Errors in Chemical Analysis

“Lies, damn lies, and statistics...”
Accuracy versus Precision

In casual conversation we use the words “accurate” and “precise” interchangeably - not so in Analytical Chemistry.
Accuracy versus Precision

In casual conversation we use the words “accurate” and “precise” interchangeably - not so in Analytical Chemistry.

Accuracy: The closeness of a measurement, or the mean of multiple measurements, to its true or accepted value.
Accuracy versus Precision

In casual conversation we use the words “accurate” and “precise” interchangeably - not so in Analytical Chemistry.

Accuracy: The closeness of a measurement, or the mean of multiple measurements, to its true or accepted value.

Precision: The agreement between multiple measurements made in the same way.
Accuracy versus Precision

Neither Accurate nor Precise
Low accuracy, low precision
Low accuracy, high precision

Only Precise

Only Accurate
High accuracy, low precision
High accuracy, high precision

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Determinate versus Indeterminate Error

In any measurement, there are two types of errors: determinate and indeterminate.
Determinate versus Indeterminate Error

In any measurement, there are two types of errors: determinate and indeterminate.

**Determinate Error**

Errors that cause the measured mean value ($x$ bar) for any series of measurements to be displaced, in one particular direction by one particular amount, from the true mean value ($\mu$).
Determinate versus Indeterminate Error

In any measurement, there are two types of errors: determinate and indeterminate.

**Determinate Error**

Errors that cause the measured mean value ($x$ bar) for any series of measurements to be displaced, in one particular direction by one particular amount, from the true mean value ($\mu$).

**Indeterminate Error**

Errors that cause the measured value for each measurement to be scattered randomly about $\mu$. 
In other words:

**Accurate measurements have little **Determinate Error**.

**Determinate error degrades Accuracy**  
- but has no effect on precision.
In other words:

**Accurate** measurements have little **Determinate Error**.

**Determinate error** degrades **Accuracy**
- but has no effect on **precision**.

**Precise** measurements have little **Indeterminate Error**.

**Indeterminate error** degrades **Precision**
- but it does not influence **accuracy**.
Another way to look at this: you want to be analyst 1.
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Determinate error is exposed by calibration against a sample with a known value, aka a STANDARD.
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For example: standard weights

If determinate error is present at an unacceptable level, you must track down its source and eliminate it.
**Determinate error** is exposed by calibration against a sample with a known value, aka a STANDARD.

For example: standard weights

If determinate error is present at an unacceptable level, you must track down its source and eliminate it.
**Determinate error** is exposed by calibration against a sample with a known value, aka a STANDARD.

For example: standard weights

one kilogram - exactly!

If determinate error is present at an unacceptable level, you must track down its source and eliminate it.
**Determinate errors** can be removed by changing your experimental procedure to account for them.

A common example in analysis: the *indicator error.*

<table>
<thead>
<tr>
<th>Indicator</th>
<th>pH range for color change</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Methyl violet</td>
<td>Yellow</td>
</tr>
<tr>
<td>Thymol blue</td>
<td>Red</td>
</tr>
<tr>
<td>Methyl orange</td>
<td>Red</td>
</tr>
<tr>
<td>Methyl red</td>
<td>Red</td>
</tr>
<tr>
<td>Bromthymol blue</td>
<td>Yellow</td>
</tr>
<tr>
<td>Phenolphthalein</td>
<td>Colorless</td>
</tr>
<tr>
<td>Alizarin yellow R</td>
<td>Yellow</td>
</tr>
</tbody>
</table>

[http://www.colby.edu/chemistry/CH142/notes/FG16_07.JPG](http://www.colby.edu/chemistry/CH142/notes/FG16_07.JPG)
the indicator in a titration should transition between two colors at the equivalence point.
an example that you will soon be encountering: *indicator error*.

Warder titration - solution of 0.1M NaOH and 0.1M Na₂CO₃ titrated with 0.1M solution of strong acid. Carbonic acid dissociation constants: pKₐ₁=6.37, pKₐ₂=10.25.

http://www.titrations.info/acid-base-titration-sodium-hydroxide-and-carbonate
an example that you will soon be encountering: *indicator error*.

Your eye detects a pink color here... 50 µl after the eq. point...

http://www.titrations.info/acid-base-titration-sodium-hydroxide-and-carbonate
an example that you will soon be encountering: *indicator error.*

...but not here, at the eq. point.

Warder titration - solution of 0.1M NaOH and 0.1M Na2CO3 titrated with 0.1M solution of strong acid. Carbonic acid dissociation constants: pKa1=6.37, pKa2=10.25.

http://www.titrations.info/acid-base-titration-sodium-hydroxide-and-carbonate
an example that you will soon be encountering: *indicator error*.

Warder titration - solution of 0.1M NaOH and 0.1M Na₂CO₃ titrated with 0.1M solution of strong acid. Carbonic acid dissociation constants: pKₐ₁=6.37, pKₐ₂=10.25.

So the indicator error is the difference, 50 µl.

---

http://www.titrations.info/acid-base-titration-sodium-hydroxide-and-carbonate
an example that you will soon be encountering: *indicator error.*

so the indicator error is the difference, 50 µl - about 1 drop.

Create your own Standard!

If you standardize your NaOH titrant against a *known* concentration of H$_2$CO$_3$ using phenolphthalein, you *exactly* compensate for this determinate error.

http://www.titrations.info/acid-base-titration-sodium-hydroxide-and-carbonate
Understanding the Nature of **Indeterminate Error**

Random errors behave under the laws of large numbers called “Gaussian Statistics”
Say you flip a coin ten times, you tally the results, and you do this 395 times (3950 coin flips)...

μ = 5.04
σ = 1.62
this distribution is Gaussian...

Gaussian distribution function

\[ y = \frac{\exp\left[\frac{-(x - \mu)^2}{2\sigma^2}\right]}{\sigma\sqrt{2\pi}} \]

\(\mu = 5.04\)
\(\sigma = 1.62\)
this distribution is Gaussian...

\[ y = \exp \left[ \frac{-(x - \mu)^2}{2\sigma^2} \right] \]

\( \mu \) is called the mean.

\[ \mu = 5.04 \]

\[ \sigma = 1.62 \]
this distribution is Gaussian...

\[
y = \exp \left( \frac{- (x - \mu)^2}{2\sigma^2} \right) / \sigma \sqrt{2\pi}
\]

\(\sigma\) is called the standard deviation
this distribution is Gaussian...

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

\[ \sigma = \sqrt{\frac{\sum_{i=1}^{N} (x_i - \mu)^2}{N}} \]
this distribution is Gaussian...

\[ y = \frac{\exp\left[-\frac{(x - \mu)^2}{2\sigma^2}\right]}{\sigma\sqrt{2\pi}} \]
±1σ encompasses 68.3% of the measurements...
±2σ encompasses 95.4% of the measurements...
$\pm 3\sigma$ encompasses 99.7% of the measurements.
We distinguish between two flavors of means:

\[ \mu \] - the \textit{true or population mean}. 

You know what the mean should be. Or, if you’ve got more than 19 measurements (i.e. \(N \geq 20\)), you have a good estimate of \(\mu\).
We distinguish between two flavors of means:

\[ \mu \] - the \textit{true or population mean}.  
You know what the mean should be. Or, if you’ve got more than 19 measurements (i.e. \( N \geq 20 \)), you have a good estimate of \( \mu \).

\[ \bar{X} \] - the \textit{sample mean}. (\textit{“x-bar”})
You have no idea what the value of the mean should be. And you’ve made less than 20 measurements (\( N < 20 \)).
and this means we’ve got two flavors of standard deviations too:

when you know the true or population mean:

\[
\sigma = \sqrt{\frac{\sum_{i=1}^{N} (x_i - \mu)^2}{N}}
\]
and this means we’ve got two flavors of \textit{standard deviations} too:

when you know the \textbf{true or population mean}:

\[ \sigma = \sqrt{\frac{\sum_{i=1}^{N} (x_i - \mu)^2}{N}} \]

...and when you don’t:

\[ s = \sqrt{\frac{\sum_{i=1}^{N} (x_i - \bar{x})^2}{N - 1}} \]

We will use “standard deviation” to mean $s$, and “true standard deviation” to mean $\sigma$. 
and this means we’ve got two flavors of standard deviations too:

when you know the true or population mean:

\[ \sigma = \sqrt{\frac{\sum_{i=1}^{N} (x_i - \mu)^2}{N}} \]

...and when you don’t:

\[ s = \sqrt{\frac{\sum_{i=1}^{N} (x_i - \bar{x})^2}{N - 1}} \]

N-1 is called the “degrees of freedom”

read more about the “degrees of freedom” in any statistics book...
Calculating the Standard Deviation for multiple measurements:

### Table 6-4

<table>
<thead>
<tr>
<th>Type of Calculation</th>
<th>Example*</th>
<th>Standard Deviation of $y$†</th>
</tr>
</thead>
<tbody>
<tr>
<td>Addition or subtraction</td>
<td>$y = a + b - c$</td>
<td>$s_y = \sqrt{s_a^2 + s_b^2 + s_c^2}$ (1)</td>
</tr>
<tr>
<td>Multiplication or division</td>
<td>$y = a \times b/c$</td>
<td>$\frac{s_y}{y} = \sqrt{\left(\frac{s_a}{a}\right)^2 + \left(\frac{s_b}{b}\right)^2 + \left(\frac{s_c}{c}\right)^2}$ (2)</td>
</tr>
<tr>
<td>Exponentiation</td>
<td>$y = a^x$</td>
<td>$\frac{s_y}{y} = x \left(\frac{s_a}{a}\right)$ (3)</td>
</tr>
<tr>
<td>Logarithm</td>
<td>$y = \log_{10} a$</td>
<td>$s_y = 0.434 \frac{s_a}{a}$ (4)</td>
</tr>
<tr>
<td>Antilogarithm</td>
<td>$y = \text{antilog}_{10} a$</td>
<td>$\frac{s_y}{y} = 2.303 \ s_a$ (5)</td>
</tr>
</tbody>
</table>
The Confidence Interval and Level.

What are they? Well:
The Confidence Interval and Level.

“The confidence interval for the mean is the range of values within which the population mean is expected to lie with a certain probability.”

“The confidence level is the probability that the true mean lies within a certain interval and is often expressed as a percentage.”

Clear?
Confidence intervals (CIs). Since the mean is involved, there are two flavors of these:

If you know \( \mu \) and can calculate \( \sigma \):

\[
\mu = \bar{x} \pm \frac{z \sigma}{\sqrt{N}}
\]

This is the confidence interval.
Confidence intervals (CIs). Since the mean is involved, there are two flavors of these too:

If you know $\mu$ and can calculate $\sigma$:

$$
\mu = \bar{x} \pm \frac{z\sigma}{\sqrt{N}}
$$

the mean you know or measured with $N > 19$.

$z$ : this specifies the probability.

- e.g., $z=1$ means 68.3%
- $z=2$ means 95.4%
- $z=3$ means 99.7%

$\sigma$ : the population st. dev.
This is a table of confidence levels.

<table>
<thead>
<tr>
<th>Confidence Level, %</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.67</td>
</tr>
<tr>
<td>68</td>
<td>1.00</td>
</tr>
<tr>
<td>80</td>
<td>1.28</td>
</tr>
<tr>
<td>90</td>
<td>1.64</td>
</tr>
<tr>
<td>95</td>
<td>1.96</td>
</tr>
<tr>
<td>95.4</td>
<td>2.00</td>
</tr>
<tr>
<td>99</td>
<td>2.58</td>
</tr>
<tr>
<td>99.7</td>
<td>3.00</td>
</tr>
<tr>
<td>99.9</td>
<td>3.29</td>
</tr>
</tbody>
</table>

We will say that z=2 is the “95% confidence level”
Confidence intervals (CIs). Since the mean is involved, there are two flavors of these too:

if you do not know $\mu$ and you’ve just got $s$:

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{N}}$$
Confidence intervals (CIs). Since the mean is involved, there are two flavors of these too:

if you do not know \( \mu \) and you’ve just got \( s \):

\[ \mu = \bar{x} \pm \frac{t s}{\sqrt{N}} \]

this is the confidence interval.

\( t \) is called the “Student T factor.”
Confidence intervals (CIs). Since the mean is involved, there are two flavors of these too:

If you do not know \( \mu \) and you've just got \( s \):

- The sample st. dev.
- "t" which is always greater than the corresponding "z".
- The mean you measured with \( N < 20 \).

\[
\mu = \bar{X} \pm \frac{ts}{\sqrt{N}}
\]

Well, ahem, \( N \).
again, taken from Skoog (8th ed).

<table>
<thead>
<tr>
<th>Degrees of Freedom</th>
<th>80%</th>
<th>90%</th>
<th>95%</th>
<th>99%</th>
<th>99.9%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.08</td>
<td>6.31</td>
<td>12.7</td>
<td>63.7</td>
<td>637</td>
</tr>
<tr>
<td>2</td>
<td>1.89</td>
<td>2.92</td>
<td>4.30</td>
<td>9.92</td>
<td>31.6</td>
</tr>
<tr>
<td>3</td>
<td>1.64</td>
<td>2.35</td>
<td>3.18</td>
<td>5.84</td>
<td>12.9</td>
</tr>
<tr>
<td>4</td>
<td>1.53</td>
<td>2.13</td>
<td>2.78</td>
<td>4.60</td>
<td>8.61</td>
</tr>
<tr>
<td>5</td>
<td>1.48</td>
<td>2.02</td>
<td>2.57</td>
<td>4.03</td>
<td>6.87</td>
</tr>
<tr>
<td>6</td>
<td>1.44</td>
<td>1.94</td>
<td>2.45</td>
<td>3.71</td>
<td>5.96</td>
</tr>
<tr>
<td>7</td>
<td>1.42</td>
<td>1.90</td>
<td>2.36</td>
<td>3.50</td>
<td>5.41</td>
</tr>
<tr>
<td>8</td>
<td>1.40</td>
<td>1.86</td>
<td>2.31</td>
<td>3.36</td>
<td>5.04</td>
</tr>
<tr>
<td>9</td>
<td>1.38</td>
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<td>3.25</td>
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</tr>
<tr>
<td>10</td>
<td>1.37</td>
<td>1.81</td>
<td>2.23</td>
<td>3.17</td>
<td>4.59</td>
</tr>
<tr>
<td>15</td>
<td>1.34</td>
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<td>2.13</td>
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<tr>
<td>20</td>
<td>1.32</td>
<td>1.73</td>
<td>2.09</td>
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<tr>
<td>40</td>
<td>1.30</td>
<td>1.68</td>
<td>2.02</td>
<td>2.70</td>
<td>3.55</td>
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<tr>
<td>60</td>
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<td>2.00</td>
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you represent the confidence interval in your presentation of data as an error bar. **Every data point should have one (or two).**
you represent the confidence interval in your presentation of data as an *error bar*. **Every data point should have one (or two).**
Calculating 95% Confidence intervals (CIs).

if you do not know \( \mu \) and you’ve just got \( s \):

\[
\mu = \bar{x} \pm \frac{ts}{\sqrt{N}}
\]

I made \( N \) measurements (\( N < 20 \)).
Calculating 95% Confidence intervals (CIs).

If you do not know $\mu$ and you’ve just got $s$:  

$$
\mu = \bar{x} \pm \frac{ts}{\sqrt{N}}
$$

I made N measurements ($N < 20$).

1. calculate the mean ($x$-bar).
Calculating 95% Confidence intervals (CIs).

if you do not know \( \mu \) and you’ve just got \( s \):

\[
\mu = \bar{x} \pm \frac{ts}{\sqrt{N}}
\]

I made \( N \) measurements.
1. calculate the mean (\( \bar{x} \)-bar).
2. calculate the standard deviation (\( s \)).
Calculating 95% Confidence intervals (CIs).

if you do not know $\mu$ and you’ve just got s:

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{N}}$$

I made $N$ measurements.
1. calculate the mean ($\bar{x}$-bar).
2. calculate the standard deviation ($s$).
3. then get $t$ from the table using $N-1$ as the degrees of freedom.
again, taken from Skoog (8th ed).

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Confidence intervals (CIs) determine the number of sig figs in a result.

**example:** You calculate a mean value of 26.2345 mg/ml for a series of measurements, and a confidence interval of 0.0245 mg/ml.

**question:** What do you report?
Confidence intervals (CIs) determine the number of sig figs in a result.

**example:** You calculate a mean value of 26.2345 mg/ml for a series of measurements, and a confidence interval of 0.0245 mg/ml.

**question:** What do you report?

**answer:** 26.23 ± 0.02 mg/ml.
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**example:** You calculate a mean value of 26.2345 mg/ml for a series of measurements, and a confidence interval of 0.0245 mg/ml.

**question:** What do you report?

**answer:** 26.23 ± 0.02 mg/ml.

One nonzero digit here. always. round if necessary.
Confidence intervals (CIs) determine the number of sig figs in a result.

**example:** You calculate a mean value of 26.2345 mg/ml for a series of measurements, and a confidence interval of 0.0245 mg/ml.

**question:** What do you report?

**answer:** 26.23 ± 0.02 mg/ml.

*one* nonzero digit here. always. If you are performing additional calculations with the CI, then keep the trailing digits and use them to generate a final answer before rounding.
Confidence intervals (CIs) determine the number of sig figs in a result.

**example:** You calculate a mean value of 26.2345 mg/ml for a series of measurements, and a confidence interval of 0.0245 mg/ml.

**question:** What do you report?

**answer:** 26.23 ± 0.02 mg/ml.

↑ the last sig. fig. here...

↑ ...occupies the same decimal place as the only sig. fig. here.
answer: 26.23 ± 0.02 mg/ml.
Also ok: 26.23 (± 0.02) mg/ml.
**answer:** 26.23 ± 0.02 mg/ml.
Also ok: 26.23 (± 0.02) mg/ml.

**incorrect answers:** 26.2345 ± 0.0245 mg/ml
answer: 26.23 ± 0.02 mg/ml.
Also ok: 26.23 (± 0.02) mg/ml.

incorrect answers: 26.2345 ± 0.0245 mg/ml

1 sig fig only.
answer: 26.23 ± 0.02 mg/ml.
Also ok: 26.23 (± 0.02) mg/ml.

incorrect answers: 26.2345 ± 0.0245 mg/ml
26.2 ± 0.02 mg/ml
answer: 26.23 ± 0.02 mg/ml.
Also ok: 26.23 (± 0.02) mg/ml.

incorrect answers: 26.2345 ± 0.0245 mg/ml
26.2 ± 0.02 mg/ml

decimal place of last digit of mean does not match CI.
answer: 26.23 ± 0.02 mg/ml.
Also ok: 26.23 (± 0.02) mg/ml.

incorrect answers: 26.2345 ± 0.0245 mg/ml
26.2 ± 0.02 mg/ml
26.234 ± 0.024 mg/ml
answer: 26.23 ± 0.02 mg/ml.
Also ok: 26.23 (± 0.02) mg/ml.

incorrect answers: 26.2345 ± 0.0245 mg/ml
26.2 ± 0.02 mg/ml
26.234 ± 0.024 mg/ml

1 sig fig only.
Let’s do an example Confidence Interval Calculation
Suppose you have a new analytical method for measuring %Ni in a metal sample. You make four measurements of the nickel concentration and get the following results:

<table>
<thead>
<tr>
<th>sample</th>
<th>%Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0329</td>
</tr>
<tr>
<td>2</td>
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</tr>
<tr>
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<td>0.0330</td>
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<tr>
<td>4</td>
<td>0.0323</td>
</tr>
<tr>
<td>avg</td>
<td>0.03260</td>
</tr>
<tr>
<td>s</td>
<td>0.00041</td>
</tr>
</tbody>
</table>

What do you report as the 95% Confidence Interval?
what's the value of $t$?

$N=4$, and thus the d.o.f. = 3.

<table>
<thead>
<tr>
<th>sample</th>
<th>%Ni</th>
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<tbody>
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</tr>
<tr>
<td><strong>s</strong></td>
<td><strong>0.00041</strong></td>
</tr>
</tbody>
</table>

$$
\mu = \bar{X} \pm \frac{ts}{\sqrt{N}}
$$
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<tr>
<th>Degrees of Freedom</th>
<th>80%</th>
<th>90%</th>
<th>95%</th>
<th>99%</th>
<th>99.9%</th>
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**Solution:**

95% confidence interval:

\[
\mu = 0.03260 \pm \frac{(3.18)(0.00041)}{\sqrt{4}} = 0.03260 \pm 0.00065
\]

You will report this value as:

\[0.0326 \pm 0.0007 \text{ %Ni}\]
Other Calculations from Gaussian Statistics:

1. **Q-Test for the rejection of data points**

   \[ Q = \frac{gap}{range} \]

   Compare to the tabulated value of \( Q_{\text{crit}} \)

   reject if \( Q > Q_{\text{crit}} \)

   Used to determine whether a data point can be rejected on the basis of determinate error.
Example of a Q-test:

\[ d = x_6 - x_5 \]
\[ w = x_6 - x_1 \]
\[ Q = \frac{d}{w} \]

If \( Q > Q_{\text{crit}} \), reject \( x_6 \)
At a 95% Confidence Level, Q must be greater than 0.625 to reject the data point.
Other Calculations from Gaussian Statistics:

2. Comparison of two experimental means

\[
t = \frac{\bar{x}_i - \bar{x}_j}{s_{\text{pooled}} \sqrt{\frac{N_i + N_j}{N_i N_j}}}
\]

\[
d.o.f. = N_i + N_j - 2
\]

Compare to the tabulated value of t

Different if \( t > t_{\text{tab}} \)

\[
s_{\text{pooled}} = \sqrt{\frac{\sum_{i=1}^{N_i} (x_i - \bar{x}_i)^2 + \sum_{j=1}^{N_j} (x_j - \bar{x}_j)^2}{N_i + N_j - 2}}
\]

Used to determine whether two experimentally measured values are statistically different.