

VI. Treatment of Analytical Data

Types of Error

Systematic (Determinate) errors effect each individual measurement in the same manner and often arise from a defect in the analytical procedure or measuring instrument.

Example: Use of uncorrected temperatures that were measured with the thermometer for Cup Z in Experiment #5 would lead to a systematic error in the heats of solution.

Random (Indeterminate) error affects each individual measurement in a random manner and results from uncertainties associated with every physical measurement.

Example: Calibration of the 20 mL pipet

Run:	I	II	III
Volume (mL):	19.95	19.97	19.99

Variation in volumes results from the uncertainty in reading the position of the meniscus relative to the mark on the pipet.

Accuracy refers to the nearness of the arithmetic mean of a set of measurements to the true value.

Precision refers to the agreement of a set of measurements among themselves. The precision of a set of measurements is indicated by the deviation of the individual measurements from the arithmetic mean.

$$\text{deviation} = d_i = |x_i - \bar{x}|$$

Average Deviation

$$\bar{d} = \frac{\sum_i^N |x_i - \bar{x}|}{N}$$

where \sum is the summation over all N values, N is the number of measurements, x_i is the i^{th} measurement, $| \quad |$ is the absolute value of the quantity inside the vertical lines, and

$$\bar{x} = \text{arithmetic mean} = \frac{\sum_i^N x_i}{N} = \frac{x_1 + x_2 + \dots + x_N}{N}$$

Example: Determine the average deviation for the volumes delivered by a 20 mL pipet.

Run:	I	II	III
Volume (mL):	19.95	19.97	19.99

$$\bar{x} = \frac{\sum_i^N x_i}{N} = \frac{(19.95 + 19.97 + 19.99)mL}{3} = 19.97mL$$

$$\bar{d} = \frac{\sum_i^N |x_i - \bar{x}|}{N} = \frac{|19.95 - 19.97| + |19.97 - 19.97| + |19.99 - 19.97| mL}{3} = 0.013mL$$

$$\text{arithmetic mean} \pm \text{average deviation} \Rightarrow 19.97 \pm 0.01 mL$$

Relative Average Deviation (RAD)

$$RAD = \left[\frac{\bar{d}}{\bar{x}} \right] 1000 \quad \text{units: ppt (parts per thousand)}$$

Example: Determine the relative average deviation for the volumes delivered by a 20 mL pipet. See data in previous example.

$$RAD = \left[\frac{\bar{d}}{\bar{x}} \right] 1000 = \left[\frac{0.013mL}{19.97mL} \right] 1000 = 0.65ppt$$

Sample Standard Deviation

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

Example: Determine the standard deviation for the volumes delivered by a 20 mL pipet. See data in previous example.

$$s = \sqrt{\frac{\sum_i^N (x_i - \bar{x})^2}{N - 1}} = \sqrt{\frac{(-0.02 mL)^2 + (0.00 mL)^2 + (0.02 mL)^2}{3 - 1}} = 0.02 mL$$

$$\text{arithmetic mean} \pm \text{standard deviation} \Rightarrow 19.97 \pm 0.02 mL$$

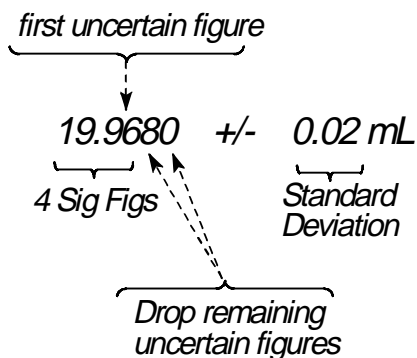
There is a 68% probability that the next volume delivered will fall in the range of 19.95 to 19.99 mL (19.97 ± 0.02 mL).

Significant Figures

Exact numbers are numbers that describe indivisible objects such as people, cars, atoms, and molecules.

Inexact numbers express the results of measurements of divisible entities. The number of digits in an inexact number should express the accuracy of the measuring instrument or the precision of a set of repetitive measurements. These digits are called *significant figures* and include all figures that are known with certainty and the first uncertain figure.

Example: Volume delivered by 20 mL pipet



$$19.97 \text{ +/- } 0.02 \text{ mL}$$

The standard deviation of 0.02 mL indicates that the fourth figure in the number 19.9680 is uncertain. All figures to the right of this figure are dropped.

A zero is significant only if it is preceded by a number other than zero.

Example:

0.00100 (3 sig figs)

100.10 (5 sig figs)

Use scientific notation to avoid confusion.

$$1.00 \cdot 10^{-3}$$

$$1.0010 \cdot 10^2$$

Rules

Addition or Subtraction: The sum or difference is rounded off at the last common figure that occurs farthest to the right in all the component numbers.

Example:

$$\begin{array}{r} 20.020 \\ 0.2 \\ 6.44 \\ \hline 26.7 \end{array}$$

Multiplication or Division: The product or quotient is rounded off in order that it contains the same number of significant figures as the component number with the smallest number

of significant figures.

Example:

$$\frac{(4.000)(50.5)}{0.2} = 1.\overline{01} \cdot 10^3 = 1 \cdot 10^3$$

Insignificant figures are indicated with an overline.

Round Off

If the number to be dropped is > 5 , then the last retained digit is increased by one.

If the number to be dropped is < 5 , then the last retained digit is left unchanged.

If the number to be dropped is 5, then the last retained digit is increased by one if odd and left unchanged if even.