Some Advanced Statistics

Confidence Intervals and the Comparison of Two Means

Confidence Intervals

For a finite number of measurements, the sample mean, $\bar{x}$ and the sample standard deviation, s, are only estimates of the true mean, μ, and standard deviation, σ. The confidence interval is a calculated range within which there is a given probability that the true mean lies. The confidence interval is calculated as follows:

Confidence interval: $$\mu(\%) = \bar{x} \pm \frac{ts}{\sqrt{n}}$$

where s is the sample standard deviation, n is the number of measurements, t is Student's t value (see attached table) and $\bar{x}$ is the sample mean. When referring to Student's t-table, the degrees of freedom (df) is n-1 for these calculations. An example calculation is below:

Five replicate samples were titrated with MnO_4^{1-} to determine the concentration of Fe^{2+}. The calculated molar concentrations for the samples are:

$[Fe^{2+}]$	0.2605	0.2610	0.2600	0.2601	0.2610

The sample mean $\bar{x}$ =0.2605 and s=0.0005.

The 50% confidence interval is calculated as follows:

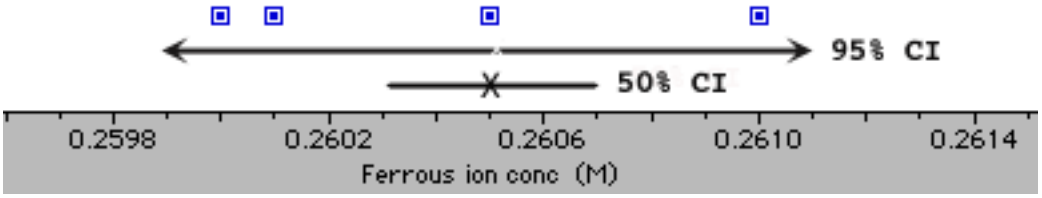
$$\mu(50\%) = 0.2605 \pm \frac{(0.741)(0.0005)}{\sqrt{5}} = 0.2605 \pm 0.0002$$

where 0.741 is the table value for the 50% level with df=4.

The 95% CI is:

$$\mu(95\%) = 0.2605 \pm \frac{(2.776)(0.0005)}{\sqrt{5}} = 0.2605 \pm 0.0006$$

The CI values mean that there is a 50% chance that the true value of $[Fe^{2+}]$ lies between 0.2603 M and 0.2607 M. In order to report a range that we are 95% certain contains the true value, the range must be enlarged to cover the interval from 0.2599 M to 0.2611 M.



In the figure, the individual values are represented by the dotted squares (remember, 0.2610 M occurs twice). The lower line (X denotes the mean) represents the range for the 50% confidence interval. In other words, there is a 50% probability that the true value for $[Fe^{2+}]$ lies within the range 0.2603 to 0.2607. To be 95% certain that the reported range contains the true mean, the interval must be enlarged to contain values from 0.2599 to 0.2611.

Comparison of Two means

Student's t values may also be used to compare two sets of measurements to determine if the measurements are the same or different. A t value is calculated as below (subscripts 1 and 2 refer to measurement sets 1 and 2).

$$t = \frac{|\overline{x_1} - \overline{x_2}|}{s_{pooled}} \sqrt{\frac{n_1 n_2}{n_1 + n_2}}$$

where

$$s_{pooled} = \sqrt{\frac{s_1^2(n_1 - 1) + s_2^2(n_2 - 1)}{n_1 + n_2 - 2}}$$

The calculated value of t is compared to the table value for n_1+n_2-2 df. If the calculated t is greater than the table t at the desired confidence level, the means are considered to be significantly different.

Here is another set of measurements of Fe^{2+} ion in aqueous solution:

$[Fe^{2+}]$	0.2609	0.2615	0.2613	0.2620	0.2618

Compare the mean of this set of measurements with those used above in the CI calculation. Can you be 50%, 95%, 99.5% and 99.9% certain that the two samples were different?