Experimental Error: What is the "truth"?

We don't (and can't) determine the "true value" of any component in a mixture.

- All measurements have some associated error (*uncertainty*).

We can work to understand (and improve) the *precision* of a measurement.

Precision =

Comparing multiple methods increases confidence in the *accuracy* of our results.

Accuracy =

1

Representation of Analytical Data

Significant Figures: Number of digits necessary to present a result with the appropriate accuracy.

Last digit has uncertainty, at least ±1!

Results are presented to the appropriate number of significant figures, and accompanied by the error in the final digit.

Value ± Error

e.g. 102.5 ± 0.1 ppm

When rounding, look at all digits beyond the last place needed.

Always round values that are exactly halfway to the nearest ***even*** digit.

12.250 → 12.2

12.350 → 12.4

12.250001 → 12.3

2

Guidelines for Sig. Figs

1. all nonzero digits are significant,
2. all zeros that appear between nonzero digits of a number are significant,
3. all zeros at the end of a number on the right hand side of the decimal point are significant,
4. all other zeros are not significant.

Examples:

Value	# Significant Figures
14600	
0.0146	
1406	
0.010460	

3

Sig Figs in Calculations

In doing calculations, the number significant figures is limited by the least certain piece of data.

Addition/Subtraction

Multiplication/Division

Example:

How many sig. figs. should be in the answers to the following:

126.23 + 0.0147 =

58.6 x 3.1 =

4

Sig Figs in Calculations

Logarithms: *if $n = 10^a$, then $\log n = a$*

The number of sig. figs. in ***a*** should be the same as the number of sig. figs. in ***n***.

BUT, the only significant figures in ***a*** are in the mantissa (after the decimal point).

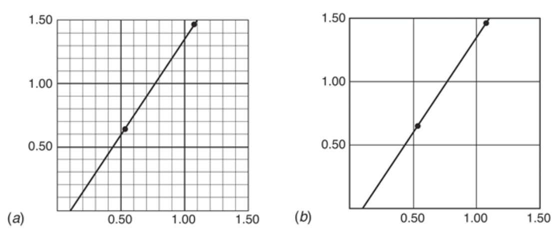
Example: What is the log of 3250? 0.01370?

5

Sig Figs in Calculations

Graphing:

- If someone is going to need to extract data from your graph, it must be set up to allow the appropriate accuracy (# sig. figs) to be read as well.



Experimentally-Determined Values:

The *real rule for sig. figs.*: The first digit that has some associated uncertainty is the last significant digit.

6

Types of Error

Systematic Error:

Detecting Systematic Error…How?

Random Error

Absolute Uncertainty

Relative Uncertainty, Percent Relative Uncertainty

Error Propagation

How do errors in individual values affect an analysis?

- Effects depend on how the data is used.

Overall uncertainty is often dominated by one component

- The “weakest link”
- If we understand the contribution of each component to uncertainty, we can predict what “reasonable” precision is for a measurement.

Error Propagation in Addition and Subtraction:

- Overall error is based on the absolute uncertainties of individual values.

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

- Example:

$$\begin{array}{rr} & 12.4 \pm 0.2 \\ & 5.7 \pm 0.1 \\ + & 1.43 \pm 0.04 \\ \hline & 19.53 \pm ??? \end{array}$$

Error Propagation

Error Propagation in Multiplication and Division

- Concept is the same as addition and subtraction, except *relative uncertainties* are used

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

  - Actually, *relative* uncertainties work fine (and may make the calculation easier).

- Let's say we have a product to consider, how do we determine the uncertainty in C (e_C)?

$$(A \pm e_A) \times (B \pm e_B) = C \pm e_C$$

$$\frac{e_C}{C} = \sqrt{\left(\frac{e_A}{A}\right)^2 + \left(\frac{e_B}{B}\right)^2}$$

9

Error Propagation

Example: What is the concentration of a hydrochloric acid solution made by diluting 10.4 ± 0.1 mL of concentrated HCl (12.1 ± 0.3 M) to 250.0 ± 0.24 mL?

10

Error Propagation

Logs, exponents, powers, etc. have varying rules (Table 3-1). You should know how to use the rules if you are given this table.

TABLE 3-1 Summary of rules for propagation of uncertainty

Function	Uncertainty	Function[a]	Uncertainty[b]
$y = x_1 + x_2$	$e_y = \sqrt{e_{x_1}^2 + e_{x_2}^2}$	$y = x^a$	$\%e_y = a\%e_x$
$y = x_1 - x_2$	$e_y = \sqrt{e_{x_1}^2 + e_{x_2}^2}$	$y = \log x$	$e_y = \frac{1}{\ln 10}\frac{e_x}{x} \approx 0.434\,29\,\frac{e_x}{x}$
$y = x_1 \cdot x_2$	$\%e_y = \sqrt{\%e_{x_1}^2 + \%e_{x_2}^2}$	$y = \ln x$	$e_y = \frac{e_x}{x}$
$y = \frac{x_1}{x_2}$	$\%e_y = \sqrt{\%e_{x_1}^2 + \%e_{x_2}^2}$	$y = 10^x$	$\frac{e_y}{y} = (\ln 10)e_x \approx 2.302\,6\,e_x$
		$y = e^x$	$\frac{e_y}{y} = e_x$

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

Harris, *Quantitative Chemical Analysis*, 8e