Experimental Error

Chapter 3

Errors Matter (Zika Epidemic)

Microcephaly

- Abnormally small head associated with incomplete brain development
- Can be caused by infections from the mosquito-borne virus Zika during a mother's pregnancy
- CDC recommends that pregnant women who travel/live in areas with known Zika outbreaks be tested for the virus

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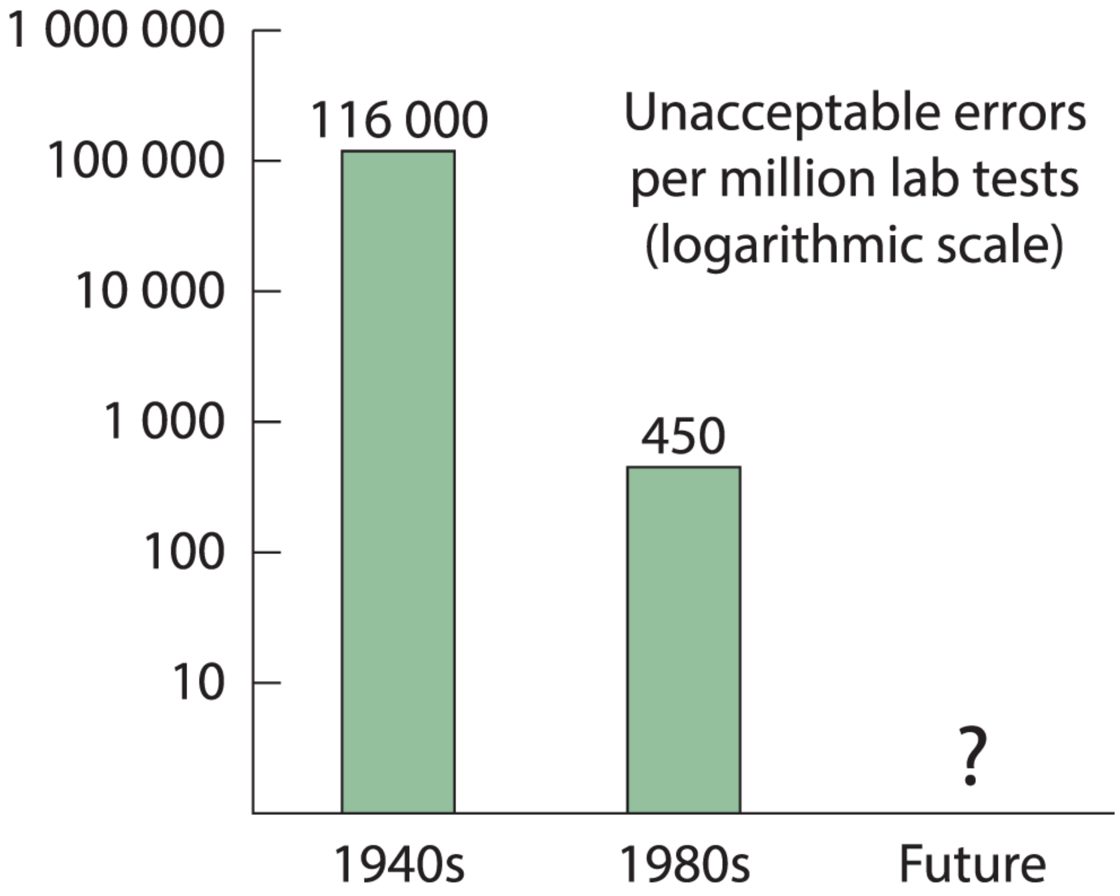
"Botched" Testing

- Technicians at a Washington DC testing lab mistakenly diluted lab reagents, resulting in 409 Zika tests all coming back "negative."
- Retesting identified pregnant women who had the Zika virus.
- Standard operating procedures (SOP) outline specific procedures to ensure the quality of the chemical analysis.

Errors Matter

More than 13 billion clinical tests are performed each year in the United States.

- Some results will be wrong
- Improving reliability depends on the scientist's ability to recognize and prevent errors . . .
- . . . and to make intelligent decisions despite uncertainty.



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Section 3-1
Significant Figures

Significant Figures

Significant figures: minimum number of digits needed to write a given value in scientific notation without loss of precision

$\mathbf{9.25 \times 10^4}$	**3 significant figures**
$\mathbf{9.250 \times 10^4}$	**4 significant figures**
$\mathbf{9.250\,0 \times 10^4}$	**5 significant figures**
0.000 925	**3 significant figures**

Zeros are significant when they occur (1) in the middle of the number or (2) at the end of the number to the right of the decimal point

Uncertainty in Measured Quantities

There is uncertainty in any *measured* quantity.

- Even instruments with digital readouts that do not fluctuate

When reading the scale on any apparatus, estimate all readings to the nearest tenth of the distance between scale divisions (**interpolation**).

Within calculations, **rounding** of numbers should only be done at the *final answer* (after all calculations are complete, not at intermediate steps).

- Subscript extra digits during calculations to remember which decimals are significant.

Section 3-2
Significant Figures in Arithmetic

Significant Figures: Addition and Subtraction (1 of 2)

- Express all numbers with the same exponent.
- Align all numbers with respect to the decimal point.
- Round the answer according to the number with the *fewest decimal places.*

$$\begin{array}{r} 1.632 \times 10^5 \\ +\ 4.107 \times 10^3 \\ \underline{+\ 0.984 \times 10^6} \end{array} \Rightarrow \begin{array}{r} 1.632 \qquad \times 10^5 \\ +\ 0.041\ 07 \times 10^5 \\ \underline{+\ 9.84 \qquad \times 10^5} \\ \mathbf{11.51\ _{307} \times 10^5} \end{array}$$

$$\begin{array}{r|l} 18.998 & 403\ 163\ (F) \\ +\ \ 18.998 & 403\ 163\ (F) \\ \underline{+\ \ 83.795} & \underline{\qquad\qquad (Kr)} \\ 121.794 & _{806\ 326}\ (KrF_2) \end{array}$$

$$= \mathbf{121.795}$$

Significant Figures: Addition and Subtraction (2 of 2)

After addition or subtraction, the number of significant figures in the answer may *exceed* or be *less than* the number of significant figures in the original data.

5.345	4 sig figs	7.26×10^{14}	3 sig figs
+ 6.728	4 sig figs	$- 6.69 \times 10^{14}$	3 sig figs
12.073	**5 sig figs**	0.57×10^{14}	**2 sig figs**

Significant Figures: Multiplication and Division

- Answer is limited to the number of digits in the number with the *fewest* significant figures

$$3.26 \times 10^{-5}$$
$$\times\ 1.78$$
$$\mathbf{5.80 \times 10^{-5}}$$

$$4.317\,9 \times 10^{12}$$
$$\times\ 3.6 \quad \times 10^{-19}$$
$$\mathbf{1.6 \quad \times 10^{-6}}$$

$$34.60$$
$$\div\ 2.462\,87$$
$$\mathbf{14.05}$$

Significant Figures: Logarithms and Antilogarithms (1 of 2)

$$n = 10^a \qquad \text{means that} \qquad \log n = a$$

- Number of digits in **mantissa** of log *x* = number of significant figures in *x*

Characteristic = 2

Mantissa = 0.530

$$\log 339 = 2.530$$

3 sig figs

3 digits

Characteristic = −4

Mantissa = 0.470

$$\log 3.39 \times 10^{-5} = -4.470$$

3 sig figs

3 digits

Significant Figures: Logarithms and Antilogarithms (2 of 2)

$$\boldsymbol{n = 10^{a}} \qquad \textbf{means that} \qquad \boldsymbol{\log n = a}$$

- Number of digits in antilog *x* (=10^x) = number of significant figures in mantissa of *x*

$$\textbf{antilog}(-3.42) = 10^{-3.42} = 3.8 \times 10^{-4} \qquad 10^{6.142} = 1.39 \times 10^{6}$$

2 digits → 2 sig figs

3 digits → 3 sig figs

Section 3-3
Types of Error

Types of Error

- *Every* measurement has some uncertainty.
- **Experimental error:** difference between the “true” value and the measured value
- Three types of experimental error:
  - **Systematic**
  - **Random**
  - **Gross (blunders)**

Systematic Error

Systematic error (**determinate error**): arises from a flaw in equipment or experiment design

- If conduct experiment again in exact manner, error is reproducible
- Can be discovered and corrected (in theory)

Ways to Detect

- Analyze a known sample (certified reference material).
- Use different method to measure same quantity.
- Different labs analyze identical samples ("round robin").
- Analyze blank sample. If observe nonzero result, method has systematic error.

Ways to Correct

- Calibrate glassware and instruments (Section 2-9).
- Use standard addition (Section 5-3) or internal standards (Section 5-4) to correct for matrix effects.

Random Error

Random error (**indeterminate error**): arises from uncontrolled variables in measurement

- Equal chance of being positive or negative
- *Always* present; cannot be eliminated
- Might be reduced with better technique

Examples of Random Error

- Subjective reading of a scale (varies with individual)
- Electrical noise in an instrument

Gross Error (Blunder)

Gross error (**blunder**): due to accidental but significant departures from procedure

- Caused by procedural, instrumental, or clerical mistakes (unrecoverable)
- Should be recorded in the lab notebook
- May be so serious that data are rejected or experiment is redone

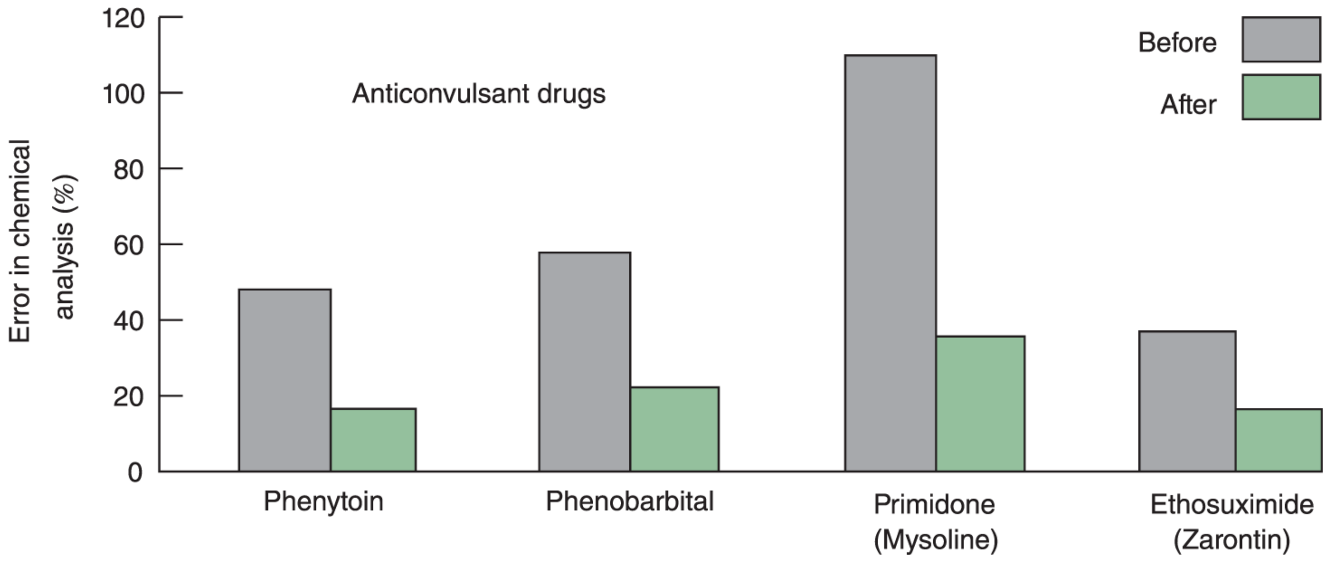
Examples of Blunders

- Calculation errors
- Overshooting a titration end point
- Dropping, discarding, or contaminating a sample
- Instrument failure

Box 3-1 Certified Reference Materials

National standards laboratories distribute **certified reference materials**.

- *Standard reference materials* are certified with painstaking care.
- Anticonvulsant drugs for patients with epilepsy require specific concentrations.
  - [drug] too low can lead to seizures
  - [drug] too high can be toxic
- Reference materials enable different laboratories to detect and correct errors in assay procedures.



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Precision and Accuracy

Precision: describes the reproducibility of a result

- If measure several times and values agree = precise
- If measure several times and values vary widely = not precise

Uncertainty: the variability within a set of measurements

Accuracy: how close a measured value is to the “true” value

Note: A measurement might be reproducible but wrong.

Absolute and Relative Uncertainty

Absolute uncertainty: expresses the margin of uncertainty associated with any measurement (with units)

- Typically written as a $\pm$ value
- Buret reading of **12.35 $\pm$ 0.02 mL** means the true value could be in the range **12.33 mL to 12.37 mL**

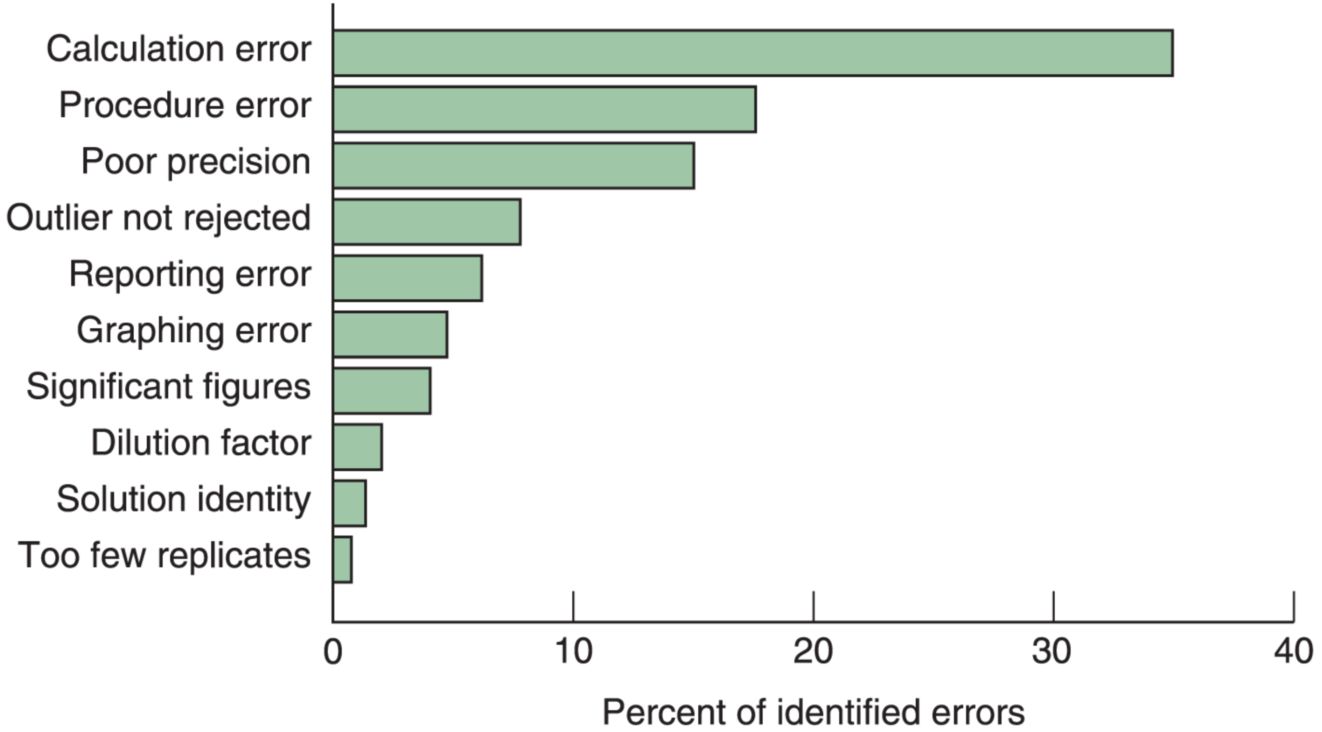
Relative uncertainty: compares the size of the absolute uncertainty with the size of its associated measurement

$$\textbf{Relative uncertainty} = \frac{\textbf{absolute uncertainty}}{\textbf{magnitude of the measurement}} = \frac{0.02\ \text{mL}}{12.35\ \text{mL}} = 0.002$$

$$\textbf{Percent relative uncertainty} = \frac{\textbf{absolute uncertainty}}{\textbf{magnitude of the measurement}} \times 100 = 0.002 \times 100 = 0.2\%$$

Box 3-2 Post-mortems of Failed Quant Labs

Students analyzed a series of unknown samples using proven titration procedures.



What could go wrong?

- 15% failed experiments due to *random errors*
- 85% failed experiments due to *blunders*