

## Error Analysis Example

Error analysis is always a difficult area for students. However, the careful consideration of experimental error is one of the important skills that we need to learn to be effective scientists. In the following discussion, the errors in a titration experiment are considered. The first section is a detailed look at how to determine the most important errors. The second section is an example of the corresponding text that would be written in a lab report for CH141-142.

### Determining the Important Errors

- The **purpose** of the error analysis section of the lab report is to determine the most important errors and the effect that those errors have on the final result.
- **Random Errors:** Random errors cause positive and negative deviations from the average value of a measurement. Random errors cancel by averaging, if the experiment is repeated many times. Upon averaging many trials, random errors have an effect only on the precision of a measurement. The effect of random errors is primarily on the precision. Every non-integer experimental measurement is a source of random error. The random error is estimated from the readability of the device. A table of typical measurements and the associated precision, under practical circumstances, is given below. For instrument readings, to avoid round-off error, report one extra significant figure and then underline the digit that is not significant.

Volumetric flasks and pipettes	precision (relative)	significant figures	
10 mL	± 0.03 mL	3	i.e. 10.0 mL
25 mL	± 0.03 mL	3	25.0 mL
50 mL	± 0.05 mL	3	50.0 mL
100 mL	± 0.08 mL	4	100.0 mL
<u>Auto-pipettors</u>			
10 µL	± 0.05 µL (0.5%)	3	i.e. 10.0 µL
100 µL	± 0.3 µL (0.3%)	3	100. µL
1000 µL	± 2 µL (0.2%)	3	1000. µL
<u>Analytical Balance</u>			
0.1000 g	± 0.0001 g	4	e.g. 0.3456 g
1.0000 g	± 0.0001 g	5	2.3456 g
10.0000 g	± 0.0001 g	6	12.3456 g
<u>Spectrophotometer (Spectro-Viz*)</u>			
0.100	± 0.003 (± 3%)	2	e.g. 0.12 <u>3</u>
0.500	± 0.003 (± 0.6%)	2	0.45 <u>6</u>
1.000	± 0.004 (± 0.4%)	3	1.12 <u>3</u>
1.500 (1 sign. fig. for A>2)	± 0.015 (± 1%)	2	1.5 <u>67</u>
<u>pH Meter</u>			
7.00	± 0.02	~3	e.g. 6.12 <u>3</u>
<u>Electronic Pressure Sensor</u>			
1.0 atm (760 torr)	± 0.0005 atm (± 0.4 torr)	3-4	e.g. 826. <u>4</u> torr
<u>Constant Current Power Supply</u>			
0.400 amp	± 0.0004 amp (± 0.1 %)	3	0.416 <u>2</u> amp

\* Spectro-Viz plus photometric accuracy is ± 13%, but standard curve calibration decreases the systematic error to approximately equal the averaged precision (about 3 sign. figures), assuming the range of A is 0.1 to 1.0.

• **Systematic Errors:** Without any changes in the procedure, systematic errors are repeated if the experiment is repeated. Systematic errors have a biased effect on the final results; systematic errors make the final result high or low, but not both. Instrument calibration errors are examples of systematic errors. Environmental effects can also be causes of systematic error, for example a change in lab temperature changing the calibration of a balance or the volume of a flask. An example of a systematic error from the  $\text{CaCO}_3$  precipitation experiment is that small particles pass through the glass frits in a Gooch crucible, making the final precipitate mass too small. Systematic errors affect the accuracy of the final results.

A given measurement can contribute to both random and systematic error. Non-integer measurements always contribute to the random error. For example, a miscalibrated balance is a source of random and systematic error. Systematic errors are often corrected by completing a determination using a different method or by comparing results among different laboratories.

• **Student Mistakes:** Student mistakes are just student mistakes; they are neither random nor systematic errors. Examples in this category are spills, misreading a device such as a burette, misinterpretation of the procedure, incorrect handling of a micro-pipettor, and forgetting to rinse out a beaker when doing a quantitative transfer. These errors are known and easily preventable, if the experiment is repeated. Systematic errors occur with each repetition of the experiment, assuming no changes in instrumentation. Mistakes should be noted in the Results section of your report as mistakes.

***Example:*** *Titration of an Unknown Acid:*

A 25.0-mL sample of an unknown acid is titrated with 15.67 mL of 0.1042 M NaOH. The volume of the acid is determined using a volumetric pipette and the burette used in the experiment has scale divisions every 0.1 mL. The standard base solution was made using an analytical balance and a 100.0-mL volumetric flask. The end point is determined by visually detecting the pink color of phenolphthalein.

***Answer:***

Random Measurement Errors: Every measurement is a source of random error. However, we must identify those errors that have a significant effect on the final result. The effects on the final result are determined using significant figure rules. The concentration of the unknown acid is:

$$M_{\text{unknown}} = V_{\text{titrant}}M_{\text{titrant}}/V_{\text{unknown}} = 0.01567 \text{ L}(0.1042 \text{ mol/L})/0.0250 \text{ L} = 0.4821 \text{ M}$$

Since only multiplications and divisions are involved, the number of significant figures in the final result is equal to the smallest number of significant figures of the terms in the calculation. We next discuss the errors associated with each term.

*Volumetric Glassware and Analytical Balance Measurements:* Large volume standard volumetric glassware typically has a precision and accuracy of four significant figures. The accuracy and precision of mass measurements on an analytical balance are also typically to four significant figures ( $\pm 0.0001$ ). The expected precision in the NaOH solution, using the analytical balance and volumetric glassware, is four significant figures. The number of significant figures in the 25.0-mL volumetric pipette is three. At best the final concentration is known to three significant figures.

*Measurements that are Interpolated between Scale Markings:* The burette readings are not as precise. To determine the volume of titrant delivered, two readings are made. Each reading is recorded to the nearest 0.01 mL. However, visually estimating the volume to better than  $\pm 0.02$

mL is difficult. Consequently the precision of the volume delivered by the burette is poorer than  $\pm 0.02$  mL, since two readings are necessary. Correspondingly in the titration example, the volume delivered by the buret at best is  $15.67 \pm 0.03$  mL, or three significant figures. Correspondingly, the final unknown concentration is officially known to three significant figures. The conclusion is that the precision is determined primarily by the random error in the burette readings and pipette. The random error in the other volume and mass determinations are not consequential.

Systematic Measurement Errors: Every measurement is a potential source of systematic error. However, with thoughtful construction of the procedure many measurements can be discounted as significant sources of systematic error. So while the calibration of the glassware and the balance used in a titration experiment are technically sources of systematic error, these errors are easily avoided. The calibration of the balances is periodically checked using a registered calibration mass. Standard volumetric glassware is certified by the manufacturer through calibration against National Institute of Standards and Technology (NIST) traceable procedures. In a titration experiment the only significant systematic errors are in the purity of the reagents and the visual determination of the end point. The purity of the reagents also includes absorption of moisture from the ambient air. So reagents that are susceptible to atmospheric moisture absorption are usually kept in low humidity desiccators. In a titration, the primary systematic error is the endpoint determination. The difference between the **equivalence point** and the measured **end point** is called the titration error. A visual end point is always slightly beyond the equivalence point because of the necessity of seeing the color change by eye. The result is that the volume of titrant delivered is too large, giving a larger final concentration than the true value. The conclusion is that the accuracy is determined primarily by systematic error in the end point.

### Example Lab Report Section on Error Analysis

The discussion, above, gives the complete thought process for determining the most important errors in the experiment. The section in the lab report that presents your conclusions is disappointingly short, by comparison. For the titration example:

The precision is dominated by the random error of the volume readings of the burette and volumetric pipette. The other volumetric glassware contribute insignificant random error. The accuracy is determined by the systematic error in the visual detection of the end point. The visual end point is at a volume larger than the equivalence point, giving a higher final result than the true concentration value.