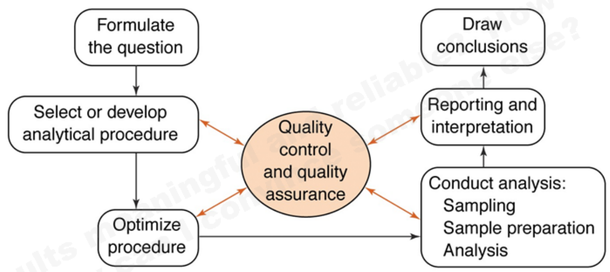
Statistics and Chemical Measurements: Quantifying Uncertainty

The bottom line: ***Do we trust our results?***
Should we (or anyone else)? Why?



What is Quality Assurance?

What is Quality Control?

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Normal or Gaussian Distribution – The “Bell Curve”

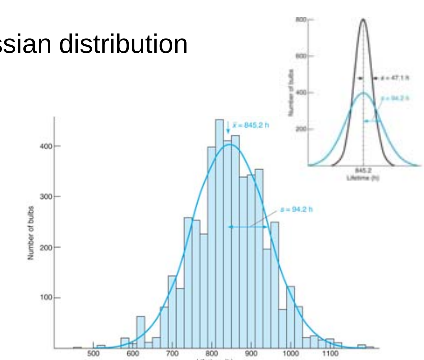
IF only *random errors* are present, data will follow a Gaussian Distribution

This distribution is described by: $$y = \frac{1}{\sigma\sqrt{2\pi}} e^{-(x-\mu)^2/2\sigma^2}$$

Two important parameters for a Gaussian distribution

μ: population *mean* or average
The mean defines

σ: population *standard deviation*
The standard deviation defines



Harris, *Quantitative Chemical Analysis*, 8e
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Normal or Gaussian Distribution – The "Bell Curve"

- Experimental determination of μ and σ is unrealistic, because they are based on an infinite data set.
- SO, a more realistic goal is to calculate an arithmetic mean:

$$\bar{x} = \frac{\sum_i x_i}{n}$$, where *n* is the number of samples.

- It is also more realistic to calculate a sample standard deviation:

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

Why "n-1"?
Remember e^2?
Know how to calculate s on your calculator!

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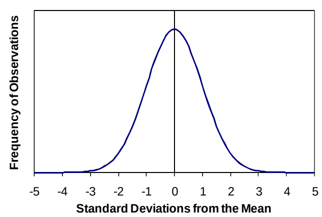
Relating Standard Deviation, Gaussian Distribution and Probability

For ANY Gaussian curve ("normal distribution", random errors):

- 68.3% of measurements are within ± 1 std. dev.
- 95.5% of measurements are within ± 2 std. dev.
- 99.7% of measurements are within ± 3 std. dev.



We can predict the odds of finding a value within a specific range. It all boils down to area under the curve!

1. Pick a range on the x-axis of the curve
2. Integrate the area under this range (Table 4-1)
3. This area is the probability of observing a value somewhere in this range.

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Relating Standard Deviation, Gaussian Distribution and Probability

For example:

50% of the values should be > the mean, and 49.8650% should be between the mean and +3s.

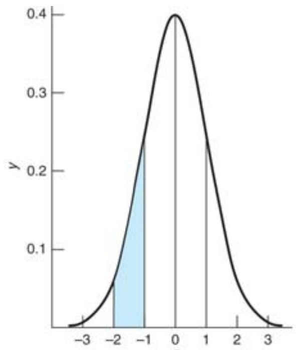
Since 34.13% of the observations fall between the mean and +1s, and 47.73% fall between the mean and +2s, what fraction falls between +1s and +2s?

TABLE 4–1 Ordinate and area for the normal (Gaussian) error curve, $y = \frac{1}{\sqrt{2\pi}} e^{-z^2/2}$

$\lvert z \rvert$[a]	y	Area[b]	$\lvert z \rvert$	y	Area	$\lvert z \rvert$	y	Area
0.0	0.398 9	0.000 0	1.4	0.149 7	0.419 2	2.8	0.007 9	0.497 4
0.1	0.397 0	0.039 8	1.5	0.129 5	0.433 2	2.9	0.006 0	0.498 1
0.2	0.391 0	0.079 3	1.6	0.110 9	0.445 2	3.0	0.004 4	0.498 650
0.3	0.381 4	0.117 9	1.7	0.094 1	0.455 4	3.1	0.003 3	0.499 032
0.4	0.368 3	0.155 4	1.8	0.079 0	0.464 1	3.2	0.002 4	0.499 313
0.5	0.352 1	0.191 5	1.9	0.065 6	0.471 3	3.3	0.001 7	0.499 517
0.6	0.333 2	0.225 8	2.0	0.054 0	0.477 3	3.4	0.001 2	0.499 663
0.7	0.312 3	0.258 0	2.1	0.044 0	0.482 1	3.5	0.000 9	0.499 767
0.8	0.289 7	0.288 1	2.2	0.035 5	0.486 1	3.6	0.000 6	0.499 841
0.9	0.266 1	0.315 9	2.3	0.028 3	0.489 3	3.7	0.000 4	0.499 904
1.0	0.242 0	0.341 3	2.4	0.022 4	0.491 8	3.8	0.000 3	0.499 928
1.1	0.217 9	0.364 3	2.5	0.017 5	0.493 8	3.9	0.000 2	0.499 952
1.2	0.194 2	0.384 9	2.6	0.013 6	0.495 3	4.0	0.000 1	0.499 968
1.3	0.171 4	0.403 2	2.7	0.010 4	0.496 5	∞	0	0.5

a. $z = (x - \mu)/\sigma$.
b. The area refers to the area between $z = 0$ and $z =$ the value in the table. Thus the area from $z = 0$ to $z = 1.4$ is 0.419 2. The area from $z = -0.7$ to $z = 0$ is the same as from $z = 0$ to $z = 0.7$. The area from $z = -0.5$ to $z = +0.3$ is (0.191 5 + 0.117 9) = 0.309 4. The total area between $z = -\infty$ and $z = +\infty$ is unity.

Harris, Quantitative Chemical Analysis, 8e



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So just how good are your data? How do you know (statistically)?

When we determine an average (with some associated error), how sure are we that the "true value" is close to this average?

- What factors influence this confidence?

The most common statistical tool for determining that the "true" value is close to our calculated mean is the **confidence interval.**

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{n}}$$

The *confidence interval* presents a range about the mean within which there is a fixed probability of finding μ.

WITH ONE KEY ASSUMPTION!

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Confidence Intervals

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{n}}$$

- Values for t are tabulated based on several confidence levels and various numbers of degrees of freedom.

	Confidence Level (%)						
Degrees of Freedom	**50**	**90**	***95***	**98**	**99**	**99.5**	**99.9**
3	0.765	2.353	*3.182*	4.541	5.841	7.453	12.924
120	0.677	1.658	*1.980*	2.358	2.617	2.860	3.373

- **NOTE:** even though the number of measurements (n) is used in the CI calculation, t is determined based on the *degrees of freedom* (n-1).
  - How can we work to minimize the range calculated at a given confidence interval?
  - How would you cut the CI in half experimentally?

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Significance Testing: Are two sets of data really "different"?

- Significance testing is built around evaluating a statement about the data, the *"Null Hypothesis"*
  - "Null Hypothesis" is generally a statement that the items being compared are statistically the same (from the same population of a given distribution).
  - The result of the significance test suggests whether the null hypothesis should be accepted (the data are not statistically different) or rejected (the data are statistically different).

Three different considerations typically encountered in lab:

1. Comparing a measured result with a "Known" or "True" value.
2. Comparing two different methods/datasets.
3. Comparing differences of multiple samples and two or more methods.

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Significance Testing: General Steps in Significance Testing

1. State the null hypothesis
2. Select the appropriate test (for the scenario and for the data distribution)
3. Choose the level of significance for the test
   - Generally base our determination of the 95% confidence interval.
     - If there is greater than 95% probability that the data are the same, we say they do not differ. Less than 95% probability indicates statistically different results.
4. Choose the number of "tails" for the test
   - Two tailed: Difference in either direction (too large or too small)
   - One tailed: Difference in only one direction (**either** too large **or** too small)
5. Calculate the test statistic
   - "t" tests compare means, "F" tests compare standard deviations
6. Compare the test statistic with the critical value for the test
   - Critical values can be found in reference tables
     - *Use correct number of degrees of freedom.*
   - Accept or reject the null hypothesis based on this comparison

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Comparing a measured result with a "Known" or "True" value.

Null hypothesis: measured value and true value are the "same"

Key question:

Does the true value fall within our confidence limits?

- Useful for comparing a result to a standard (i.e. SRM)
- Rearrange confidence limit calculation

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{n}} \longrightarrow t_{calculated} = \frac{|\text{known value} - \bar{x}|}{s}\sqrt{n}$$

- If $t_{calculated} > t_{table}$ at 95% confidence, the results are *statistically different*.
  - Typically two-tailed test
  - n – 1 degrees of freedom!

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Comparing Two Different Methods

If the results of method A ($\bar{x}_1$, s_1) are different from the results of method B ($\bar{x}_2$, s_2), is this difference significant?

- Must consider both the *means* and *standard deviations*
- *Null Hypothesis:* $\bar{x}_1 = \bar{x}_2$

- Still compare $t_{calculated}$ and t_{table}, but use new calculation

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

$$s_{pooled} = \sqrt{\frac{\sum_{\text{set A}}(x_i - \bar{x}_1)^2 + \sum_{\text{set B}}(x_j - \bar{x}_2)^2}{n_1 + n_2 - 2}} = \sqrt{\frac{s_1^2(n_1 - 1) + s_2^2(n_2 - 1)}{n_1 + n_2 - 2}}$$

- $n_1 + n_2 - 2$ = number of degrees of freedom
- If $t_{calculated} > t_{table}$ at 95% confidence, the results *are statistically different*.

This assumes σ is the "same" for both data sets. If not, the calculation changes. How do we know? **F-Test**

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F-Test for Comparing Standard Deviations

$$F_{calc} = \frac{(s_1)^2}{(s_2)^2} \qquad \text{F always} \geq 1$$

- Null hypothesis: $s_1 = s_2$
- Compare F_{calc} with $F_{table,}$ if $F_{calc} > F_{table,}$ difference is significant!

TABLE 4-4 Critical values of $F = s_1^2/s_2^2$ at 95% confidence level

Degrees of freedom for s_2	Degrees of freedom for s_1: 2	3	4	5	6	7	8	9	10	12	15	20	30	∞
2	19.0	19.2	19.2	19.3	19.3	19.4	19.4	19.4	19.4	19.4	19.4	19.4	19.5	19.5
3	9.55	9.28	9.12	9.01	8.94	8.89	8.84	8.81	8.79	8.74	8.70	8.66	8.62	8.53
4	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.91	5.86	5.80	5.75	5.63
5	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77	4.74	4.68	4.62	4.56	4.50	4.36
6	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06	4.00	3.94	3.87	3.81	3.67
7	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64	3.58	3.51	3.44	3.38	3.23
8	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35	3.28	3.22	3.15	3.08	2.93
9	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14	3.07	3.01	2.94	2.86	2.71
10	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98	2.91	2.84	2.77	2.70	2.54
11	3.98	3.59	3.36	3.20	3.10	3.01	2.95	2.90	2.85	2.79	2.72	2.65	2.57	2.40
12	3.88	3.49	3.26	3.11	3.00	2.91	2.85	2.80	2.75	2.69	2.62	2.54	2.47	2.30
13	3.81	3.41	3.18	3.02	2.92	2.83	2.77	2.71	2.67	2.60	2.53	2.46	2.38	2.21
14	3.74	3.34	3.11	2.96	2.85	2.76	2.70	2.65	2.60	2.53	2.46	2.39	2.31	2.13
15	3.68	3.29	3.06	2.90	2.79	2.71	2.64	2.59	2.54	2.48	2.40	2.33	2.25	2.07
16	3.63	3.24	3.01	2.85	2.74	2.66	2.59	2.54	2.49	2.42	2.35	2.28	2.19	2.01
17	3.59	3.20	2.96	2.81	2.70	2.61	2.55	2.49	2.45	2.38	2.31	2.23	2.15	1.96
18	3.56	3.16	2.93	2.77	2.66	2.58	2.51	2.46	2.41	2.34	2.27	2.19	2.11	1.92
19	3.52	3.13	2.90	2.74	2.63	2.54	2.48	2.42	2.38	2.31	2.23	2.16	2.07	1.88
20	3.49	3.10	2.87	2.71	2.60	2.51	2.45	2.39	2.35	2.28	2.20	2.12	2.04	1.84
30	3.32	2.92	2.69	2.53	2.42	2.33	2.27	2.21	2.16	2.09	2.01	1.93	1.84	1.62
∞	3.00	2.60	2.37	2.21	2.10	2.01	1.94	1.88	1.83	1.75	1.67	1.57	1.46	1.00

Critical values of F for a one-tailed test of the hypothesis that $s_1 > s_2$. There is a 5% probability of observing F above the tabulated value.

You can compute F for a chosen level of confidence with the Excel function FINV(probability,deg_freedom1,deg_freedom2). The statement "=FINV(0.05,7,6)" reproduces the value F = 4.21 in this table. The statement "=FINV(0.1,7,6)" gives F = 3.01 for 90% confidence.

Harris, *Quantitative Chemical Analysis*, 8e

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Comparing Differences of Multiple Samples and Two or More Methods.

- Only individual samples have been run, no replicates.
- The basis for our decision becomes the average difference between the two methods.
  - Null hypothesis: difference in the two methods is "zero"

$$t_{calculated} = \frac{\bar{d}}{s_d}\sqrt{n} \qquad s_d = \sqrt{\frac{\sum_i \left(d_i - \bar{d}\right)^2}{n-1}}$$

n = number of pairs of measurements

If $t_{calculated} > t_{table}$ at 95% confidence, the results *are statistically different*.

n – 1 degrees of freedom

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Tests for Data Validity: Testing for "outliers"

Useful when one piece of data appears to be outside a reasonable range.

- Tests for statistical probability that the outlier is a member of the same population of the consistent data
- These are statistical tests, but are still subjective and should be used carefully to avoid eliminating useful data!!!

I. Q-Test

$$Q_{calculated} = \frac{|gap|}{|range|}$$

gap is the difference b/w outlier and nearest value

range is total spread of the data.

Compare $Q_{calculated}$ with Q_{table} (typically use 90% confidence)

- If $Q_{calculated}$ is *greater* than Q_{table}, there is a statistical probability that the outlier is an invalid data point and should be discarded.
- If $Q_{calculated}$ is *less* than Q_{table}, the data point should be retained.

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Tests for Data Validity: Testing for "outliers"

II. Grubbs Test

$$G_{calculated} = \frac{|\text{suspect value} - \bar{x}|}{s}$$

Compare $G_{calculated}$ with G_{table}

- If $G_{calculated}$ is *greater* than G_{table}, there is a statistical probability that the outlier is an invalid data point and should be discarded.
- If $G_{calculated}$ is *less* than G_{table}, the data point should be retained.

TABLE 4-5 Critical values of *G* for rejection of outlier

Number of observations	*G* (95% confidence)
4	1.463
5	1.672
6	1.822
7	1.938
8	2.032
9	2.110
10	2.176
11	2.234
12	2.285
15	2.409
20	2.557

Care must be taken to avoid dismissing useful data!

Common Sense should be the guide!

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Spreadsheet Tips and Hints

Excel is great, but no amount of calculation can salvage bad data!

- When entering calculations, use parentheses at will!
  SQRT(23+A5/2) is different than SQRT((25+A5)/2)!!
- Be sure order of operations will be followed correctly
  1. Exponents
  2. Multiplication and Division (left to right)
  3. Addition and Subtraction
- Document your spreadsheet by including cell formulas for critical calculations
- Use absolute references when helpful
  - The dollar sign "locks" a row or column
  - i.e. B5 will refer to cell B5 in any calculation, but B$5 will allow the column to vary while the row stays locked at 5
- Learn common built-in functions
  - Things like SUM, STDEV, AVERAGE (version dependent)
  - Check out the Insert→Function menu in Excel
  - "Help" or right-clicking can come in handy, too!

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