Gaussian Distribution

- If the errors for a set of measurements are random, then the measurements can be represented by a Gaussian distribution
- Two quantities are used to describe a Gaussian curve
  - The *Mean*—the arithmetic average of all measurements
  - The *Standard Deviation*—a measure of the spread in the measurements

Gaussian Distribution

- Mean:

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

n = total number of measurements

- Standard deviation

$$s = \sqrt{\frac{1}{(n-1)}\sum_{i=1}^{n}(x_i - \bar{x})^2}$$

the factor n-1 in the denominator is called the degrees of freedom

Gaussian Distribution

Measurement	Value	Measurement	Value
1	0.3410	9	0.3430
2	0.3350	10	0.3420
3	0.3470	11	0.3560
4	0.3590	12	0.3500
5	0.3530	13	0.3630
6	0.3460	14	0.3530
7	0.3470	15	0.3480
8	0.3460		

x = .3486

s = $.0073_1$

Gaussian Distribution

- For a small, finite number of measurements, the mean and standard deviation are only approximations of the "true" mean (μ) and standard deviation of the sample (σ)
- For a large number of measurements:

$$\lim_{n\to\infty} \bar{x} = \mu$$

$$\lim_{n\to\infty} s = \sigma$$

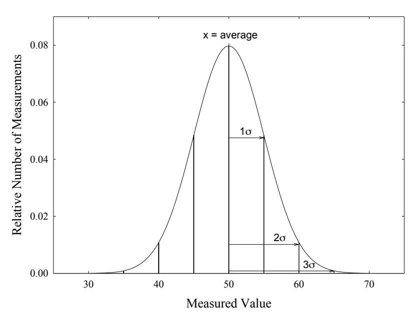
Gaussian Distribution

- The mathematical expression for a Gaussian distribution is:

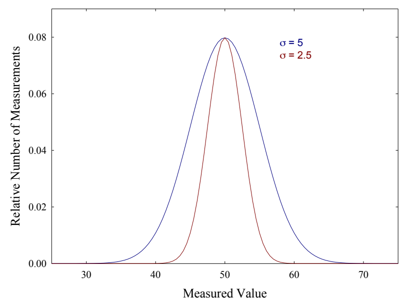
$$y = \frac{1}{\sigma\sqrt{2\pi}}\exp\left\{-\frac{(x-\mu)^2}{2\sigma^2}\right\}$$

The factor $1/\sigma(2\pi)^{1/2}$ is a normalization constant and assures that the area under the curve for the Gaussian function equal unity

Gaussian Distribution



Gaussian Distribution



Gaussian Distribution

- 68.3% of measurements fall within $\pm 1\sigma$ of the mean for a Gaussian distribution
  - If we report the error bars of a measurement as $\pm 1\sigma$, we are confident that 68% of our results will lie within $\pm 1\sigma$ of the true value
- 95.5% of measurements fall within $\pm 2\sigma$ of the mean
- 99.7% of measurements fall within $\pm 3\sigma$ of the mean

Confidence Intervals

- Reported confidence intervals can be calculated using the *student's t* values (found in Table 4-1)

  $\mu = x_{avg} \pm (t \cdot s)/n^{1/2}$

  the value of t depends on the number of degrees of freedom and the confidence level you want to report

Confidence Intervals

Values of student t at 95% confidence level

d.f.s	95% confidence
1	12.706
2	4.303
3	3.182
4	2.776
5	2.571
10	2.228
40	2.021

Confidence Intervals

Example: The following data were determined for analysis of Ca^{2+} in water:

6.34 ppm 5.87 ppm 6.12 ppm 5.71 ppm 6.48 ppm

Report average and uncertainty at 95% confidence level

$x = 6.10_4$ $s = 0.31_9$

$t = 2.776$

$t \cdot s/n^{1/2} = (2.776)(0.31_9)/5^{1/2} = 0.39_6$

$[Ca^{2+}] = 6.10_4 \pm 0.39_6$ ppm

Student t's

- Student t's can also be used to compare different measurements to see if they give the same results within experimental errors
- There are three different cases to consider:
  - Comparing measured result with "true" value
  - Comparing results from replicate measurements
  - Comparing individual differences from alternate experimental techniques

Student t's

- Comparing measured result with "true" value
- Use confidence interval expression at desired level of confidence to see if "true" value lies within prescribed range for results

$$\mu = x_{avg} \pm (t \cdot s)/n^{1/2}$$

Student t's

- Comparing results from replicate measurements

$$t_{calc} = \frac{|\bar{x}_1 - \bar{x}_2|}{s_{pooled}} \sqrt{\frac{n_1 n_2}{n_1 + n_2}}$$

$$s_{pooled} = \sqrt{\frac{\sum_{set\ 1} (x_i - \bar{x}_1)^2 + \sum_{set\ 2} (x_j - \bar{x}_2)^2}{n_1 + n_2 - 2}}$$

If $t_{calc} > t_{table}$, the two results are statistically different

Student t's

- Comparing individual differences from alternate experimental techniques

  Define d_i as the difference between results for same sample by different experimental methods

$$s_d = \sqrt{\frac{\sum (d_i - \bar{d})^2}{n - 1}}$$

$$t_{calc} = \frac{|\bar{d}|}{s_d} \sqrt{n}$$

$|\bar{d}|$ is the absolute value of the mean differences

If $t_{calc} > t_{table}$, the results are statistically different

Exclusion of Data Points—the Q Test

- Suppose you have a series of measurements for a given sample, and one data point seems to be far outside the average range of the other data
- We use the Q test to see if that point can be excluded from the calculation of the mean and standard deviation
  - Calculated range between extremes of data—highest data value minus lowest data value
  - Calculate gap between suspect data and nearest neighbor

Exclusion of Data Points—the Q Test

- We need two quantities to determine whether a data can be excluded from the results:
  - Calculated range between extremes of data—highest data value minus lowest data value

    $\text{range} \equiv x_{max} - x_{min}$
  - Calculate gap between suspect data and nearest neighbor

    $\text{gap} \equiv x_i - x_j$

    where x_i is the data point of interest, and x_j is the nearest data point

Exclusion of Data Points—the Q Test

- Q is defined as ratio of data gap to data range

$$Q_{calc} = \frac{\text{gap}}{\text{range}}$$

- If $Q_{calc} > Q_{table}$, the point may be excluded

Q (90%)	n
0.765	4
0.642	5
0.560	6
0.507	7
0.468	8
0.437	9

Exclusion of Data Points—the Q Test

Example: The following data were measured for analysis of X in a sample:

5.678 5.589 5.431 4.998 5.486

Decide if the point, 4.998, can be discarded:

range = 5.678 – 4.998 = 0.680

gap = 5.431 – 4.998 = 0.433

Q_{calc} = 0.433/0.680 = 0.637

Q_{table} = 0.642

$Q_{calc} < Q_{table} \Rightarrow$ value may not be discarded

Exclusion of Data Points—the Q Test

Example: The following data were measured for analysis of X in a sample:

Result including low value:

x = 5.436 ± 0.326 (95% confidence level)

Result excluding low value:

x = 5.546 ± 0.175 (95% confidence level)

Excluding low point gives much tighter uncertainty, but it is not justified in this case.