Error Analysis in Experimentation

Experimentation involves observations, measurements, and analyses.

The quality of the final results, assessed by the reliability of data, depends on the quality of the measurements and the rigor with which the data are analyzed.

Central to the critical analysis of experimental data is a thorough understanding of the sources and the magnitudes of the errors associated with it.

There are always limitations in discovering the "ultimate reality" about a system that we wish to characterize.

These limitations cause discrepancies between our experimental result and the "true value" of the quantity of interest.

The fact is that the true value is defined in statistics as the mean of the sample population composed of an infinite number of measurements.

Implication: that any result obtained from a finite set of data may be in error to some extent.

The sources of error are categorized as systematic and random.

A systematic error arises from a bias that is placed on the measurement either by the instrument itself or by a consistently improper method of reading the instrument.

Random errors arise from intrinsic limitations in the sensitivity of the instrument and in the ability of the user to interpret the instrument's output.

Many measurements of a quantity are likely to be slightly different each time the measurement is made.

These fluctuations in the reading would be caused by the inherent inability of the electronic and mechanical components of the balance to function absolutely reproducibly.

Accuracy and Precision

An experimental measurement has high precision if the random errors (fluctuations) are small. Many significant figures are justified.

A measurement is accurate if there are small systematic errors. If so there is no intrinsic bias to the measurement, and its value approaches the true or accepted one.

There is no relationship between accuracy and precision. An experiment can have small random errors and still give inaccurate results due to large systematic errors.

An experiment with large random errors may still be accurate in the sense that the "true" or accepted value lies within the limits of error reported.

It is possible to observe a pattern in the observed random fluctuations of the measurements and they can be characterized.

There exists a distribution of such measured values and it can be expressed in a definite mathematical way (Gaussian distribution).
Another type of error is sometimes referred to as a "blunder"; a mistake. It is often evidenced by way the data point "sticks out".

It is considered acceptable to throw this data point out, and there are rigorous statistical tests that can be applied to justify this decision.

Systematic errors can also be minimized through proper instrument calibration and more careful experimental practices.

Yet another type of error, sometimes referred to as a "model error," is less obvious and potentially more serious than a blunder.

Model errors can be difficult to detect because it is often easier to mistrust your data than to question the validity of the theory that is supposed to be demonstrated by them.

Data are the facts on which science is built, and theories that do not conform to the facts must be modified or rejected.

Estimating Properties

Mean

If a measurement of some property \( x \) of a system is repeated several times the mean or average value of \( x \), on which \( n \) independent measurements have been made is defined as:

\[
\overline{x} = \frac{1}{n} \sum_{i=1}^{n} x_i
\]

If the errors associated with the measurements are completely random in nature, the data distribution follows a Gaussian distribution and mean is the best estimate of the true value of the property that can be obtained.

Standard Deviation, \( S \)

\[
f(x) = \frac{1}{\sqrt{2\pi}} e^{-\frac{1}{2} \left( \frac{x-\mu}{\sigma} \right)^2}
\]

\( \sigma = \) population standard deviation

The sample variance, \( S^2 \), which is defined as:

\[
S^2 = \frac{1}{n-1} \sum_{i=1}^{n} (x_i - \overline{x})^2
= \frac{n}{n-1} \left( \overline{x^2} - \overline{x}^2 \right)
\]

\( S = \) sample standard deviation

\( S \rightarrow \sigma \) as \( N \rightarrow \infty \).

\( S \) quantifies the precision/uncertainty/error (dispersion of data about the mean). For large \( n \) and data randomly distributed, \(~68\%\) of the data fall within \( \pm \sigma \) units of the mean.

Standard Error (Standard Error of the mean) \( S_m \)

If two series of measurements are made on the same system, the average value determined from the first series will in all likelihood be different from the value obtained from the second.

If a large number of these series were performed, the respective mean values would be symmetrically distributed about the "true value," and the standard deviation of the such a distribution is defined as the standard error of the mean would be given by:

\[
S_m = \frac{S}{\sqrt{n}}
\]

The precision of the mean can be raised by increasing \( n \).
Confidence Limits

Once \( S_m \) is determined, confidence limits can be obtained. The range on both sides of the mean within which the "true value, \( \mu \)" can be expected to be found for a degree of "confidence of c%"

The range \( \pm \delta \) is calculated from error/uncertainty \( \delta \), calculated from,

\[
\delta = \frac{S}{\sqrt{n}} t_{c, n}
\]

\( t = \) Students' t value taken from Students' t table.

Student’s t Distribution

In practice the replications, \( n \neq \infty \), and is finite, often \( n < 20 \). The best estimate of true value is still the average, and even though \( S \) and \( S_m \) can be calculated its usefulness is unclear because the probability distribution (Gaussian) is unknown.

The distribution function that would apply to limited \( n \) (therefore limited \( \nu = n-1 \) with an unknown \( \sigma \) is the Student's t distribution \( P(t) \).

\[
\delta = \frac{S}{\sqrt{n}} t_{c, n} = c\% \text{ CL}
\]

\( \Delta = t_{0.05, \infty} \frac{S}{\sqrt{n}} = 95\% \text{ CL} \)

Student’s t distributions \( P(t) \) for \( \nu = 1, 3, 5, .. \)

Expression of numerical results:

Sample mean \( \pm \Delta \) (95% Confidence level, \( n = \# \))

True mean \( = \mu \).

Confidence Limits

Within what values would \( \mu \) (the population mean) be, so that one can be \( c\% \) confident that \( \mu \) is indeed in that interval?

The confidence limits and interval are calculated using,

\[
\mu = \bar{x} \pm \delta
\]

confidence limits \( \bar{x} - \frac{tS}{\sqrt{n}} \leq \mu \leq \bar{x} + \frac{tS}{\sqrt{n}} \)

confidence interval \( \bar{x} - \frac{tS}{\sqrt{n}} \text{ and } \bar{x} + \frac{tS}{\sqrt{n}} \)

Find the value of \( \text{Student's } t \) from tables relevant to (n-1) degrees of freedom at desired c\% confidence.

\( n = \# \text{ replications} \)

Rejection of outliers: Q Test

Outliers are not always obvious. To reject a suspicious data point from set of \( n \) data points, where there is no obvious gross error, the Q test is used.

a. Arrange the data in the order of increasing value.
b. Determine the range = \( (X_{\text{max}} - X_{\text{min}}) \)
c. Find the difference between the data point in question, and its nearest neighbor. \( \text{gap} = |X_q - X_n| \)
d. Calculate the rejection quotient \( Q_{\text{calc}} \) as; \( Q_{\text{calc}} = \frac{\text{gap}}{\text{range}} \)
e. If \( Q_{\text{calc}} < Q_{\text{table}} \) for the \( n \), accept \( x_q \) for a given confidence level, 90% - norm. (> i.e 10% chance it is an outlier).
Outliers, if exists appear at the extremes.

Rejection of outliers: Grubbs Test

Calculate the Grubbs statistic.

\[ G_{calc} = \frac{\text{questionable value} - \bar{x}}{S} \]

Compare \( G_{calc} \) vs Critical table values for \( G \) for \( n \) observations

If \( G_{calc} < G_{table} \); accept the questionable value at 95% CL.

Discarding Data

Another method for deciding whether a data point can be justifiably discarded is to evaluate the mean without the ‘suspect data point’.

Then determine if this point deviates from the mean by more than four times the average deviation of the other points.

The average deviation is defined as,

\[ d_{av} = \frac{1}{n} \sum_{i=1}^{n} |x_i - \bar{x}| \]

Propagation of (Random) Errors

Once measurements \((x, y, z, \ldots)\) are made and estimates of the uncertainties associated with each of the individual measurements have been obtained \(\Delta x, \Delta y, \Delta z, \ldots\), their combined effect on the quantity of interest, \(F\), must be assessed.

This procedure is known as the propagation of errors.

\[ F = f(x, y, z, \ldots) \]

Then, \( dF = \frac{\partial F}{\partial x} \, dx + \frac{\partial F}{\partial y} \, dy + \frac{\partial F}{\partial z} \, dz + \ldots \) for infinitesimal changes

\[ \Delta F = \frac{\partial F}{\partial x} \, \Delta x + \frac{\partial F}{\partial y} \, \Delta y + \frac{\partial F}{\partial z} \, \Delta z + \ldots \] for finite changes

i.e. error in \(F\), \( \Delta F = \varepsilon(F) = \frac{\partial F}{\partial x} \varepsilon(x) + \frac{\partial F}{\partial y} \varepsilon(y) + \frac{\partial F}{\partial z} \varepsilon(z) + \ldots \)
Squaring and eliminating the high order terms leads to,

\[
\left[ \varepsilon'(F) \right]^2 = \left( \frac{\partial F}{\partial x} \right)^2 \varepsilon'(x) + \left( \frac{\partial F}{\partial y} \right)^2 \varepsilon'(y) + \left( \frac{\partial F}{\partial z} \right)^2 \varepsilon'(z) + \ldots
\]

Assuming uncertainty \( \varepsilon(F) = S(F) \); \( \varepsilon'(F) \) = \( S'(F) \)

analogously, \( S'^2(F) = \left( \frac{\partial F}{\partial x} \right)^2 S^2(x) + \left( \frac{\partial F}{\partial y} \right)^2 S^2(y) + \left( \frac{\partial F}{\partial z} \right)^2 S^2(z) + \ldots \)

and \( \Delta'^2(F) = \left( \frac{\partial F}{\partial x} \right)^2 \Delta^2(x) + \left( \frac{\partial F}{\partial y} \right)^2 \Delta^2(y) + \left( \frac{\partial F}{\partial z} \right)^2 \Delta^2(z) + \ldots \)

Only variances are additive, not standard deviations!

Some general examples:

1. For \( F = ax + z \ln z \),
   \[ \Delta'^2(F) = a^2 \Delta^2(x) + a \Delta(x) + \Delta^2(z) \]

2. For \( F = ax + \text{any} + ay \) or \( ax + ay + ax + ay \),
   \[ \Delta'^2(F) = \left( \frac{\partial F}{\partial x} \right)^2 \Delta^2(x) + \left( \frac{\partial F}{\partial y} \right)^2 \Delta^2(y) + \Delta^2(z) \]

3. For \( F = ax \),
   \[ \Delta'^2(F) = \frac{a}{x} \Delta^2(x) + \Delta^2(y) + \Delta^2(z) \]

4. For \( F = ay \),
   \[ \Delta'^2(F) = a \Delta^2(x) + \frac{a}{y} \Delta^2(y) + \Delta^2(z) \]

5. For \( F = a \ln x \),
   \[ \Delta'^2(F) = \frac{a}{x} \Delta^2(x) + \Delta^2(y) + \Delta^2(z) \]

\[ F = \frac{\Delta^2(x)}{y} \Delta'^2(F) = \left( \frac{\partial F}{\partial x} \right)^2 \Delta^2(x) + \left( \frac{\partial F}{\partial y} \right)^2 \Delta^2(y) \]

The expression for \( F \) is can be such that the functional form requires care to justify a breakdown of the procedure into steps.

If the terms \( A, B, \ldots \) are not independent the error calculated in this manner will be incorrect.

\[ \Delta'^2(F) = \left( \frac{\partial F}{\partial A} \right)^2 \Delta^2(A) + \left( \frac{\partial F}{\partial B} \right)^2 \Delta^2(B) \]

\[ \Delta^2(A) = (a e^{xy} - 1) + b(1 - xy) = A + B \]

\[ \Delta^2(B) = (\Delta A) \]

\[ \Delta^2(B) = b^2 \Delta^2(y) + b^2 \Delta^2(y) \]

Would result in, \( \Delta^2(F) = (a e^{xy} - bc)^2 \Delta^2(x) + b^2 \Delta^2(y) \)
Single measurements:

measurement: number unit

The accuracy of the measurement is limited by the capability of the measuring instrument.

The last digit of the number of a measurement is a considered judgment, estimate. (a source of uncertainty).

58.4 means actual value is between 58.0 and 59.0.
0.235 means actual value is between 0.230 and 0.240.

Estimation in Weighing

Better instruments will allow more precise measurements - better estimates - uncertainty can be minimized but never eliminated.

Significant figures:

measurement - 104.036 m

1) All non-zero digits are significant
   1.5 has 2 sig. figs.

2) Interior zeros are significant
   1.05 has 3 sig. figs.

3) Leading zeros are NOT significant
   0.001050 has 4 sig. figs.
   1.050 x 10^3 has 4 sig. figs.

4) Trailing zeros may or may not be significant
   i. Trailing zeros after a decimal point are significant
      1.050 has 4 sig. figs.
   ii. Zeros at the end of a number without a written decimal point are ambiguous and should be avoided by using scientific notation
      if 150 has 2 sig. figs. then 1.5 x 10^2
      but if 150 has 3 sig. figs. then 1.50 x 10^2
ALL DIGITS OF A MEASUREMENT INCLUDING THE UNCERTAIN ONE are called SIGNIFICANT FIGURES.

Or

Significant figures is the proper number of digits in the number.

Exact numbers have an unlimited number of significant figures (meaning there are no uncertainties – do not worry about it’s sig. figs.).

A number (e.g. integers) whose value is known with complete certainty (exactly) are

a. integral powers of 10
b. numbers from counting individual objects (integers)
c. numbers from definitions and defined constants
   1 cm = 0.01 m; c = 299792458 m s⁻¹ (vacuum)
   http://physics.nist.gov/cuu/Constants/
and d. integer values (in equations)
   radius of a circle = \( \frac{\text{diameter of a circle}}{2} \)

Express all numbers with same exponent

### Addition and Subtraction

<table>
<thead>
<tr>
<th>a.</th>
<th>b.</th>
<th>c.</th>
<th>d.</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.0</td>
<td>3.0045</td>
<td>61.830452</td>
<td>76.834952 (calculator)</td>
</tr>
<tr>
<td>61.830452</td>
<td>76.834952 (roundoff); 76.8</td>
<td>Express all numbers with same exponent</td>
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<tr>
<td>1.632 \times 10^5</td>
<td>1.632 \times 10^5</td>
<td>0.04107 \times 10^5</td>
<td>9.34 \times 10^5</td>
</tr>
<tr>
<td>4.107 \times 10^3</td>
<td>4.107 \times 10^3</td>
<td>11.51 \times 10^5</td>
<td>11.51 \times 10^5</td>
</tr>
</tbody>
</table>

### Multiplication and Division

Result has decimal places same as the # with the least decimals

\[
x = \frac{41.3600 \times 0.02328 \times 122.123}{1000 \times 100} = 3.4842
\]

\[
x = 3.374876 \quad \rightarrow \quad 3.375 \quad \text{(note rounding off)}
\]

Result has the same # sig. fig. as the # with the least # sig. fig.

Integers and powers of 10 has no uncertainty

### Rounding Off

Look at the left most digit to be dropped

- <5, no change of retained digit
- >5, increase retained digit by 1
- =5, increase retained digit as is, if it is odd

\[
69.5 \text{ in} \times \frac{1 \text{ yd}}{36 \text{ in}} \times \frac{1 \text{ m}}{1.0936 \text{ yd}} = 1.76 \times 10^1 \text{ m} = 1.76 \text{ m}
\]

mantissa has the same # sig.fig. as that of the number. round off at the correct position.

### Antilogs

will carry sig. figs. equal to the number of digits in the mantissa.

\[
antilog (1.4007) = 25.16
\]

round off such that it contains same # sig. fig. as mantissa

### Logarithms

\[
\log 25.158 = 1.40070
\]

characteristic \( \uparrow \) mantissa

e. \( y = \sqrt{x} \) \( y \) has same # sig. figs. as \( x \)
Arithmetic operations:

The precision of a calculated result is determined by the number with the lowest precision.

a. addition and subtraction:

Result has decimal places same as the # with the least decimals.

b. multiplication and division:

Result has the same # sig. fig. as the # with the least # sig. fig.

Disregard the uncertainty of integers and powers of 10, because they are exact.

b. multiplication & division

\[ y = \frac{k \cdot a_1 \cdot a_2}{a_1 a_2} \]  

(first calculate y and the relative errors,

\[ s = \sqrt{\left( \frac{\Delta a_1}{a_1} \right)^2 + \left( \frac{\Delta a_2}{a_2} \right)^2} \times y \]

(same approach for s, use \( s \) in place of \( a \))

Rounding Off:

Look at the left most digit to be dropped

<5, no change of retained digit  
>5, increase retained digit by 1  
=5, increase retained digit by 1, if it is odd

\[ 69.5 \text{ in} \times \frac{1 \text{yd}}{36 \text{ in}} \times \frac{1 \text{m}}{1.0936 \text{yd}} = 1.765321466 \text{ m} = 1.77 \text{ m} \]


c. logarithms:  \( \log 25.158 = 1.40070 \)  

mantissa has the same # sig.fig. as that of the number. round off at the correct position.

d. antilogs:  \( \text{antilog} \ (1.4007) = 25.158 \)  

will carry sig. figs. equal to the number of digits in the mantissa.

antilog (1.4007) = 25.16  

round off such that it contains same # sig. fig. as mantissa

e. \( y = \sqrt{x} \)  

y has same # sig. figs. as x

<table>
<thead>
<tr>
<th>Tolerances of Class A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Buret volume (mL)</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>10</td>
</tr>
<tr>
<td>25</td>
</tr>
<tr>
<td>50</td>
</tr>
<tr>
<td>100</td>
</tr>
</tbody>
</table>
Significant figures of a calculated result is determined by the first non zero digit of the uncertainty (σ or s) associated with it. Calculate the uncertainty first before deciding on the significant figures of the final computed value. Both the computed result and the uncertainty must be consistent in terms of the number of digits beyond the decimal point.

\[ 0.002364 \pm 0.000003 \]
\[ 0.0946 \pm 0.0002 \]
\[ 0.02500 \pm 0.00005 \]
\[ 0.821 \pm 0.002 \]
\[ 1.022 \pm 0.004 \]

**Estimating uncertainty of a single measurement**

Sometimes the uncertainty is not expressed explicitly, for a single measurement. Then the error is considered to be at the last digit (or last two digits) of the significant digits of the measurement given. Uncertainty has one significant digit, usually. The number of decimals of both value and error are same.

e.g. a single measurement like 1.047 m has an uncertainty of ± 0.001 m.

\[ R = 8.3144621 \pm 0.0000075 \text{ JK}^{-1}\text{mol}^{-1} \text{ (best available, n large)} \]
\[ R = 8.3145 \pm 0.0001 \text{ JK}^{-1}\text{mol}^{-1} \]

Unit conversion relations are not considered in significant digit assignments. [http://www.onlineconversion.com/](http://www.onlineconversion.com/)