Quantification
The simplest method of quantification is through the calibration of an instrument represent a signal vs. the parameter of interest (i.e. analyte concentration)

Sensitivity
- The sensitivity of an instrument or method describes the ability to discriminate between small differences in analyte concentration
- Calibration Sensitivity = the slope of a calibration curve at the concentration of interest
- The greater the slope the higher the sensitivity
**Dynamic Range or Calibration Range**

- Reported as the range in concentration from the lowest to the highest analyte concentration that can reliably be quantified
  - Low end – detection limit
  - High end – end of linear region or the highest standard used
- Multiple detectors expand range
- Limiting factors
  - Beer’s Law
  - Sample/Standard residuals (memory effect)

**Graphing Linear Relationships**

\[ y = mx + b \]

**Quantification**

The best calibrations provide a very strong “fit” between a measurement of a signal and the concentrations of standards. How do we determine the “level of fitness”?

**Correlation:**

What is the variation (“error”) around the relationship?
Correlation:

The **sample mean** is:

\[ \bar{x} = \frac{1}{n} \sum_{i=1}^{n} x_i \]

Sum of squares for variable \( x \). This statistics quantifies the spread of variable \( x \):

\[ SS_{xx} = \sum_{i=1}^{n} (x_i - \bar{x})^2 \]

Sum of squares for variable \( y \). This statistics quantifies the spread of variable \( y \):

\[ SS_{yy} = \sum_{i=1}^{n} (y_i - \bar{y})^2 \]

Correlation:

Sum of the cross-products. This statistics is analogous to the other sums of squares except that it quantifies the extent to which the two variables go together or apart:

\[ SS_{xy} = \sum_{i=1}^{n} (x_i - \bar{x})(y_i - \bar{y}) \]

Graphing Linear Relationships

Let’s assume we have a real fish population

<table>
<thead>
<tr>
<th>Weight (lb)</th>
<th>Length (in)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.18</td>
<td>13.53</td>
</tr>
<tr>
<td>1.35</td>
<td>14.5</td>
</tr>
<tr>
<td>1.71</td>
<td>13.5</td>
</tr>
<tr>
<td>1.72</td>
<td>16.03</td>
</tr>
<tr>
<td>1.99</td>
<td>16.42</td>
</tr>
<tr>
<td>2.02</td>
<td>15.83</td>
</tr>
<tr>
<td>2.58</td>
<td>15.72</td>
</tr>
<tr>
<td>4.26</td>
<td>21.1</td>
</tr>
<tr>
<td>4.5</td>
<td>21.47</td>
</tr>
<tr>
<td>7.31</td>
<td>22.96</td>
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<td>7.99</td>
<td>24.39</td>
</tr>
<tr>
<td>8.1</td>
<td>23.17</td>
</tr>
</tbody>
</table>

Should we expect any relationship between the selected parameters? If yes, which and why?
Fish Data:

Weight (lb) | Length (in) |
---|---|
1.18 | 13.53 |
1.35 | 14.5 |
1.71 | 13.5 |
1.72 | 16.03 |
1.99 | 16.42 |
2.02 | 15.83 |
2.58 | 15.72 |
4.26 | 21.1 |
4.5 | 21.47 |
7.31 | 22.96 |
7.99 | 24.39 |
8.1 | 23.17 |

SSxx: 78.5
SSyy: 182.0
SSxy: 113.8

The correlation coefficient is:

\[ r = \frac{SS_{XY}}{\sqrt{(SS_{XX})(SS_{YY})}} \]

Here \( r = 0.95 \)

The correlation coefficient is positive.

Correlation:

the correlation coefficient has no inherent value, and in the exception of strong relationships as in the case presented, \( r \) is hard to use to determine correlational strength. Another statistics is much more useful: the coefficient of determination \( (r^2) \)

\[ r^2 = 0.91 \]

This statistic quantifies the proportion of the variance of one variable that is explained by the other – Functional?
Correlation: Functional Relationships?

- **Correlation:** Here $r^2 = 0.82$

- **B) Whole data set**

**Data Table:**

<table>
<thead>
<tr>
<th>Weight (lb)</th>
<th>Length (in)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.015</td>
<td>3.16</td>
</tr>
<tr>
<td>0.05</td>
<td>6.07</td>
</tr>
<tr>
<td>0.06</td>
<td>5.72</td>
</tr>
<tr>
<td>0.07</td>
<td>6.57</td>
</tr>
<tr>
<td>0.08</td>
<td>4.32</td>
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<td>0.09</td>
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<tr>
<td>0.12</td>
<td>8.39</td>
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<tr>
<td>0.15</td>
<td>8.32</td>
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<tr>
<td>0.16</td>
<td>7.79</td>
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<tr>
<td>0.42</td>
<td>10.13</td>
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<tr>
<td>0.44</td>
<td>10.97</td>
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<tr>
<td>0.5</td>
<td>9.72</td>
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<tr>
<td>0.53</td>
<td>11.02</td>
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<tr>
<td>0.6</td>
<td>11.33</td>
</tr>
<tr>
<td>0.83</td>
<td>13</td>
</tr>
</tbody>
</table>

**Equations:**

- $y = 10.339x + 5.1588$ with $R^2 = 0.815$
- $\hat{y} = 1.4492x + 12.819$ with $R^2 = 0.9058$

Ooops, we forgot a section of the fish data set
B) Non-linear relationship

Let’s make a statement about the relationship:

- The weight is \( \propto \) to the volume

\[ W \propto V \]

Where:

\[ V = A \times L \]

\[ A = \alpha \times L^2 \]

\[ V = \alpha \times L^3 \]

\[ W = \rho \times V \]

Therefore

\[ W = \alpha \times \rho \times L^3 \]
$L = k^3 \sqrt{W} = kW^{1/3}$

Log $L = \log (k \times W^{1/3})$

$\log L = \log k + \frac{1}{3} \log W$

$y = b + mx$

**Correlation: Residuals**

Where: $\hat{y} = ax + b$

- $\hat{y}$ represents the *predicted* value of $Y$
- $a$ represents the slope of the line
- $b$ represents the intercept of the line

**B) Correlation: Linear?**

Testing the “spread” of the residuals

$\text{residuals} = (y_i - y')$
B) Correlation: Linear?
Testing the “spread” of the residuals

$\text{residuals} = (y_i - y')$

Determining the concentration of an unknown: Standard Addition

- Standard Addition: Useful method for analyzing complex sample in which matrix effect can be substantial
- Common form: Adding one or more increments of a standard solution (solid) to sample aliquots of the same size \( \Rightarrow \) "spiking" the sample.

Let $C_{\text{unk}}$ = concentrations and $V$ = volume
- “unk” = unknown; “std” = standard

\[
C_{\text{unk}} = \frac{C_{\text{unk}}V_{\text{unk}} + C_{\text{std}}V_{\text{std}}}{V_{\text{tot}}} = \frac{C_{\text{unk}}V_{\text{unk}}}{V_{\text{tot}}} + \frac{C_{\text{std}}V_{\text{std}}}{V_{\text{flask}}}
\]

Let $S$ = instrument signal and $k$ = proportionality constant

\[
S = k \frac{C_{\text{unk}}V_{\text{unk}}}{V_{\text{tot}}} + k \frac{C_{\text{std}}V_{\text{std}}}{V_{\text{tot}}}
\]
Determining the concentration of an unknown:

**Standard Addition**

- Let “S” = instrument signal and “k” = proportionality constant

\[
S = k \frac{C_{\text{std}} V_{\text{std}}}{V_{\text{tot}}} + k \frac{C_{\text{unk}} V_{\text{unk}}}{V_{\text{tot}}}
\]

\[
S = m V_{\text{std}} + b
\]

\[
m = k \frac{C_{\text{std}}}{V_{\text{tot}}} \\
b = k \frac{V_{\text{unk}} C_{\text{unk}}}{V_{\text{tot}}}
\]

**Standard Addition**

- Standard Additions can also be applied to solids:

\[
C_{\text{tot}} = \frac{\left( [C]_{\text{unk}} M_{\text{unk}} \right) + \left( [C]_{\text{tot}} M_{\text{std}} \right)}{M_{\text{unk}} + M_{\text{std}}} \\
\]

\[
[C]_{\text{unk}} = \frac{\left( [C]_{\text{tot}} \times (M_{\text{unk}} + M_{\text{std}}) \right) - \left( [C]_{\text{tot}} M_{\text{std}} \right)}{M_{\text{unk}}}
\]