ERRORS IN CHEMICAL ANALYSIS

I. Introduction

A. It is impossible to perform a chemical analysis that is error free or without uncertainty.

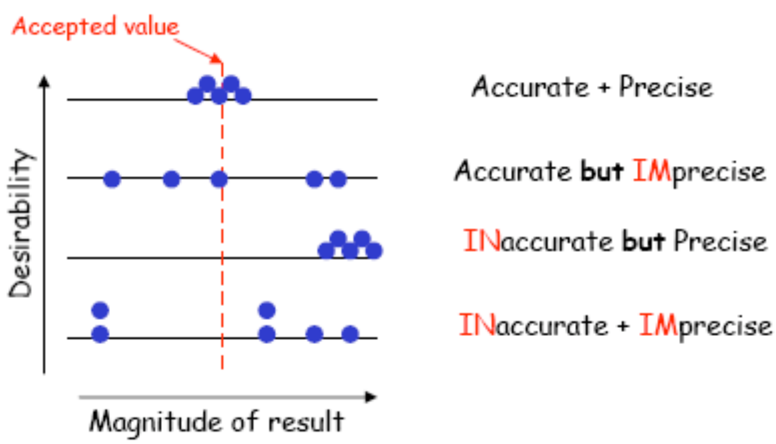
B. Our goals are to minimize errors and to calculate the size of the errors.

Errors

Systematic: glassware, instrumentation…

Random: environment, analyst…

C. Examples of errors in chemical analysis include:



Precision: reproducibility of multiple measurements

Accuracy: nearness of the measured value to the "true" value.

D. Must establish the reliability of the data (i.e., establish limits within which the true value lies with a known probability).

E. The limits and reliability must be determined by statistically valid methods.

F. We will concern ourselves with:

1. Methods of recognizing errors.
2. Techniques for estimating and reporting of errors.

II. Significant Figures

A. Must review significant figures before considering errors and error analysis.

B. Significant figures in a measurement include all certain digits plus the first uncertain digit.

1. For lined scales, estimate one digit smaller than the smallest division on the scale. For example:
   a. Graduated cylinders.
   b. Mohr pipets.

2. For electronic/digital readouts, all displayed digits are assumed significant, and the last digit is assumed to be only uncertain digit.

C. Significant figure "rules" for reporting data.

1. All non-zero digits are significant.
2. Zeros used to locate a decimal point are never significant (i.e., zeros to the left of a nonzero digit).
3. Zeros used to indicate the accuracy of the measurement are significant (i.e., zeros to the right of a nonzero digit in the presence of a decimal point).
4. Trailing zeros (not indicating accuracy) may or may not be significant.
   a. If a decimal is present, they are significant.
   b. If a decimal is not present, they are not significant.
   c. It is always best to use scientific notation.

III. Math Operations with Significant Figures

A. Addition and subtraction - the absolute error (uncertainty) of the result is equal to the largest absolute uncertainty of the quantities added/subtracted. (Simply stated: "line 'em up and cut 'em off."). For example,

1.256
0.2
9.31245
Sum = 10.96845 = 11.0

B. Rounding off convention:

3.2456 ==> 3 significant figures ==> 3.25
3.2450 ==> 3 significant figures ==> 3.24
3.2449 ==> 3 significant figures ==> 3.24
3.151 ==> 2 significant figures ==> 3.2
3.150 ==> 2 significant figures ==> 3.2
3.149 ==> 2 significant figures ==> 3.1
Note that if the number is exactly halfway between numbers (i.e., like 3.150 in the example above), the last digit to be kept is rounded up if odd and rounded down if even.

C. Multiplication/division - the usual method is that the quotient/product should have the same number of significant figures as the quantity multiplied/divided with the least number of significant figures.

1. By strict interpretation, the answer should have the same relative uncertainty as the factor with the largest relative uncertainty (i.e., the fewest significant digits). For example:
   (5,845)(98) = 572,810 (calculator)
   = 570,000 (rounded to 2 significant figures)
   = 573,000 (rounded to 3 significant figures)
   Note that 98 *almost* has three significant figures (i.e., it's nearly 100).

D. Logarithms and Antilogarithms

1. A logarithm of "A" is a number "B" whose value is such that...

   $A = 10^B$ and $\log(A) = B$ (common log or log base 10)

   $A = e^B$ and $\ln(A) = B$ (natural log)

2. We will work exclusively with common logs.

3. Logarithms are composed of a mantissa and a character. For example...

   log(523) = 2.7185017 = 2.719 (with appropriate significant figures)

   2 ==> the character

.7185017 ==> the mantissa

Note that in scientific notation,

$523 = 5.23 \times 10^{+2}$

log(5.23) = 0.7185017 ==> the mantissa

$\log(10^{+2}) = 2$ ==> the character

4. Significant figure rules for logs/antilogs:

a. In a logarithm, keep as many significant figures in the ***mantissa*** as there are in the original number.

b. In an antilogarithm, report as many significant figures as are to the right of the decimal in the original number.

c. For example,
log(1,293) = 3.1115985 = 3.1116
antilog(15.92) = $8.3176 \times 10^{+15} = 8.3 \times 10^{+15}$

E. Exact numbers have infinite significance.

1. Exact numbers usually refer to a quantity that has a discrete amount (e.g., counted items).
2. Defined numbers are exact (e.g., 1 centimeter = 10 millimeters is a defined relationship).
3. π (3.1415926535....) is considered to be an exact number.

IV. Significant Figures in Graphing

A. A graph should be as accurate as the data plotted.

1. The last certain digit in the numbers plotted should be the smallest line division on the graph.

2. The uncertain digit (the estimated digit) should correspond to the estimates between lines of the graph.

3. For example, consider a plot of two points: (0.65 g, 1.47 mL) and (0.53 g, 1.08 mL). The smallest x-axis division should be 0.1 g, and the smallest y-axis division should be 0.1 mL.

V. Elementary Statistics Relevant to Analytical Chemistry

A. Definition of Terms:

1. Mean (average):

a. Of a sample (i.e., if N, the number of measurements, is ≤ 20)...

$$\overline{X} = \frac{\sum_{i=1}^{N} X_i}{N} =$$

= (sum of all measurements)/(number of measurements)

b. Of a population (i.e., if N>20)...

μ = population mean = $\overline{X}$

2. Median = middle result when the data are arranged by size.

a. If the data is an odd numbered set, the median is the middle value.

b. If the data is an even numbered set, the median is the average of the middle two values. For example,

An odd-numbered set:
2.9
2.6
2.4
2.3
2.2
Sum = 12.4
Average = 12.4/5 = 2.5
Median = 2.4

An even-numbered set:
0.1000
0.0902
0.0886
0.0884
Sum = 0.3672
Average = 0.3672/4 = 0.0918
Median = (0.0902+0.0886)/2 = 0.0894

B. Precision - the agreement between two or more measurements performed in exactly the same way (i.e., repeatability). Mathematically precision can be determined as:

$$s = \sqrt{\frac{\sum_i (x_i - \overline{x})^2}{n-1}}$$

C. Accuracy versus precision.

1. Accuracy is the closeness of a measurement to the true (or accepted) value.

2. Accuracy is expressed by the absolute error or the relative error:

Absolute error (E) = $X_i - X_t$ where X_t is the "true" value.

Relative error (E_r) = $[(X_i - X_t)/X_t] \times 100\%$ (expressed as a percentage)

Relative error (E_r) = $[(X_i - X_t)/X_t] \times 1000$ppt (expressed as a ppt)

VI. Uncertainties in Analytical Chemistry

Absolute: expresses the margin, or range of values associated with the measurement

Relative: compares the size of the absolute uncertainty with the associated measurement

Absolute uncertainty is an expression of the uncertainty of a measurement. Usually, it is plus-or-minus the last digit = absolute uncertainty. For example,

10.20 g ==> implies that the measurement is +/- 0.01 g

Absolute uncertainty = +/- 0.01 g

Relative uncertainty = $RU = \dfrac{Absolute\ uncertainty}{Magnitude\ of\ measurements}$

If we multiply it by 100 we get percent relative uncertainty.

For example,

10.20 g ==> absolute uncertainty = +/- 0.01 g
relative uncertainty = (0.01 g)/10.20)
= 0.0009803
= 0.001

1. Relative uncertainty can be expressed as in a variety of methods:

a. % (or pph) = [(absolute uncertainty)/measurement]x100%

b. ppt = [(absolute uncertainty)/measurement]x1000ppt

c. ppm = [(absolute uncertainty)/measurement]x10^{+6}ppm
In the example above,
10.20 +/- 0.01 ==> relative uncertainty in ppt is:
ppt = [(absolute uncertainty)/measurement]x1000ppt
= [0.01/10.20]x1000ppt
= 1 ppt

d. Sample problem: A burette is used to measure 5.00 mL.

5.00 +/- 0.01 mL ==>
absolute uncertainty = 0.01
relative uncertainty(%) = [0.01/5.00]x100%
= 0.2%

e. Sample problem: Use the same burette to measure 43.82 mL.
43.82 +/- 0.01 mL ==>
absolute uncertainty = 0.01
relative uncertainty(%) = [0.01/43.82]x100%
= 0.02%

**Note that this is 10X better than for the smaller volume above!

VII. Propagation of error

Arithmetic operations (subtraction, addition, division, multiplication, etc.) with numbers are performed in analytical chemistry all the time. Each parameter, or variable, has its own uncertainty level. And therefore, their resulting uncertainty might be different from uncertainty of the single variable.

1. Addition/Subtraction

$1.76\ (\pm 0.03) + 1.89\ (\pm 0.02) - 0.059\ (\pm 0.02) = 3.06\ (\pm e_4)$

$$e_4 = \sqrt{e_1^2 + e_2^2 + e_3^2} = 0.04_1$$

2. Multiplication/Division

   First thing to do is to convert all uncertainties into relative uncertainties and the use the following formula to calculate the error:

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

Summary of all equations to calculate other functions are given in the table below:

Table 1. Summary of rules for propagation of errors (p.56 course textbook)

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