1 Significant Figures

3-2 Significant Figures in Arithmetic

3-3 Types of Error

3-4 Propagation of Uncertainty from Random Error

3-5 Propagation of Uncertainty from Systematic Error

3-3: Experimental Error

- Some laboratory errors are more obvious than others, but there is error associated with every measurement.
- There is no way to measure the “true” value of anything.
- The best we can do in a chemical analysis is to carefully apply a technique that experience tells us is reliable.

3-3: Experimental Error

- Repetition of one method of measurement several times tells us the **precision** (reproducibility) of the measurement.

- If the results of measuring the same quantity by different methods agree with one another, then we become confident that the results are **accurate**, which means they are near the "true" value.

Precision *vs*. accuracy

Q. Does small random error imply accuracy in an experimental measurement?

A. The ability to reproduce a measurement does not make it correct.

Definitions:

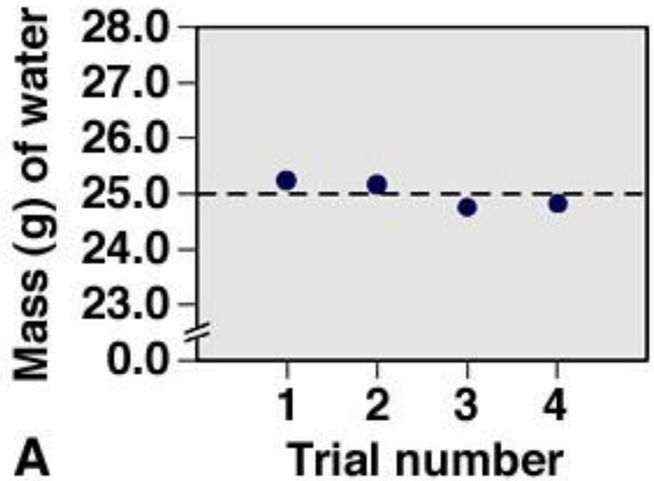
Accuracy

How close is the measured value to the ”true” value?

Precision

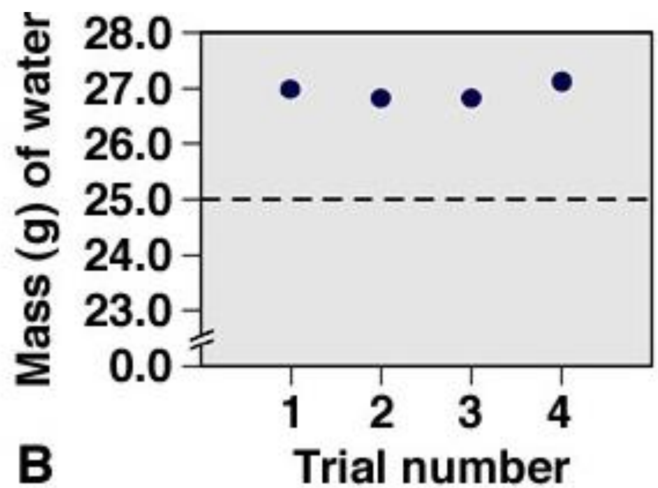
How reproducible (*i.e*., repeatable) is the result?

Precision *vs*. accuracy



precise and accurate

precise but not accurate



3-2: Significant Figures: Addition/Subtraction

In addition and subtraction, the **last significant figure** is determined by the number with the **fewest decimal places** (when all exponents are equal).

Example:

$$\begin{array}{r} 1.362 \times 10^{-4} \\ \underline{+\ 3.111 \times 10^{-4}} \\ 4.473 \times 10^{-4} \end{array}$$

3-2: Multiplication / Division

Multiplication and division

- The number of figures is limited by the factor with the **smallest** number of digits.

Example:

$$\begin{array}{r} 34.60 \\ \underline{\div\ 2.462\ 87} \\ 14.05 \end{array}$$

3-2: Significant Figures: Logarithms

Logarithm of a quantity

- The number of figures in the **mantissa** should equal the number of significant figures in the quantity.
- What is the pH of a solution that is 0.0255 M in H^+?

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

$$\mathrm{pH} = -\log[0.0255\mathrm{M}] \quad \text{3signicicant figures}$$

$$\mathrm{pH} = 1.\mathbf{593}_5$$

Matissa: Is the decimal part in the answer of a logarithmic operation.
Example: Log 339 = 2.530. The integer part (2) is called the **characteristic**, while the decimal part (530) is called the mantissa.

3-2: Rounding

- Always retain **more digits** than necessary during a calculation and round off to the appropriate number of digits at the end.
- Look at ***all* the digits** *beyond* the last place desired.
  - **Round up** if this number is more than halfway to the next higher digit. $121.794_{806\,4}$ is rounded to 121.795.
  - **Round down** if the insignificant figures is less than halfway. 121.794_{3} is rounded to 121.794.
  - **Round to the nearest *even* digit** if the number is exactly halfway.
    - 43.5_{5} is rounded to 43.6
    - 43.4_{5} is rounded to 43.4

Experimental error

No analytical result is ever absolutely and completely certain.

Error

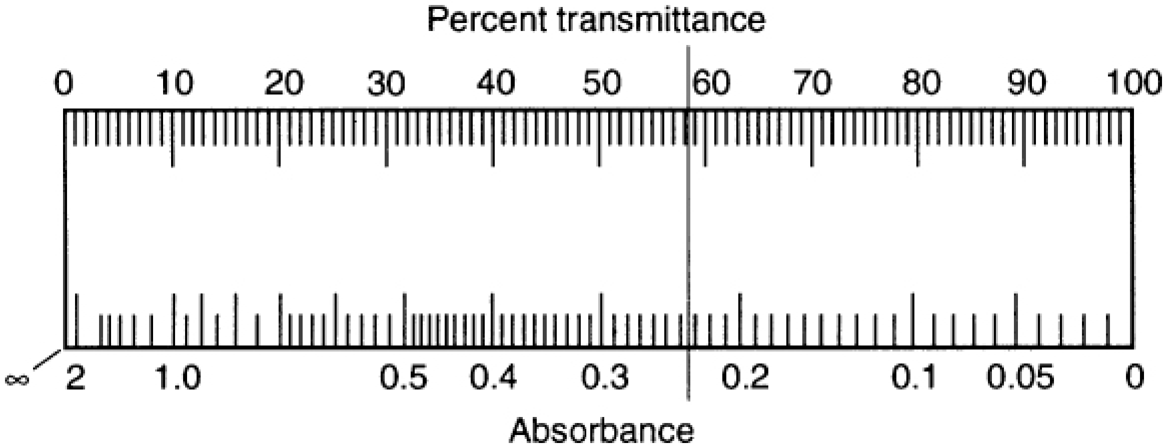
systematic (determinate) | random (indeterminate)

constant | proportionate

Systematic error refers to consistent error that appears each and every time a given measurement is made in the same way.

3-3: Random and Systematic Errors

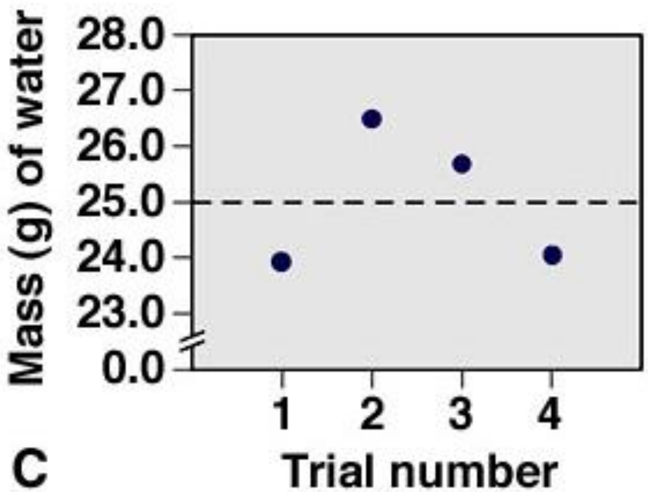
- **Random** (indeterminate) error affects the precision (reproducibility) of a result.
  - Arises from uncontrolled (and uncontrollable) variables in the measurement.
  - Has an equal chance of being positive or negative.
  - Is always present and cannot be corrected.
- Example: Random error associated with reading a scale.



3-3: Random and Systematic Errors

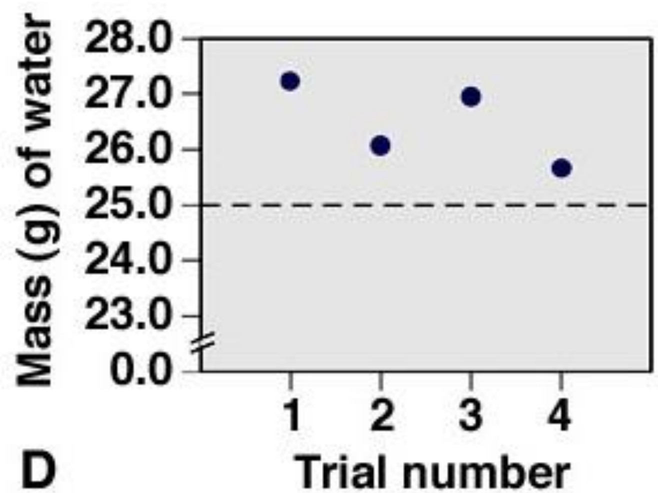
- **Systematic** (determinate) error affects the accuracy (nearness to the "true" value).
  - Arises from a flaw in equipment or the design of an experiment.
  - Reproducible.
- Example: An incorrectly standardized pH meter. You think that the pH of the buffer used to standardize the meter is 7.00, but it is really 7.08. Then all your pH readings will be 0.08 pH unit too low. pH reading of 5.60 is actually 5.68.
- With diligence, systematic error can be discovered and eliminated, but some **random error** is **always** present.
- We strive to **eliminate systematic errors** in all measurements.

Random *vs*. Systematic Error



random error

systematic error



Sources of systematic error

- Improper experimental design ("procedural" errors)
- Improper calibration of the experimental apparatus

Result: Data are systematically skewed.

∴ Reduced accuracy

In principal at least, the source of a systematic error can be identified and the error eliminated.

3-3: Detecting Systematic Error

1. Analyze a known sample, such as a **certified reference material**.
2. Analyze blank samples containing no analyte being sought. If you observe a nonzero result, your method responds to more than you intend.
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.
5. Disagreement beyond the estimated **random error** is **systematic error**.

Detection of systematic error

- Analysis of a "known" sample

National Institute of Standards and Technology (NIST)
"Standard Reference Materials" (SRMs)

- Analysis of a blank sample

Blank ≅ Sample containing no analyte

Expected: No analyte $\longrightarrow$ No response

If… No analyte $\longrightarrow$ Non-zero response

Then… Possible problem with method!

Detection of systematic error (cont'd)

- Analysis of same sample by multiple analytical methods

  Poor agreement implies an error in one (or more) of the techniques employed.

- "Round Robin" experiments

  Identical sample is analyzed by same (or several) methods in multiple laboratories by multiple analysts.

  Disagreement exceeding random error indicates systematic error.

- Varying the sample size

  Sample size reduction can make the presence of a constant systematic error more apparent.

Sources of random error

- Fluctuations in quantity measured
- Limitations on our ability to make physical measurements in a consistent way

Why are we limited?

Fluctuations in the behavior of measuring instrument with changing experimental conditions

Inability to control variations in experimental conditions (*e.g.*, random electrical noise).

Sources of random error (cont’d)

- Operator subjectivity

  A given operator making the same measurement repeatedly over a period of time will likely generate a data set comprising a random collection of values scattered about the true value, some higher, some lower.

  Unlike systematic error, random error cannot be eliminated.

If all systematic error were eliminated, there would still be uncertainty in the experimental measurement.

3-3: Uncertainties for Random Errors

- 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.

- Express as the *standard deviation, standard deviation of the mean*, or a *confidence interval*, which we will discuss in Chapter 4.

- We assume that systematic error has been detected and corrected.

3-4: Propagation of Uncertainties from Random Errors

Data treatment in many experiments involves arithmetic operations on several numbers, each of which has some uncertainty associated with it.

Total random error ≠ sum of individual errors.

Why?

Because random error has an equal chance of be positive or negative, some error cancellation is to be expected.

3-4: Propagation of Uncertainties

For **random errors**, propagation of uncertainty in addition and subtraction requires **absolute uncertainties**.

$$e_3 = \sqrt{e_1^{\,2} + e_2^{\,2}}$$

Multiplication and division utilize **relative uncertainties**.

$$\%e_3 = \sqrt{\%e_1^{\,2} + \%e_2^{\,2}}$$

Other rules for propagation of random error are found in Table 3-1,

3-4: Propagation of Uncertainties

TABLE 3-1 Summary of rules for propagation of uncertainty

Function	Uncertainty	Function[a]	Uncertainty[b]
$y = x_1 + x_2$	$e_y = \sqrt{e_{x_1}^2 + e_{x_2}^2}$	$y = x^a$	$\%e_y = a\%e_x$
$y = x_1 - x_2$	$e_y = \sqrt{e_{x_1}^2 + e_{x_2}^2}$	$y = \log x$	$e_y = \frac{1}{\ln 10}\frac{e_x}{x} \approx 0.434\,29\,\frac{e_x}{x}$
$y = x_1 \cdot x_2$	$\%e_y = \sqrt{\%e_{x_1}^2 + \%e_{x_2}^2}$	$y = \ln x$	$e_y = \frac{e_x}{x}$
$y = \frac{x_1}{x_2}$	$\%e_y = \sqrt{\%e_{x_1}^2 + \%e_{x_2}^2}$	$y = 10^x$	$\frac{e_y}{y} = (\ln 10)\, e_x \approx 2.302\,6\, e_x$
		$y = e^x$	$\frac{e_y}{y} = e_x$

a. x represents a variable and a represents a constant that has no uncertainty.
b. e_x/x is the relative error in x and $\%e_x$ is $100 \times e_x/x$.

Addition & Subtraction

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:

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

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

Ex. What is the most probable uncertainty for this computation?

$$\underset{e_1}{1.76\ (\pm\ 0.03)} \times \underset{e_2}{1.89\ (\pm\ 0.02)} \div \underset{e_3}{0.59\ (\pm\ 0.02)} = 5.6_4 \pm\ ?? \quad e_4$$

Relative uncertainty, $\%e_4 = [(\%e_1)^2 + (\%e_2)^2 + (\%e_3)^2]^{½}$

Here, $\%e_4 = [(1._7)^2 + (1._1)^2 + (3._4)^2]^{½} = 4._0\%$

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

$\therefore$ Answer is $5.6_4 \pm 0.2_3$ or, after dropping insignificant digits:

5.6 ± 0.2

3-4:Propagation of Uncertainty

EXAMPLE **Uncertainty in H^+ Concentration**

Consider the function pH = $-\log [H^+]$, where $[H^+]$ is the molarity of H^+. For pH = 5.21 ± 0.03, find $[H^+]$ and its uncertainty.

Solution First solve the equation pH $= -\log[H^+]$ for $[H^+]$: If $a = b$, then $10^a = 10^b$. If pH $= -\log[H^+]$, then $\log[H^+] = -$pH and $10^{\log[H^+]} = 10^{-\text{pH}}$. But $10^{\log[H^+]} = [H^+]$. We therefore need to find the uncertainty in the equation

$$[H^+] = 10^{-\text{pH}} = 10^{-(5.21 \pm 0.03)}$$

In Table 3-1, the relevant function is $y = 10^x$, in which $y = [H^+]$ and $x = -(5.21 \pm 0.03)$. For $y = 10^x$, the table tells us that

$$\frac{e_y}{y} = 2.302\,6\, e_x$$

$$\frac{e_{[H^+]}}{[H^+]} = 2.302\,6\, e_{\text{pH}} = (2.302\,6)(0.03) = 0.069\,1 \qquad \text{(3-12)}$$

The relative uncertainty in $[H^+]$ is 0.069 1. For $[H^+] = 10^{-\text{pH}} = 10^{-5.21} = 6.17 \times 10^{-6}$ M, we find

$$\frac{e_{[H^+]}}{[H^+]} = \frac{e_{[H^+]}}{6.17 \times 10^{-6}\text{ M}} = 0.069\,1 \Rightarrow e_{[H^+]} = 4.26 \times 10^{-7}\text{ M}$$

The concentration of H^+ is $6.17\,(\pm 0.426) \times 10^{-6}$ M $= 6.2\,(\pm 0.4) \times 10^{-6}$ M. An uncertainty of 0.03 in pH gives an uncertainty of 7% in $[H^+]$. Notice that extra digits were retained in the intermediate results and were not rounded off until the final answer.

TEST YOURSELF If uncertainty in pH is doubled to ±0.06, what is the relative uncertainty in $[H^+]$? (***Answer:*** 14%)

3-4:Propagation of Uncertainty

EXAMPLE **Propagation of Uncertainty in the Product $x \cdot x$**

If an object falls for t seconds, the distance it travels is $\frac{1}{2}gt^2$, where g is the acceleration of gravity (9.8 m/s ^{2}) at the surface of the Earth. (This equation ignores the effect of drag produced by air, which slows the falling object.) If the object falls for 2.34 s, the distance traveled is $\frac{1}{2}(9.8\ \text{m/s}^2)(2.34\ \text{s})^2 = 26.8$ m. If the relative uncertainty in time is $\pm 1.0\%$, what is the relative uncertainty in distance?

Solution Equation 3-7 tells us that for $y = x^a$, the relative uncertainty in y is a times the relative uncertainty in x:

$$y = x^a \Rightarrow \%e_y = a(\%e_x)$$

$$\text{Distance} = \tfrac{1}{2}gt^2 \Rightarrow \%e_{\text{distance}} = 2(\%e_t) = 2(1.0\%) = 2.0\%$$

If you write distance $= \frac{1}{2}gt \cdot t$, you might be tempted to say that the relative uncertainty in distance is $\sqrt{1.0^2 + 1.0^2} = 1.4\%$. This answer is wrong because the error in a single, measured value of t is always positive or always negative. If t is 1.0% high, then t^2 is 2% high because we are multiplying a high value by a high value: $(1.01)^2 = 1.02$.

Equation 3-6 presumes that the uncertainty in each factor of the product $x \cdot z$ is random and independent of the other. In the product $x \cdot z$, the measured value of x could be high sometimes and the measured value of z could be low sometimes. In the majority of cases, the uncertainty in the product $x \cdot z$ is not as great as the uncertainty in x^2.

TEST YOURSELF You can calculate the time it will take for an object to fall from the top of a building to the ground if you know the height of the building. If the height has an uncertainty of 1.0%, what is the uncertainty in time? (***Answer:*** 0.5%)

3-4: The Real Rule on Significant Figures

The real rule: The first uncertain figure is the last significant figure.

$$\frac{0.821(\pm 0.002)}{0.803(\pm 0.002)} = 1.022(\pm 0.004)$$

- The quotient above is expressed with *four* figures even though the dividend and divisor each have *three* figures.

3-5: Propagation of Systematic Error

- Systematic error occurs in some common situations (molecular mass and volumetric glassware calculations).
- It is treated differently from random error in arithmetic operations.
- *For systematic uncertainty, we add the uncertainties of each term in a sum or difference.*

- Systematic error in the mass of **n** atoms of one element is **n** times the uncertainty in mass of that element.
- **Uncertainty** in the mass of a molecule with several elements is computed from the sum of squares of the **systematic uncertainty** for each element.

3-5: Propagation of Systematic Error: Molecular Mass

Uncertainty in molecular mass of O_2

- The mass of O_2 is somewhere in the range 31.998 8 ± 0.000 8 g/mol.
- The uncertainty in the mass of *n* atoms is

  $n \times$ (uncertainty of one atom) = 2 $\times$ (± 0.000 8) = ± 0.0016

The uncertainty is **not** $\pm\sqrt{(0.0008)^2 + (0.0008)^2} = \pm 0.001_1$

For systematic uncertainty, we add the uncertainties of each term in a sum or difference.

3-5: Propagation of Systematic Error – Volume Delivered

- A 25-mL Class A volumetric pipet is certified to deliver 25.00 ± 0.03 mL.
- The volume delivered is in the range 24.97 to 25.03 mL. If you use the **uncalibrated** pipet four times to deliver a total of 100 mL, what is the uncertainty in 100 mL?
- The uncertainty is a systematic error, so the uncertainty in four pipet volumes is ± 4 × (0.03) = **± 0.12 mL**, **not**

$$\pm\sqrt{(0.03)^2+(0.03)^2+(0.03)^2+(0.03)^2}=\pm 0.06$$

- The difference between 25.00 mL and the actual volume delivered is a *systematic* error. It is always the same.
- *Calibration of the pipet eliminates systematic error.*

3-5:Calibration Removes Systematic Error

- If a calibrated pipet delivers a mean volume of 24.991 mL with an uncertainty of ± 0.006 mL, and you deliver four aliquots, the volume delivered is 4 × 24.991 = 99.964 mL and the uncertainty is ± 0.0012 mL.

$$e_{\text{del. vol.}} = \sqrt{(0.006)^2 + (0.006)^2 + (0.006)^2 + (0.006)^2}$$
$$e_{\text{del. vol.}} = \pm\, 0.0012 \text{ mL}$$

- For an uncalibrated pipet, the uncertainty is ± 4 × 0.03 = 0.12 mL because it is a systematic uncertainty.

Calibrated pipet volume = 99.964 ± 0.012 mL
Uncalibrated pipet volume = 100.00 ± 0.12 mL