

## **Error Analysis Revisited**

Topics to Master:

- 1) Means and variances
- 2) Standard error and confidence limits
- 3) Comparison of mean values
- 4) Reporting results and significant figures
- 4) Estimation and propagation of error
  - a) general form for error propagation
  - b) addition and subtraction
  - c) multiplication and division

## 1: Means and Variances

The sample mean, or average value, for a group of measurements  $p_1, p_2, p_3, \dots$ , denoted  $\langle p \rangle$ , is defined by:

$$\langle p \rangle = \frac{\sum_i p_i}{n}$$

where  $n$  represents the number of measurements. The command for the sample mean in Excel is `AVERAGE(p1, p2, p3...)`.

The sample variance of the measurements is defined as:

$$s^2 = \frac{\sum_i (p_i - \langle p \rangle)^2}{n - 1}$$

The "-1" in the denominator can be dropped when  $n$  is large. Then the sample variance can be replaced by the population variance,  $\sigma^2$ , and the sample mean can be replaced by the population mean,  $\mu$ . The square root of the variance is called the standard deviation. The standard deviation gives an indication of the magnitude of random errors associated with the measurement. The command for the sample standard deviation,  $s$ , in Excel is `STDEV(p1, p2, p3...)`.

On occasion, the standard deviation for a set of data is artificially increased owing to the influence of one or more outlying points. We shall use the rejection quotient,  $Q$ , to determine whether an outlying point can be removed from the data set. To define  $Q$ , determine the difference between the suspected outlying point,  $p$ , and the point closest to it in the data set,  $p_{\text{close}}$ . Divide this by the range of the data,  $p - p_{\text{far}}$ , where  $p_{\text{far}}$  is the farthest point from the suspected outlying point. Then

$$Q_{\text{exp}} = \frac{p - p_{\text{close}}}{p - p_{\text{far}}}$$

If  $Q_{\text{exp}}$  is greater than the value of  $Q_{\text{crit}}$ , given in the table on the following page, the suspected point can be rejected. The table is divided into columns denoted by confidence values. A 95% confidence level means that there is a 5% chance that the rejected point is actually a "good" value and should not have been excluded. We'll talk more about confidence values in a moment. First, let's use these statistical tools in an example problem.

Critical value of the Rejection Quotient,  $Q_{\text{crit}}$ 

| # Data Points | 90% Confidence | 95% Confidence | 99% Confidence |
|---------------|----------------|----------------|----------------|
| 3             | 0.94           | 0.98           | 0.99           |
| 4             | 0.76           | 0.85           | 0.93           |
| 5             | 0.64           | 0.73           | 0.82           |
| 6             | 0.56           | 0.64           | 0.74           |
| 7             | 0.51           | 0.59           | 0.68           |
| 8             | 0.47           | 0.54           | 0.63           |
| 9             | 0.44           | 0.51           | 0.60           |
| 10            | 0.41           | 0.48           | 0.57           |

**Exercise 1:** Base your answers to the following questions on the data set given below.

Pressure measurements in mmHg.

983.5, 984.6, 982.7, 989.2, 983.6, 984.7, 983.0

- Determine the mean value for the set of measurements.
- Determine the standard deviation for the measurements.
- Determine whether any data points can be ignored among these measurements.
- If the answer to part "c" is true, recalculate parts "a" and "b". Put your answers in scientific notation with the correct number of significant figures and the appropriate units.

## 2: Standard Error and Confidence Limits

The standard deviation gives an idea of how precise a series of measurements is. Often a result is reported as  $\langle p \rangle \pm s$ , or  $2s$ . The problem with this approach is that the true standard deviation,  $\sigma$ , for the measurement cannot be determined from a limited number of measurements. To circumvent this problem, a confidence interval,  $\lambda$ , is used instead of  $\sigma$ . A result reported as  $10.2 \pm 0.4$  (95% confidence) has a 5% chance of lying outside the range 9.8 - 10.6. The boundaries of the range are called the confidence limits of the measurement. Confidence levels are often defined as  $100\%(1 - \alpha)$ . An  $\alpha = 0.05$  gives a 95% confidence level.

To define the confidence limits requires a two-step procedure. First we define the standard error of the estimate. In our case the estimate is the mean, so the standard error of the mean becomes:

$$\sigma_{<p>} = \sqrt{\frac{s^2}{n-1}}$$

The standard error of the mean is essentially the average absolute deviation from the mean. Once this value is determined it is multiplied by an appropriate t-value. Critical t-values are available in statistical reference tables. However, it's easier to use the TINV command in Excel.

**Example:** Determine the t-value at 95% confidence for 7 degrees of freedom. The term “degrees of freedom” refers to the number of independent values being considered. Since the mean already relates the measurements, only n-1 measurements can be varied for a given mean.

Use the Excel command =TINV(0.05,7) to get 2.365

The value for the confidence interval is then defined as  $\lambda = \sigma_{<p>}t_{(\alpha)}$ .

**Exercise 2:** Base your responses to the following questions on the pressure data given in exercise 1.

- a) Determine the standard error of the mean for the pressure measurements (use the data set determined in part 1c). Give appropriate units.
- b) Determine the 95% confidence interval for the same set of pressure measurements. Give appropriate units.
- c) How does your value of  $\lambda$  compare to the value of the standard deviation for the set of pressure measurements?
- d) What information does  $\lambda$  give you that the standard deviation does not?

### Exercise 3: Calibration of a Volumetric Pipet.

You have all used volumetric pipets to prepare solutions of a specific concentration. In this exercise you will determine the accuracy and precision of using this tool.

- a) Obtain approximately 200 mL of deionized water in a clean beaker and allow the temperature to stabilize.
- b) Record the temperature and refer to the water density tables found on the course's web site to find the density of water at that temperature.
- c) Tare a clean, dry 50 mL beaker.
- d) Using a 25 mL volumetric pipet, add 25 mL of the deionized water to the beaker. Record the mass and determine the volume based on the density of water.
- e) Repeat step (d) four more times.
- f) Determine the sample mean and 95% confidence interval of your volume determination. Report your result as  $\langle V \rangle \pm \lambda$ .
- g) Does 25 mL lie within the confidence limits determined in part (f)? If it doesn't, you will incur a systematic error whenever you use this pipet.
- h) Determine the relative error of your volume measurement based on the 95% confidence interval determined in part (f). Simply take  $100 \lambda / \langle V \rangle$  as the percent relative error.

### 3: Comparison of Mean Values

In this section we address the question, "are two mean values statistically different?" As an example, consider the difference between two density measurements that are reported by two investigators. We are then interested in determining whether the difference

$$\Delta\rho = \langle\rho_1\rangle - \langle\rho_2\rangle$$

is statistically different than zero. To accomplish this, we define the pooled sample variance

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

Here  $s_1^2$  and  $n_1$  refer to the sample variance and number of measurements for the mean  $\langle\rho_1\rangle$ . The standard error of  $\Delta\rho$  then becomes

$$\sigma_{\Delta\rho} = \sqrt{\frac{s_p^2}{n_1} + \frac{s_p^2}{n_2}}$$

The confidence interval,  $\lambda$ , is then defined as before (i.e.  $\lambda = \sigma_{\Delta\rho}t_{0.05}$ ). The critical t-value should be calculated at  $n_1+n_2-2$  degrees of freedom.

#### **Exercise 4: Calibration of a Volumetric Flask**

You have all used volumetric flasks to make up solutions of a specific concentration. You simply add your solute to the flask and fill it to the fiduciary mark with the solvent. The mass of solute can usually be determined to high precision. In this exercise you will determine the accuracy and precision of the volume determination.

- Using a method similar to that in Exercise 3, determine the volume of a clean 25-mL volumetric flask. Repeat the measurement for a total of 5 times.
- Determine the sample mean and 95% confidence interval of your volume determination. Report your result as  $\langle V \rangle \pm \lambda$ .
- Does 25 mL lie within the confidence limits determined in (b)? If it doesn't, a systematic error results whenever you use this flask.
- Calculate the sample variance and 95% confidence interval for the difference between the volume measured using the volumetric pipet and the volume measured using the volumetric flask.
- Using the pooled variance, determine whether the difference between the volume determined by the two techniques is significant at 95% confidence?

#### **4: Reporting Results and Significant Figures**

The calibration procedure for the volumetric glassware relied on knowing the density of water, a standard. The result of the measurement could be referenced to the manufacturer's claim that the volume was 25 mL. Most of physical chemistry, and science in general, is not about measuring known quantities. Rather, the goal of science is to measure and understand

the unknown. Now we have a problem. If you don't know the answer, how do you know you are right?

Experimental science is messy, it's not exact. It is very difficult to prove the accuracy of an experimental result. Only after the same result has been reproduced numerous times, by different researchers is it accepted as being accurate. Precision; however, is easy to report, and should be reported. As stated before, the confidence interval gives a straightforward way of stating that, "the chance that the result of this measurement is outside the specified confidence limits is 5%" (for 95% confidence). To announce the quality of the data in a succinct way requires the use of the appropriate number of significant figures. The magnitude of the confidence interval dictates the number of significant figures that should be used.

**Example:** An average result from a series of pressure measurements was 956.23768 mmHg with a confidence interval of 0.04567 mmHg. The result should be reported as 956.24 +/- 0.05 mmHg. Note, the result and the confidence interval have the same units, and both values are rounded to the same decimal place.

Although science is inherently messy, accuracy of course matters. This is particularly true when the technology is heavily regulated, like in the pharmaceutical industry. Analytical chemists devote their careers to develop instruments and methods to ensure accurate results. Physical chemists could not test their models and theories without accurate results. How do you ensure accuracy when you don't know the answer? Two steps can be followed:

- 1) establish that the laboratory technique is able to reproduce a known result before it is used on a new, related system, and
- 2) establish that the precision of the experimental result matches the expected precision of the technique. This step is affected using a propagation of error analysis.

## 5: Estimation and Propagation of Error

We generally arrive at the results of an experiment through the mathematical manipulation of the raw data, the measurements. The precision of each measurement can be determined (as was the case for the volume measurements) or estimated. Although estimating error is to some extent subjective, there are some rules of thumb that you can follow.

- 1) Look for a precision rating from the manufacturer of the equipment. (Example: A three-place digital balance is rated at  $\pm 0.001$  gram.)
- 2) Most instruments with digital readouts display the measured value with the correct number of significant figures. (e.g. A value of 5.78 should be interpreted as  $5.78 \pm 0.01$ ).
- 3) For analog scales, assume the precision is  $1/5^{\text{th}}$  the smallest graduation on the analog scale.
- 4) Assume the precision estimates correspond to standard errors,  $\sigma_{\mu}$ .

The procedure used to carry the errors in the data through a calculation is called propagation of error. Let's identify the value of a result as  $R$ . Since it is a function of several measurable quantities  $x_1, x_2, \dots$ , we can write  $R = R(x_1, x_2, \dots)$ . The error in  $R$ , identified as  $\epsilon_R$ , is obtained from the errors in the measurables as:

$$\epsilon_R^2 = \sum_j \left( \frac{\partial R}{\partial x_j} \right)^2 \epsilon_{x_j}^2$$

Here the errors,  $\epsilon_{x_j}$ , could be estimates or standard errors determined from experiment.

Addition & Subtraction: Let's first apply the general expression to the result of adding (subtracting) two measurable quantities :  $R = A + B$ .

$$\left( \frac{\partial R}{\partial A} \right)_B = 1, \quad \left( \frac{\partial R}{\partial B} \right)_A = 1$$

Therefore,  $\epsilon_R^2 = \epsilon_A^2 + \epsilon_B^2$ . **For addition and subtraction  $\epsilon_R^2 = \sum \epsilon_{x_j}^2$ .**

Multiplication and Division: Now let's apply the general expression to the result of  $R = A*B/C$ .

$$\left( \frac{\partial R}{\partial A} \right)_{B,C} = \frac{B}{C} = \frac{R}{A}, \quad \left( \frac{\partial R}{\partial B} \right)_{A,C} = \frac{R}{B}, \quad \left( \frac{\partial R}{\partial C} \right)_{A,B} = -\frac{R}{C}$$

Therefore,  $(\epsilon_R/R)^2 = (\epsilon_A/A)^2 + (\epsilon_B/B)^2 + (\epsilon_C/C)^2$ . **For multiplication and division you must add the square of the relative errors of the measurements.**

**Exercise 5:** Using the volumetric glassware that gave the better precision, determine the density of the provided “Sodium Chloride Solution”. Use five replicates to establish the 95% confidence limit for the result. If the measured volume of the chosen glassware was statistically different than 25 milliliters, use the calibrated volume not 25 mL in your calculation of density. Determine the 95% confidence interval from the five determinations. Report your result as  $\langle \rho \rangle \pm \lambda$  using the appropriate significant figures.

Using the precision of the balance and of the volumetric glassware, perform a propagation of error analysis to estimate the error of the solution density value,  $\epsilon_{\langle \rho \rangle}$ . Use the standard error of the volumetric technique for  $\epsilon_{\langle V \rangle}$ . Multiply  $\epsilon_{\langle \rho \rangle}$  by the appropriate t-value to obtain a 95% confidence interval. How does this value compare to that determined directly from the density data?