

Chapter 3 Experimental Error

Homework Due Friday January 27

Problems: 3-2, 3-5, 3-9, 3-10,
3-11, 3-12, 3-14, 3-19

Chapter 3 – Experimental Error

Uncertainties – They are everywhere!! We need to learn to understand them, manage them, and minimize them.

Significant Figures

- The minimum number of digits needed to write a given result or value without loss of accuracy.
- Each procedure, measurement, transfer, etc. has some uncertainty associated with it. Each needs to be considered in determining the overall answer.

4.3×10^4 2 sig. figs.

4.34×10^4 3 sig figs.

4.343×10^4 4 sig figs.

1200 3 sig figs.

0.0012 2 sig figs.

0.00120 3 sig figs.

0.0001200 3 sig figs.

Significant Figures

Addition and Subtraction -

Of the numbers added and/or subtracted, limited by the number with the least significant figure –

$$17.673498 + 16.3 = 33.9(73498) = 34.0$$

(when rounding, look at the digits beyond the last sig. fig.)

Very large or very small numbers (expressed in sci. notation):

$$\begin{array}{r} 7.332 \times 10^4 \\ + 5.321 \times 10^3 \\ \hline \end{array}$$

Express all numbers w/same exponent, and follow rules above.

Significant Figures

Multiplication and Division -

Of the numbers multiplied and/or divided, limited by the number with the least significant figure –

$$17.673498 \times 16.3 = 288.0(780174) =$$

(when rounding, look at the digits beyond the last sig. fig.)

Very large or very small numbers (expressed in sci. notation):

$$\begin{array}{l} 7.332 \times 10^4 \\ \underline{\times 5.321 \times 10^3} \end{array}$$

Power of 10 does not change the sig. figs. – determined by number with least sig figs.

Significant Figures

Logs and Antilogs –

Log of $x \Rightarrow x = 10^a$ means $\log x = a$

Log 4343 or $(4.343 \times 10^3) = 3.6378$

Characteristic (1 digit) \rightarrow integer (3 from the 3.6378)

mantissa (3 digits) \rightarrow decimal (6378 from the 3.6378)

The # of sig figs in $x =$ the # of sig figs in mantissa

Antilog $(4.343) = 10^{4.\underline{343}} = 22,029$ answer with too many sig figs

22,000 correct answer (3 sig figs)

also write as $\rightarrow 2.20 \times 10^4$

Types of Error

Systematic Error (determinate error) – a consistent error that can be determined and corrected. For example, if you do everything the same from trial 1 and trial 2, the error will be reproduced. Error is in one-directional (always high or always low).

Ways to determine systematic error:

- Analyze standard (known composition and concentration)
- Analyze “blank” samples
- Compare your results to results collect from different equipment or different analytical method
- Compare your results to results collect by different people and/or laboratories using similar methods

Random error (indeterminate error) – an error that arises from uncontrollable variables (or hard to control variables) in the measurement. Random error has a equal chance of making the measurement too high or too low (\pm). It is present in all measurements.

You may be able to minimize the error by:

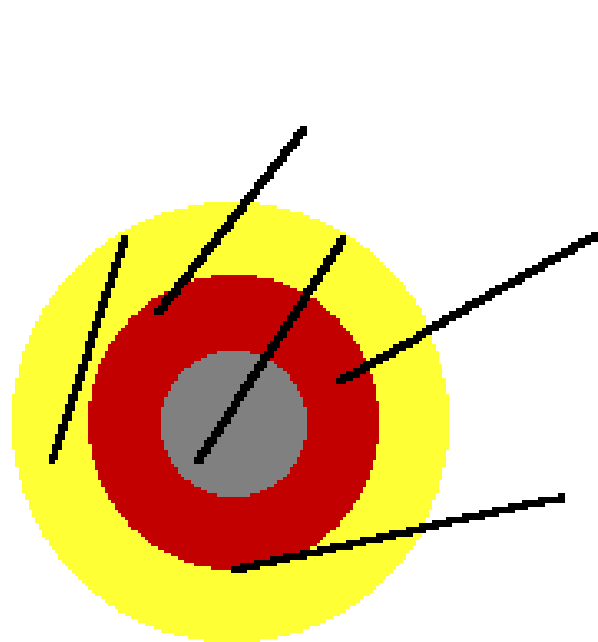
- improving your equipment (electronic noise),
- having specific procedures for reading a measurement,
- using equipment with improved precision.

Gross errors – Major mistakes by the analyst. For example, switching samples, using the wrong standards or procedures, etc.

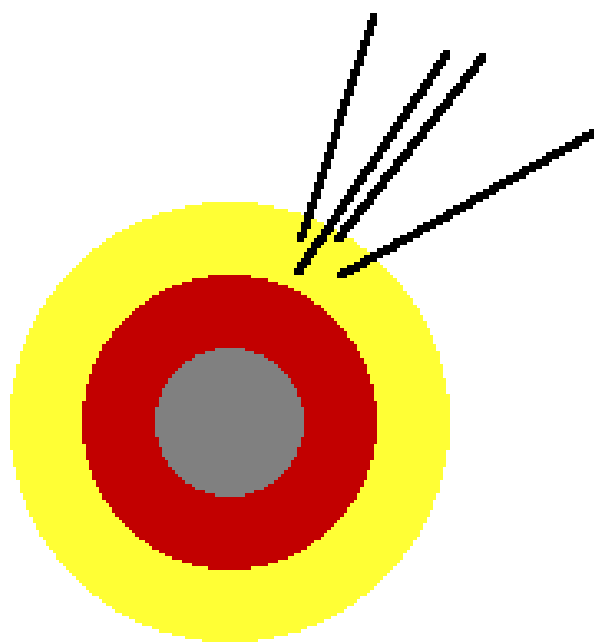
Precision and Accuracy

- **Precision:** reproducibility without regard for closeness to true value - measure via standard deviation, relative standard deviation (RSD), coefficient of variation, variance, 95% confidence interval of the mean, standard error of the mean. Essentially a measure of *dispersion or spread* of the results
- **Accuracy:** How close to the measured value is to the “true” value.
- **Bias:** Deviation of the average result from the true or accepted value - measured by relative percent deviation (RPD)

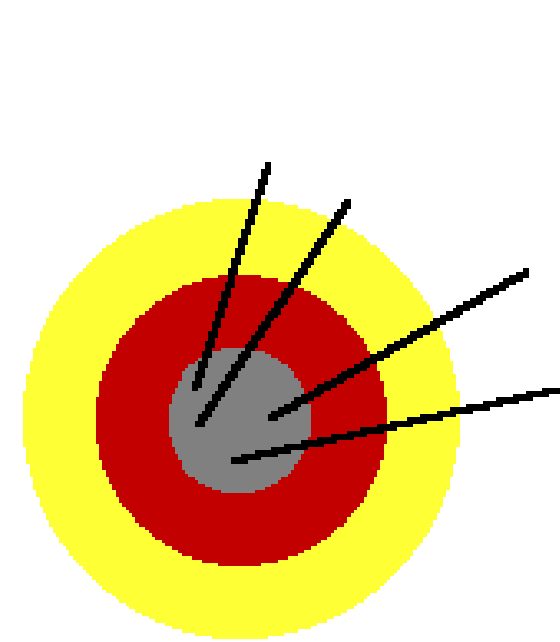
The analytical chemist goes bowhunting....



**Poor precision
but unbiased**



**Good precision
but large bias**



**Good precision
and unbiased,
therefore
accurate**

How is accuracy established ?

- While precision is easy to measure simply by replication, a measurement of accuracy involves comparing the experimental results to a “known” or “true” value



<http://ts.nist.gov/ts/htdocs/230/232/232.htm>

Uncertainty: Inexact, doubt, unsureness

Absolute uncertainty: Margin of uncertainty associated with a measurement. For example, 3.5 (± 0.01) inches. The uncertainty has the same units as the measured value.

Relative uncertainty: Compares the size of the absolute uncertainty with the size of the measured value. For example, 3.5 inches (± 0.003). The rel. uncertainty is dimensionless (no units).

Percent relative uncertainty: Relative uncertainty expressed as a percent. For example, 3.5 inches ($\pm 0.3\%$). The % rel. uncertainty is dimensionless also.

Propagation of Uncertainty – Very important!!!

You may have 10 steps in an analysis from sampling to making the final measurement. Each step has some uncertainty associated. You must be able to determine what the “total” uncertainty of the analysis is, and which steps contributed the most to the final uncertainty.

Addition and Subtraction

$$\begin{array}{r} 1.734 (\pm 0.02) \leftarrow e_1 \\ 2.837 (\pm 0.01) \leftarrow e_2 \\ + 3.278 (\pm 0.03) \leftarrow e_3 \\ \hline 7.849 (\pm e_4) \end{array}$$

Uncertainty equation (add/sub):

$$e_4 = \sqrt{e_1^2 + e_2^2 + e_3^2}$$

$$e_4 = \sqrt{(0.02)^2 + (0.01)^2 + (0.03)^2} = 0.04$$

So... answer is $7.849 (\pm 0.04)$ [absolute uncertainty]

% relative uncertainty: $(0.04 / 7.849) \times 100 = 0.05\%$

Multiplication and Division

To determine propagation of uncertainty in multiplication and division, you must convert all uncertainties to % relative uncertainties.

$$[2.34 (\pm 0.02) \times 3.33 (\pm 0.01)] / 1.27 (\pm 0.05) = 6.14 (\pm e)$$

Convert to % rel. uncert.:

$$[2.34(\pm 0.8_5\%) \times 3.33 (\pm 0.3_0\%)] / 1.27(\pm 3_9\%) = 6.14 (\pm e)$$

Determine propagated error in %:

$$\begin{aligned} \% \text{ error} &= \sqrt{0.8_5^2 + 0.3_0^2 + 3_9^2} \\ &= 4_0\% \end{aligned}$$

Convert to absolute uncertainty:

$$0.040 \times 6.14 = 0.2_4$$

Final answer: $6.14 (\pm 0.2)$

Mixed Operations (add/sub and multiply/divide):

THIS CAN BE A NIGHTMARE.

The add/sub parts are done in absolute uncertainties
and
the multiply/divide parts are done in relative uncertainties.

So...

Work the add/sub parts out first (as is the typical mathematical approach, then work the multiply/divide parts – doing the conversion from absolute uncertainties to % relative uncertainties.

Example:

$$\frac{5.67 (\pm 0.02) + 7.32 (\pm 0.04)}{2.37 (\pm 0.02)} = 5.48 (\pm e)$$

ADD FIRST:

$$\begin{aligned} 5.67 (\pm 0.02) + 7.32 (\pm 0.04) &= 12.99 (\pm \sqrt{0.02^2 + 0.04^2}) \\ &= 12.99 (\pm 0.04_5) \end{aligned}$$

NEXT CONVERT TO % REL UNCERT.:

$$\frac{12.99 (\pm 0.04_5)}{2.37 (\pm 0.02)} = \frac{12.99 (\pm 0.3_5\%)}{2.37 (\pm 0.8_4\%)}$$

$$5.48 (\pm \sqrt{0.3_5^2 + 0.8_4^2}) = 5.48 (\pm 0.9_1\%) = 5.48 (\pm 0.05_0)$$

Significant Figure Helps

Retain one or more extra insignificant figures until you have finished the entire calculation, then round to the correct significant figure in at the end.

For the uncertainties, retain the first insignificant figure (at least, if not the first and second insignificant figures) to help with determining the propagation of error. Helpful to write them as subscripts. You can drop them at the end of the calculation.

Remember – rounding too early can change the answer (sometimes slightly, sometimes more. In this class, it is important to have the correct numbers, even to the last decimal place.

Propagation of errors for log, etc.

$$y = x^a \quad \% e_y = a \% e_x$$

$$y = \log x \quad e_y = \frac{1}{\ln 10} \frac{e_x}{x} \approx 0.43429(e_x/x)$$

$$y = \ln x \quad e_y = e_x/x$$

$$y = 10^x \quad e_y/y = (\ln 10) e_x \approx 2.3026 e_x$$

$$y = e^x \quad e_y / y = e_x$$

You do not need to memorize these equations, but they have some relevance to analytical chem – particularly for pH measurements.