Measurements are affected by errors (uncertainty)

There are two general categories of errors (uncertainties) in experimental measurements:

- **Systematic errors**
- **Random errors**
Measurements are affected by errors

Random errors

1. Varies in sign and magnitude for identical conditions
2. May be due to the instrument or the process being measured
3. Must be understood and communicated with results

Sources:

Always present (need to minimize)

• Random process, instrument fluctuations
• Randomized systematic trends (e.g. operator identity, thermal drift)
• Rare events

Solutions:

Do:

• Replicate and average

Always an option

• Improve measurement methods, practices
• Isolate from rare events

Solution for Random Errors:

\( \bar{x} \) is a Good Estimate of \( x \)

Sample mean \( E(x) = \bar{x} \pm 2e_s \) with 95% confidence

Standard Error. If only random error present:

\[ e_s = \frac{s}{\sqrt{n}} \]

1. Minimize whatever is causing random errors
2. Replicate, average, construct 95% CI of mean

DONE…
But, more than random errors are present

Systematic Errors

Measurements are affected by errors

**Systematic errors**

1. Has same sign and magnitude for identical conditions
2. Must be checked for, identified, eliminated, randomized

**Sources:**

- Calibration of instruments
- Reading error (resolution, coarse scale)
- Consistent operator error
- Failure to produce experimentally conditions assumed in an analysis (e.g. steady state, isothermal, well mixed, pure component, etc.)

**Solutions:**

- Recalibrate
- Improve instrument resolution
- Apply correction for identified error
- Improve procedures, experimental design
- Shift to other methods
- Take data in random order; rotate operators

From Lecture 1: Quick Start, Replicate Errors:
Measurements are affected by errors

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- Recalibrate
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- Apply correction for identified error
- Improve procedures, experimental design
- Shift to other methods

**Always an option**

- Take data in random order; rotate operators

---

This seems complicated! Is all this work necessary?
Measurements are affected by errors

**Systematic errors**

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2. Must be checked for and eliminated

**Sources:**
- Calibration of instruments
- Reading error (resolution, coarse scale)
- Consistent operator error
- Failure to produce experimentally assumed conditions (e.g., steady state, isothermal, well mixed, pure component, etc.)

**Mistakes** (need to fix)

**Solutions:**
- Recalibrate
- Improve instrument resolution
- Apply correction for identified error
- Improve procedures, experimental design
- Shift to other methods
- Take data in random order; rotate operators

**From Lecture 1: Quick Start, Replicate Errors:**

This seems complicated! Is all this work necessary?

*Yes, if you want to (eventually) get right answers.*

Even experts have difficulty identifying sources of uncertainty

Consider the experimentally determined mass of a proton as published between 1960 and 2015:

At every stage, expert researchers did their best to determine the correct value AND estimate the error.
Even experts have difficulty identifying sources of uncertainty

Consider the experimentally determined mass of a proton as published between 1960 and 2015:

At every stage, expert researchers did their best to determine the correct value AND estimate the error.

Except for the two most recent data points, none of these error bars encompass the true value of the proton mass.

If the error bars had been correctly determined, it would have looked more like this:

All of these error bars encompass the true value of the proton mass.

The analysis that went into the error bars tells us what are the largest sources of error; the largest errors show us how to improve the process.
Even experts have difficulty identifying sources of uncertainty

If the error bars had been correctly determined, it would have looked more like this:

All of these error bars encompass the true value of the proton mass.

The analysis that went into the error bars tells us what are the largest sources of error; the largest errors show us how to improve the process.

Conclusion:
- Estimating error is not easy;
- Estimating errors drives improvements to process, which
- Ultimately leads to better results.

Measurements are affected by errors

**Systematic errors**

1. Has same sign and magnitude for identical conditions
2. Must be checked for, identified, eliminated, randomized

**Sources:**

- Unavoidable: Calibration of instruments
- Unavoidable: Reading error (resolution, coarse scale)
- Consistent operator error
- Failure to produce experimentally conditions assumed in an analysis (e.g. steady state, isothermal, well mixed, pure component, etc.)

**Mistakes (need to fix)**

**Solutions:**

- Recalibrate
- Improve instrument resolution
- Apply correction for identified error
- Improve procedures, experimental design
- Shift to other methods

**Always an option**

- Take data in random order; rotate operators
Measurements are affected by errors (uncertainty)

We have identified three sources of error:
- Random errors (replicate error)
- Reading errors
- Calibration errors

\[ e_s = \frac{s}{\sqrt{n}} \quad \text{Standard error of replicates} \]
\[ e_x = ? \quad \text{Standard reading error} \]
\[ e_z = ? \quad \text{Standard calibration error} \]

The techniques developed to understand and report replicate error can be the template that we use to account for the other two sources of uncertainty.

Now:

\[ e_s = \frac{s}{\sqrt{n}} \quad \text{Standard error of replicates} \]
\[ e_x = ? \quad \text{Standard reading error} \]
\[ e_z = ? \quad \text{Standard calibration error} \]

The techniques developed to understand and report replicate error can be the template that we use to account for the other two sources of uncertainty.
Obtaining a Good Estimate of Precision

What is the Total Error of a Measurement?

\[ e_s \equiv \text{Standard Error} \]

Part 2: Reading Errors

Three sources:
- Replicate errors
- Reading errors
- Calibration errors

We standardize the individual errors so that we can combine them (apples to apples)
Obtaining a Good Estimate of Reading Error

Sometimes a measurement is very reproducible (negligible replicate error) but there is still error/uncertainty inherent in how the reading is taken.

Example: Digital Multimeter reading a 4-20mA instrument signal

Systematic errors due to Reading errors, include:

1. Limits of instrument sensitivity (i.e. the magnitude of change required for the instrument to respond)
2. Limits of the degree of subdivision of the scale or display
3. Fluctuations of an instrument reading
Obtaining a Good Estimate of **Reading Error**

**Systematic errors due to Reading errors, include:**

1. **Limits of instrument sensitivity** (i.e. the magnitude of change required for the instrument to respond)

   **How to determine?**

   **At every range of operation, test how much signal must be received in order for the reading to change.**

   **Related concept:** *Limit of detection* (more on this later)
Obtaining a Good Estimate of Reading Error

Systematic errors due to Reading errors, include:

2. Limits of the degree of subdivision of the scale or display

How to determine?

Estimate as
• ½ the smallest subdivision on the scale or
• ½ the smallest digit on a digital readout

3. Fluctuations of an instrument reading

How to determine?

Estimate as: \( \frac{1}{2} (x_{\text{max}} - x_{\text{min}}) \) over an interval
Obtaining a Good Estimate of Reading Error

Possible reading errors:

• Determine the limits of instrument sensitivity (magnitude of change required for instrument to respond)
• Determine \( \frac{1}{2} \) the smallest subdivision of the scale or display
• Determine \( \frac{1}{2} (x_{max} - x_{min}) \) for time-fluctuating data
• Designate the reading error:

\[
e_R = \text{maximum of the possible reading errors}
\]

Question: is this way of thinking about error the same method as we used for random error?

\[
e_{\text{replicate}} = \frac{s}{\sqrt{n}}
\]

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Obtaining a Good Estimate of Reading Error

Possible reading errors:

- Determine the limits of instrument sensitivity (magnitude of change required for instrument to respond)
- Determine \( \frac{1}{2} \) the smallest subdivision of the scale or display
- Determine \( \frac{1}{2} (x_{\text{max}} - x_{\text{min}}) \) for time-fluctuating data
- Designate the reading error:

\[ e_R = \text{maximum of the possible reading errors} \]

**Question:** is this way of thinking about error the same method as we used for random error?

No. We need to **standardize** the individual errors so that we can combine them (apples to apples)

\[ e_s = \frac{e_R}{\sqrt{3}} \]

**Where does that come from?**

We have identified three sources of standard error:

- \[ e_s = \frac{s}{\sqrt{n}} \] Standard error of replicates
- \[ e_s = ? \] Standard reading error
- \[ e_s = ? \] Standard calibration error

We seek to write each in an equivalent form, so that we can combine them into a total error, taking all sources into account.

**How to proceed?**
Consider the reading on a digital multimeter (DMM):

For a DMM meter reading (mA) of:

6.7 mA

A reading of 6.7 may correspond to any of these more precise numbers with equal probability.

½ the smallest subdivision of the scale or display:

\( e_R = 0.05 \)

The variance is a well-defined statistic, designed to measure the spread of individual outcomes around the mean outcome.

The standard error\(^2\) is the variance of the sampling distribution of the error.

The sampling distribution of replicate error is the Students' t probability distribution.

We can determine the sampling distribution of reading error by considering the probability of obtaining individual readings around the true reading.

\[ e_s = \frac{e_R}{\sqrt{n}} \]

Where does that come from?

\[ e_s = \frac{s}{\sqrt{n}} \]

Standard error of replicates

\[ e_s^2 = \frac{s^2}{n} \]

Variance associated with a sample set of \( n \) measurements subject to random error

\[ x_1, x_2, x_3, x_4, x_5, ..., x_n \]

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

\[ s^2 \equiv \frac{1}{n-1} \sum_{i=1}^{n} (x_i - \bar{x})^2 \]
A reading of 6.7 may correspond to any of these more precise numbers with equal probability.

The variance of the rectangular probability distribution is \( \sigma^2 = \alpha^2 / 3 \).

The standard error of replicates is \( e_s = \frac{s}{\sqrt{n}} \).

The standard reading error is \( e_R = \frac{e_R}{\sqrt{3}} \).

The standard calibration error is \( e_s = ? \).

Measurements are affected by errors (uncertainty):

We have identified three sources of standard error:
- Random errors (replicate error)
- Reading errors
- Calibration errors

Now we know how to compute two out of three measurement standard errors.
Measurements are affected by errors (uncertainty)

We have identified three sources of standard error:

- Random errors (replicate error)
- Reading errors
- Calibration errors

\[ e_s = \frac{s}{\sqrt{n}} \]  
 Standard error of replicates

\[ e_s = \frac{e_R}{\sqrt{3}} \]  
 Standard reading error

\[ e_s = ? \]  
 Standard calibration error

For all three types of errors, we write a variance of the sampling distribution. Why? Because we know how to combine variances (see literature):

\[ \sigma^2_{\text{total}} = \sigma^2_1 + \sigma^2_2 + \sigma^2_3 + \ldots \]

They add in quadrature.

Obtaining a Good Estimate of Reading Error

Possible reading errors:

- Determine the limits of instrument sensitivity (magnitude of change required for instrument to respond)
- Determine \( \frac{1}{2} \) the smallest subdivision of the scale or display
- Determine \( \frac{1}{2} (x_{\text{max}} - x_{\text{min}}) \) for time-fluctuating data
- Designate the reading error:

\[ e_R = \text{maximum of the possible reading errors} \]

- Calculate the standard reading error,

\[ e_{s, \text{reading}} = \frac{e_R}{\sqrt{3}} \]

These steps are summarized (and you are guided through them) on the Reading Error Worksheet:

[Link to Reading Error Worksheet]
EXAMPLE 1  For a 50ml beaker weighed with the CM3215 laboratory analytical balance, what is the weight and the 95% confidence interval on the weight based on reading error?

You try.

34.4081 g

You try.

Mass, M

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### Reading Error Worksheet

This worksheet guides you through the calculation of the standard error and 95% confidence value of a digital niederer (yielding value) and subject to reading error. The reading error-related standard error, may subsequently be used in a propagation of error calculations of derived quantities.

**Device name:** Mettler analytical balance

<table>
<thead>
<tr>
<th>Measured Quantity (give symbol)</th>
<th>Mass, M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Representative value (indicate unit)</td>
<td>32.4081 g</td>
</tr>
</tbody>
</table>

**Sensitivity**

<table>
<thead>
<tr>
<th>Issue</th>
<th>Contribution to error</th>
</tr>
</thead>
<tbody>
<tr>
<td>How much signal does it take to cause the reading to change?</td>
<td>1</td>
</tr>
<tr>
<td>Peak errors - absence of marked scale or digital readout</td>
<td>2</td>
</tr>
<tr>
<td>Fluctuations with time of observation</td>
<td>4</td>
</tr>
</tbody>
</table>

**No unit of \( L, B, V \):**

\[ e_2 = 1 \times 10^{-4} \] g

**Standard error based on reading error:**

\[ e = \sqrt{e_1^2 + e_2^2} \]

\[ e = 0.58 \times 10^{-2} \] g

**With Confidence Interval on the reading:**

\[ 1.2 \times 10^{-2} \] g

---

Note: If a value is provided, for example, in a manufacturer's specification, the uncertainty, we do not use the worksheet; instead, use the Calibrated Error Worksheet.

---

www.chem.mtu.edu/~fmorriso/cm3215/ReadingErrorWorksheet.pdf
EXAMPLE 1. For a 500ml beaker weighed with the CM3215 laboratory analytical balance, what is the weight and the 99% confidence interval on the weight based on reading error?

You try.

Answer:

\[ 34.4081 \pm 0.0001 \text{ g} \]

(reading error only)

EXAMPLE 2. For height of an object measured with a meter stick as shown, what is the value and a 95% confidence interval on the height based on reading error?

You try.

Image from: www.martinaknezevic.com/events/full-sail-university-course-overview/
EXAMPLE 2 For height of an object measured with a meter stick as shown, what is the value and a 95% confidence interval on the height based on reading error?
### Reading Error Worksheet

**CM3215 Fundamentals of Chemical Engineering: Lab**  
*Prof. Faith Morrison*

This worksheet guides the user through the calculation of the standard error and 95% confidence value of a digital reads (reading value) subject to reading error. The reading error calculated standard error, may subsequently be used to propagate error in calculations of derived quantities.

#### Device name: Laboratory wooden meter stick

<table>
<thead>
<tr>
<th>Measured Quantity</th>
<th>Height, ( h )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Representative value</td>
<td>106.3 mm</td>
</tr>
</tbody>
</table>

#### Error Sources:

<table>
<thead>
<tr>
<th>Source</th>
<th>Contribution to error</th>
<th>Quantity or Not Applicable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity (scale or orientation)</td>
<td>How much does the scale itself influence the reading?</td>
<td>1</td>
</tr>
<tr>
<td>Panel position</td>
<td>How much does the panel position on the scale itself influence the reading?</td>
<td>2</td>
</tr>
<tr>
<td>Fluctuations with time of observation</td>
<td>Fluctuations due to observer variability</td>
<td>4</td>
</tr>
<tr>
<td>Maximum of ( x_2 ) &amp; ( x_4 )</td>
<td>( x_2 + x_4 )</td>
<td>( x_2 + x_4 )</td>
</tr>
<tr>
<td>Standard error based on reading error:</td>
<td>( s_e = s_p / \sqrt{3} )</td>
<td>( s_e = 0.29 ) mm</td>
</tr>
<tr>
<td>With 95% confidence interval on the reading:</td>
<td>( s_e )</td>
<td>0.58 mm</td>
</tr>
</tbody>
</table>

**Note:** If value is supplied by, for example, a manufacturer, with no indication of the variability, we do not use the worksheet. Instead, use the Calibrated Error Worksheet.

---

**Laboratory wooden meter stick**

(at the most optimistic)
Obtaining a Good Estimate of a Quantity

Summary:

**Replicate (random) error:**
- Measure the quantity several times – replicates
- The average value is a good estimate of the quantity we are measuring if only random errors are present
- The 95% confidence interval comes from $\pm (**)e_s$
- $**$ = 2 if the number of replicates is 7 or higher
- $**$ comes from the Student’s $t$ distribution if $N < 7$ ($=t.inv.2t(0.05,n-1)$)
- Report one sig fig on error limits (unless that digit is 1 or 2)

**Reading error:**
- Determine signal needed to change reading
- Determine half smallest division or decimal place
- Determine average of fluctuations
- Max of those $/\sqrt{3}$ = reading standard error
- $\pm 2e_r$ for 95% confidence interval

**Combining Errors:**

$$e^2_{combined} = e^2_{replicate} + e^2_{reading} + e^2_{calibration}$$

Answer:

$106.3 \pm 0.6 \text{ mm}$

(at the most optimistic; reading error only)
Measurements are affected by errors (uncertainty)

We have identified three sources of standard error:

- Random errors (replicate error)
- Reading errors
- Calibration errors

For all three types of errors, we write a variance.

\[ e_s = \frac{s}{\sqrt{n}} \]  
Standard error of replicates

\[ e_s = \frac{e_R}{\sqrt{3}} \]  
Standard reading error

\[ e_s = ? \]  
Standard calibration error

The variance of the sampling distribution; combine in quadrature.

Next:

Calibration Errors

Obtaining a Good Estimate of Precision

What is the Standard Error of a Measurement?

\[ e_s \equiv \text{Standard Error} \]

Part 3: Calibration Errors

Three sources:

- Replicate errors
- Reading errors
- Calibration errors

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