

# Treatment of Experimental Error

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### Motivation

Suppose you have been given two hair samples to analyze: one was found at the scene of a murder and the other is from a person accused of committing the murder. You are asked to analyze the two hair samples and determine if they came from the same person. You run your analysis, come up with your results and must present them in court.

1. You must take great care when you make the measurement, record the results and analyze the data.
2. You will want to repeat the measurement several times to increase its reliability.
3. You want to make certain that you are not making any avoidable errors when making the measurement. This can be done by running a known standard or by having another independent lab analyze the sample.
4. You also must determine the uncertainty in the measurement in order to report a meaningful number. You will be asked how certain you are that the two hairs are identical. Are you 95% certain? Are you 99% certain? You can never be 100% certain given the presence of error. Statistical methods of analysis are used to determine within what certainty the two hairs are identical.

You can see that knowing how good your results are is crucial in a court of law. Numbers are meaningless without the error associated with their measurement. If you were on the jury for this murder trial, you would want the laboratories that analyzed the hair samples to give you the error in the number and how to interpret the result.

**You must know the limits of error in your results to present or to make meaningful use of a result. This fact is true regardless of how the data are obtained.**

### Significant Figures

When calculating or reporting a result, you must use significant figures. Therefore you are responsible for the proper use of significant figures in all of your calculations. Below is a brief review of the rules:

1. The number of significant figures includes all certain digits and the first uncertain digit. If you

take a buret reading, you can tell the liquid level is say between 13.3 and 13.4 mL because the scale is marked by lines indicating every 0.1 mL. You must then estimate the position of the liquid between the graduations. When you do this, you might get a reading of 13.37 mL, where the first three digits are certain and the last is uncertain. You determine that the error in estimating the last digit is  $\pm 0.03$  mL. Therefore, you would report the number as  $13.37 \pm 0.03$  mL. This number contains four significant figures.

2. Disregard all initial zeros. Disregard all final zeros unless they follow a decimal point. All remaining digits, including zeros between nonzero digits, are significant.
3. When adding and subtracting, round off the result according to the number of decimal places in the number with the fewest decimal places.
4. When multiplying and dividing, round off the result so it has the same number of significant figures as the number with the fewest significant figures.
5. When taking the logarithm of a number, the number of significant figures to the right of the decimal point (i.e. in the mantissa) is the same as the number of significant figures in the original number.
6. When taking the antilogarithm, the number of significant figures in the result is the same as the number of significant figures to the right of the decimal point in the original number.

### Error

There are two types of error we must be concerned with when analyzing our laboratory results: **systematic** (or **determinate**) and **random** (or **indeterminate**) errors.

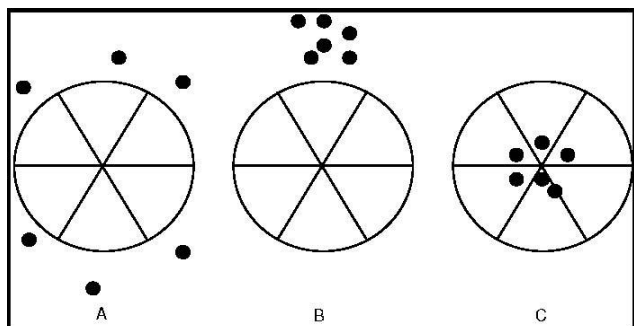
#### Systematic error

Systematic error is error that arises from a defect in an instrument or procedure and can in principle be **detected and corrected**. It is important to try to identify and correct for as many sources of systematic error as possible while making your measurements. Systematic

error is always in one direction, either higher or lower than the "true" value, thus affecting the **accuracy** (nearness of the measured value to the true value) of the measurement. These errors can be detected by using standard samples to check your method of analysis. Standards are samples that contain known amounts of the species being analyzed. You can also have someone in another laboratory independently perform the analysis to verify your results.

### Random error

Indeterminate error, often called random error, **cannot be avoided** as it is due to random fluctuations in procedures and measuring devices that are beyond your control. Because this type of error is random, it is just as likely to be too high as too low. Thus, the average of several replicate measurements will be more **precise** (how close the measured values are to each other) than any single measurement. See Figure 1 for an illustration.



**Figure1:** Target A-Accuracy, but no precision. On average, a bullseye. Target B-Precision, but no accuracy. Averaging does not help. Target C-Accurate and precise! All shots are near the bullseye.

### Determining Instrument Uncertainties

Every measurement is uncertain in that it cannot be exactly reproduced a second time. You cannot eliminate this random error, but you can estimate it. Also, making many replicate measurements and taking the average can minimize this error. Because errors fluctuate above and below the true value, results will be scattered around this central value.

As an example, if you weigh a 1990 copper penny on a balance five times, you will probably observe some variation in the last decimal place. Such a sequence of results might be 2.5227 g, 2.5227 g, 2.5226 g, 2.5227 g, and 2.5228 g. The average value is 2.5227 g, but the range of values is  $\pm 0.0001$  g from the average value. The number  $\pm 0.0001$ , the uncertainty obtained from repeated measurements, is called the absolute

uncertainty of the measurement.

Every instrument has an absolute uncertainty of measurement associated with it. For examples, Pipet See Tables 1 and 2; Buret  $\pm 0.03$  mL in any single volume reading; Mettler Balance  $\pm 0.0001$  g; 360° thermometer  $\pm \frac{1}{2}$  the difference between the smallest graduations. When you are confronted with a new instrument and need uncertainty information, it is sensible to try repeating the same measurement until some idea of the reproducibility is evident. You can also find this information for each piece of instrumentation in the specifications section of the instrument manual.

### Volumetric glassware tolerances

The National Bureau of Standards (NBS) sets the following standards for absolute error tolerable in Class A and common glassware. Any glassware labeled "Class A" must be manufactured so that the error when the glassware is properly used is no more than the tolerance set by the NBS. The tolerances for Class A and other (common) glassware are given in Tables 1 and 2.

**Table 1:** NBS Specification for Volumetric Flasks

Capacity	Tolerance Common	Tolerance Class A (TC)
10 ml	$\pm 0.04$ ml	$\pm 0.02$ ml
25 ml	$\pm 0.06$ ml	$\pm 0.03$ ml
50 ml	$\pm 0.10$ ml	$\pm 0.05$ ml
100 ml	$\pm 0.16$ ml	$\pm 0.08$ ml
200 ml	$\pm 0.20$ ml	$\pm 0.10$ ml
250 ml	$\pm 0.24$ ml	$\pm 0.12$ ml
500 ml	$\pm 0.30$ ml	$\pm 0.15$ ml
1000 ml	$\pm 0.60$ ml	$\pm 0.30$ ml

**Table 2:** NBS Specifications for Volumetric Pipets

Capacity	Tolerance Transfer = To Deliver (TD)	Tolerance Measuring
1 ml	$\pm 0.006$ ml	$\pm 0.01$ ml
2 ml	$\pm 0.006$ ml	$\pm 0.01$ ml
3 ml	$\pm 0.01$ ml	$\pm 0.01$ ml
4 ml	$\pm 0.01$ ml	$\pm 0.01$ ml
5 ml	$\pm 0.01$ ml	$\pm 0.02$ ml
10 ml	$\pm 0.02$ ml	$\pm 0.03$ ml
20 ml	$\pm 0.03$ ml	$\pm 0.03$ ml
25 ml	$\pm 0.03$ ml	$\pm 0.05$ ml