ERROR AND NOISE
SKOOG ‘N’ HOLLER CH 5A&B
ADDITIONAL READING ON WEBSITE
CHEM 314

OBJECTIVES

• Introduce sources of error in the laboratory
  • Discuss how to minimize errors
• Introduce the types of noise affecting instrumentation
• Discuss practical assessment of noise and how to minimize it (beat it to death with statistics)
• Review propagation of errors and sig figs
## SELECTING AN ANALYTICAL METHOD

<table>
<thead>
<tr>
<th>Criterion</th>
<th>Figure of Merit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Precision</td>
<td>Absolute standard deviation, relative standard deviation, coefficient of variation, variance</td>
</tr>
<tr>
<td>2. Bias</td>
<td>Absolute systematic error, relative systematic error</td>
</tr>
<tr>
<td>3. Sensitivity</td>
<td>Calibration sensitivity, analytical sensitivity</td>
</tr>
<tr>
<td>4. Detection limit</td>
<td>Blank plus three times standard deviation of the blank</td>
</tr>
<tr>
<td>5. Dynamic range</td>
<td>Concentration limit of quantitation (LOQ) to concentration limit of linearity (LOL)</td>
</tr>
<tr>
<td>6. Selectivity</td>
<td>Coefficient of selectivity</td>
</tr>
</tbody>
</table>

## ACCURACY VS PRECISION

Precision ≠ Accuracy
TYPES OF ERRORS IN THE LABORATORY

1. Random error
   - Always present, all directions
   - Often limits precision of measurements
   - Quantify: standard deviation

2. Systematic
   - Affects all measurements in the same way - Direction and magnitude
   - Assignable cause
   - Quantify: bias

3. Gross
   - Big oops!
   - Generally clear
   - Outliers?

SYSTEMATIC ERROR

Can be extremely difficult to detect

Run blanks
Run standard reference materials
Run samples by several methods or at different labs
BLANKS

Ideal blank- identical to sample except no analyte
Reagent blank- solvent + reagents used to prep sample
Solvent blank- solvent that analyte is dissolved in
Lab fortified blank- Matrix matched sample that undergoes the same procedure as the samples

STANDARD REFERENCE MATERIALS

National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2780
Hard Rock Mine Waste

Table 1. Certified Mass Fractions (Dry-Mass Basis)

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass Fraction (%)</th>
<th>k</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>8.87 ± 0.33</td>
<td>2.3</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.195 ± 0.020</td>
<td>2.6</td>
</tr>
<tr>
<td>Iron</td>
<td>2.784 ± 0.080</td>
<td>2.4</td>
</tr>
<tr>
<td>Lead</td>
<td>0.577 ± 0.041</td>
<td>2.4</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.533 ± 0.020</td>
<td>2.8</td>
</tr>
<tr>
<td>Potassium</td>
<td>3.38 ± 0.26</td>
<td>2.8</td>
</tr>
<tr>
<td>Sodium</td>
<td>0.221 ± 0.018</td>
<td>2.8</td>
</tr>
<tr>
<td>Sulfur</td>
<td>1.263 ± 0.042</td>
<td>2.6</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.257 ± 0.016</td>
<td>2.6</td>
</tr>
</tbody>
</table>

NIST Reference Material
# 2780 Hard Rock Mine Waste
https://www-s.nist.gov/srmors
RANDOM VS SYSTEMATIC ERROR
DATA OF UNKNOWN QUALITY ARE WORTHLESS

**Scenario 1:** Six equal portions of the same solution containing Fe\textsuperscript{III} were analyzed by the exact same method. The results were 19.4, 19.8, 20.3, 20.1, 19.7, 20.2.

**Scenario 2:** To assess the accuracy of your results, you measure a NIST standard (51 ppm Cu). Your results are 52.4, 53.1, 55.3, 49.6, 51.7. The average and standard deviation are 52±2.

Is there evidence of systematic or random error in the data as presented? If possible, state the magnitude of these errors.

SYSTEMATIC ERROR
Can be extremely difficult to detect

- Run blanks
- Run standard reference materials
- Run samples by several methods or at different labs

**Method errors**
**Personal errors**
**Instrument errors**

Error Family Tree
WHAT KINDS OR ERROR ARE OBSERVABLE?

Method errors
- Personal errors

SOURCES OF INSTRUMENTAL NOISE

- Chemical
- Thermal/Johnson
- Shot noise
- Flicker noise
- Environmental noise
SOURCES OF EXPERIMENTAL NOISE

Chemical
• Experiments are affected by uncontrollable environmental conditions affecting system

Instrumental noise
• Affects all components of the instrument
  • Observed noise is a complex composite of all noise sources

SOURCES OF ENVIRONMENTAL NOISE

FIGURE 5-3 Some sources of environmental noise in a university laboratory. Note the frequency dependence and regions where various types of interference occur. (From T. Coor, J. Chem. Educ., 1968, 45, A540. With permission.)
SOURCES OF INSTRUMENTAL NOISE

- Chemical
- Thermal/Johnson
- Shot noise
- Flicker noise
- Environmental noise

NOISE IN MEASUREMENTS

Unavoidable
Generally independent of signal size

\[ S = \frac{\text{max}_{\text{noise}} - \text{min}_{\text{noise}}}{5} \]

@99% CI

S/N < 2-3; signal not detectable from noise
IMPROVING S/N STATISTICS

\[
\left( \frac{S}{N} \right)_n = \sqrt{n} \left( \frac{S}{N} \right)_1
\]

To improve the signal-to-noise ratio by a factor of \( n \) requires averaging \( n^2 \) spectra.

SIGNAL TO NOISE

What is the anticipated S/N with 4 scans?

What is the anticipated S/N with 16 scans?

To improve the signal-to-noise ratio by a factor of \( n \) requires averaging \( n^2 \) spectra.
19-33. A spectrum has a signal-to-noise ratio of 8/1. How many spectra must be averaged to increase the signal-to-noise ratio to 20/1?

Improve S/N by \( \frac{20}{8} = 2.5 \)

\( 2.5^2 = 6.25 \Rightarrow 7 \) scans
COMMON SENSE RULES OF SIG FIGS

Record one more digit that you are certain of when making measurements.

A measurement can only have one uncertain digit. Example:

13.2305 \pm 0.04535 \text{ g}

13.23 \pm 0.05 \text{ g}

Rounding rules for 5's

PROPAGATION OF ERROR

TABLE 3-1 Summary of rules for propagation of uncertainty

<table>
<thead>
<tr>
<th>Function</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>y = x_1 + x_2</td>
<td>e_y = \sqrt{e_{x_1}^2 + e_{x_2}^2}</td>
</tr>
<tr>
<td>y = x_1 - x_2</td>
<td>e_y = \sqrt{e_{x_1}^2 + e_{x_2}^2}</td>
</tr>
<tr>
<td>y = x_1 \cdot x_2</td>
<td>e_y = \sqrt{e_{x_1}^2 + e_{x_2}^2}</td>
</tr>
<tr>
<td>y = \frac{x_1}{x_2}</td>
<td>e_y = \sqrt{e_{x_1}^2 + e_{x_2}^2}</td>
</tr>
</tbody>
</table>

<table>
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<tbody>
<tr>
<td>y = x^a</td>
<td>%e_y = a%e_x</td>
</tr>
<tr>
<td>y = \log x</td>
<td>e_y = \frac{1}{\ln 10} e_x = 0.434 29 \frac{e_x}{x}</td>
</tr>
<tr>
<td>y = \ln x</td>
<td>e_y = \frac{e_x}{x}</td>
</tr>
<tr>
<td>y = 10^x</td>
<td>e_y = (\ln 10)e_x = 2.302 6 e_x</td>
</tr>
<tr>
<td>y = e^x</td>
<td>\frac{e_y}{y} = e_x</td>
</tr>
</tbody>
</table>

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

3-16. Find the absolute and percent relative uncertainty and express each answer with a reasonable number of significant figures.

(d) 2.016 4 (\pm 0.000 8) + 1.233 (\pm 0.002) + 4.61 (\pm 0.01) = ?