**Fundamentals of Analytical Chemistry**

Chapter 6
Random Errors in Chemical Analysis

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**Random Error**
- Cannot eliminate!
- Causes are the same as systematic error.
  - Measurements ‘closer to the edge’
  - Many times a function of the analyst!
- Random error tends to be bi-directional
  - Tendency over the long term to cancel
- Gaussian Curve

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**Histogram**
- With a finite set of measurements, can plot a histogram
  - Values (or ranges of values) on x-axis
  - Frequency on y-axis

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**Population Statistics**
- Statistics from data for which *every value* is known!
  - Average age of students at Cameron University.
  - Population mean:
    \[ \mu = \frac{\sum x_i}{N} \]
  - Population standard deviation:
    \[ \sigma = \sqrt{\frac{\sum (x_i - \mu)^2}{N}} \]
Sample Statistics
- Sample mean: $\bar{x} = \frac{\sum x_i}{N}$
  - No difference in calculation from population mean
- Sample standard deviation: $s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{N-1}}$
  - Measure of precision
  - Note the denominator is equal to $N-1$
  - Loss of one degree of freedom.

Other Statistical Values
- Variance
  - Standard deviation squared
  - Can be population ($\sigma^2$) or sample ($s^2$)
- Standard error of the mean
  - Gaussian distribution based on single measurement
  - May improve reliability by multiple measurements.

Normalized Gaussian Curve
- Let $z = \frac{(x - \mu)}{\sigma}$
- "Normalized" Gaussian equation
- Gives plot with maximum at 0 and $z$ equal to one standard deviation unit

Area under the curve
- From calculus, we know that the integral of values from the Gaussian curve gives us the area under the curve
- From $-\infty$ to $\infty$, the integral of our normalized function is 1
- Defining points $\pm z$, area = 0.683
- Defining points $\pm 2z$, area = 0.954
- Defining points $\pm 3z$, area = 0.997

Gaussian curve
- This gives us the relative probability of finding points defined by our value of $z$
  - $\pm z$, 68.3%
  - $\pm 2z$, 95.4%
  - $\pm 3z$, 99.7%
- We can also determine percentage and calculate $z$
  - 90% = $\pm 1.64z$
  - 95% = $\pm 1.96z$

Loss of one degree of freedom.
- Note the denominator is equal to N
- Measure of precision
- No difference in calculation from population

Sample Statistics
- Unfortunately, in analytical chemistry we don't have the luxury of knowing all of the values
- Representative sample
  - May or may not be truly 'representative'
  - Must modify our approach to calculating statistical values.

$\bar{x} = \frac{\sum x_i}{N}$
$s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{N-1}}$
Comparing s and \( \sigma \)
- When \( N > 20 \), \( s \) is a pretty good estimator of \( \sigma \)
- Can assume that \( s \approx \sigma \)
- Series of measurements, with no individual set of measurements > 20, can calculate a ‘pooled’ standard deviation
- Assumption is deviation is a function of the method and not the operator!

Pooled Standard Deviation

\[ s_{\text{pooled}} = \sqrt{\frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2 + \ldots + (n_N - 1)s_N^2}{n_1 + n_2 + \ldots + n_N - N}} \]

Since most calculators can calculate a standard deviation, there is a ‘modified’ version of this equation that can be used

\[ s_{\text{pooled}} = \sqrt{\frac{\sum (n_i - 1)s_i^2}{N_1 + N_2 + \ldots + N_N}} \]

Other Measurements
- Relative standard deviation
  \[ s_r = \frac{s}{\bar{x}} \]
- Coefficient of Variation
  \[ s \times 100\% \]
- Other values
  - RSD in ppt (parts per thousand)
  - \( s_x \times 1000 \)

Rounding
- ‘Rounding’ is the process of mapping from an infinite set to a finite set.
  - Results of a calculation may be any value
  - Rounding insures the values reported have the correct number of digits
    - Significant Figures
  - Rounding is really picking the closest allowed value to your calculated value

Rounding
- First look – first unretained digit
  - 0-4: lesser of the allowed values
  - 5-9: greater of the allowed values
  - 5 – must investigate further
    - Non-terminal 5
      - Followed by other non-zero digits (16.01487)
      - ALWAYS the greater of the allowed values
    - Terminal 5
      - Not followed by a non-zero digit (16.0)
      - Round such that the last retained digit is even

Significant Figures
- Every measurement has three parts
  - Magnitude
  - Units
  - Error
- Significant figures are used to indicate the error in a measurement or the result of a calculation that uses measurements.
  - All known digits and the first interpolated digit
  - \( \pm 1 \) in the last decimal place
What Figures are Significant?
- All non-zero digits are significant figures (sf)
- Zero
  - Between sf – significant (5.04)
  - Right of dp and right of sf – significant (14.50)
- 5.00147
  - B/N meet both conditions – NOT significant!
  - Zeros in this case tell magnitude and not error
- 47,000,000 (?)

Logarithms
- To determine significant figures in logarithms, we have to understand that logarithms are aliens!
  - Anything before the decimal is not significant
  - Anything after the decimal is significant
    - 1.825
    - 0.052
    - 8.004
  - All have 3 significant figures!

Rules for Significant Figures in Calculations
- Multiplication and/or division
  - Round answer to match the factor with the fewest number of significant figures.
    - 14.2 + 8.41 = 22.61
    - 14.2 (tenths place), 8.41 (hundredths place)
    - Answer becomes 22.6 (rounded)
  - 5.87 * 15.1 = ?

Rules for Significant Figures in Calculations
- Addition and/or subtraction
  - Round answer to the ‘least reliable’ decimal place.
    - 14.2 + 8.41 = 22.61
    - 14.2 (tenths place), 8.41 (hundredths place)
    - Answer becomes 22.6 (rounded)
  - 5.87 + 15.1 = ?
**Special Situations (1)**

- **Mean**
  - Decimal places for the mean should match the decimal places of the measurements used to calculate the mean.

- **Standard Deviation**
  - Decimal places for the standard deviation should match the decimal places of the measurements used to calculate the standard deviation.

**Error Propagation**

- **Addition/subtraction**
  - Absolute error propagates
  - For $y = a \pm s_a + b \pm s_b - c \pm s_c$, $s_y = \sqrt{(s_a^2) + (s_b^2) + (s_c^2)}$

- **Multiplication/division**
  - Relative error propagates
  - For $y = s_y = a \times s_a / b \times s_b / c \times s_c$, $s_y/y = (s_a/a) + (s_b/b) + (s_c/c)$

- **Logarithms**
  - $s_y = \ln(10) \times s_a$

  - If you know $s_y$, you can calculate $s_a/r$ directly.
  - Rearrange equation to solve for $s_a$ if you know $s_y/r$.
  - Only error propagation that relates an absolute error to a relative error.
    - Absolute error (alien) to relative error (real).

**Significant Figures**

**Special Situations (2)**

- **Rounding results after error propagation**
  - First, round the error term ($s_y$) to one significant figure.
  - Second, round the answer ($y$) to the same number of decimal places as the error term.

**Goal is to find $s_y$!**

- For multiplication/division, must then multiply the result of the calculation by $y$
  - $y = (s_y/y) = s_y$
  - $y$ is the result of the calculation ignoring the standard deviation (error) terms.

- **Exponent**
  - For $y = a^x$, $s_y/y = (s_a/a)$
  - Error doesn’t “cancel”
  - Must then calculate $s_y$ as above.

**Error Propagation**

- **Also called standard deviation propagation**
  - What should the standard deviation (or error) be when numbers with a known standard deviation (or error) are manipulated? Important to consider:
    - Addition/subtraction
    - Multiplication/division
    - Exponents
    - Logarithms

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