

Measuring Density with Different Types of Glassware

Objective

In Part A of this experiment, you will measure the volume that is delivered from three pieces of laboratory glassware: a beaker, a graduated cylinder, and a volumetric pipet. In Part B, you will use the appropriate glassware to measure the density of Coke and Diet Coke. The goal is to determine the accuracy and precision for each type of glassware. The accuracy and precision for a device is determined by a method of calibration. Calibration means that the user understands the limitations inherent in a particular piece of equipment and gives a good estimate of the actual values that can be relied upon when using that equipment for measuring.

Introduction

Chemistry is an experimental science and therefore chemistry will always involve the taking of measurements. These measurements may be multiple measurements of the same object, measurements of a single object by multiple observers, or one observer's measurements of many different objects. What is the interpretation of each set of measurements? Are the measurements giving the correct answer (i.e. are they accurate)? Are they consistent (i.e. precise)? One thing scientist must keep in mind is that no matter how much care is taken when measuring; uncertainty in measurement is always present.

The rules that apply to significant figures are basically an elementary form of error analysis. For the most part, following the rules that govern significant figures are sufficient when there is a single measurement, or at most a duplicate trial. However, there may be times when we have the opportunity to carry out more exacting experiments where uncertainties in measurements can be estimated quite accurately.

Errors in Observational Data

There exists a degree of uncertainty with nearly every type of measurement. A balance that measures to the nearest gram will obviously introduce some uncertainty in the mass of objects that

weigh approximately 1.5 grams. If you try to measure the length of a board and the end of the board falls between two of the marks on your measuring tape; you would have to estimate the last fractional length. The only measurement that can be determined with certainty is counting a small set of objects, for example, the number of students in your class. However, counting large sets of objects is not an exact measurement. To determine the population of the US for example, actually counting every person is impractical and difficult to the point that estimates must be made to complete the task.

When we say that a measurement is uncertain, we mean that the measurement includes error. An **error** is the difference between a measured value and the true value. Errors are typically expressed as the uncertainty in the measurement using statistical quantities. There are two types of errors, systematic errors and random errors.

Random errors are the uncertainties associated with a measuring device; for example, an object measured for length may fall between the smallest divisions on a ruler and its value would have to be estimated. The reality is, no matter how carefully measurements are taken there is always a certain amount of “scatter” in the data. This scatter is due to the inability of an instrument or an observer of that instrument to discriminate between readings differing by less than some small amount. Random errors do not follow any regular pattern. Since random errors occur in an unpredictable manner, it is impossible to eliminate them. Fortunately, random errors can be dealt with statistically. Sometimes mistakes are made during a procedure (e.g. spilling part of a solution, dropping a piece of equipment, overfilling or underfilling a graduated cylinder, or when performing a titration you titrate each sample to a slightly different endpoint, etc.). These will all be good data points, but they will differ slightly due to random or indeterminate errors. If you average the data points, this random error is represented by the deviation of each individual measurements from the mean. These are not errors; they are *mistakes* and cannot be dealt with in any fashion, except perhaps as a learning exercise. Random errors are impossible to eliminate, but because they randomly fluctuate around the measurement the average value should reflect a good value for the measurement in the absence of systematic error.

Systematic errors (sometimes referred to as determinate error) are errors of a definite size and sign that can often be traced to specific sources introduced during the lab. Generally, such errors can be avoided or corrected. For example, this type of error may be caused by improper calibration of an instrument, uncompensated instrumental drift, leakage of material (e.g. gas in a pressure system), incomplete fulfillment of assumed conditions for a measurement (e.g. incomplete reaction in a calorimeter or incomplete drying of a weighed precipitate), personal errors in reading an instrument or a measuring device (e.g. parallax error) or, biased methods implemented during the procedure (e.g. uncompensated human reaction times). Systematic errors often announce their presence in some sort of pattern. Systematic errors must be eliminated (corrected) since there is no statistical method to handle these errors, while random errors can produce a result which is either too high or too low. When systematic errors are made, accuracy rarely matches precision. Therefore, it is important to calibrate, read instruments, etc. correctly.

Gross errors are results in a value which is far different than either the true or the mean. They may be caused by sample inconsistencies or experimental error (i.e. reading measuring instruments wrong on one trial).

Accuracy and Precision

When experimental values are discussed it is important to know the information about the quality of the data. What exactly is meant by quality? How can the size of the random and systematic

errors be determined? To answer these questions, the terms accuracy and precision need to be defined.

Accuracy is a measure of the difference between the true value and measured value. The real, true value is not always known. Absolute error is the approximate error of a single measurement:

$$\text{absolute error} = \Delta = |\text{true value} - \text{observed value}| \quad (\text{EQ 1.1})$$

Accuracy is frequently described as a percent difference or percent error between the measured value and the actual value:

$$\% \text{ error} = \frac{\text{observed value} - \text{true value}}{\text{true value}} \times 100 \% \quad (\text{EQ 1.2})$$

The difficulty with determining the error for a measured (or calculated) value is that it is often difficult or impossible to determine the true value. For measurements taken in the undergraduate laboratory, we frequently compare our results with generally accepted results published in the literature as our known or true value. In such cases the percent error is calculated.

Precision is a measure of the reproducibility of a measurement. It is a measure of the amount of random error. If we were to take many measurements, how close would they be to each other?

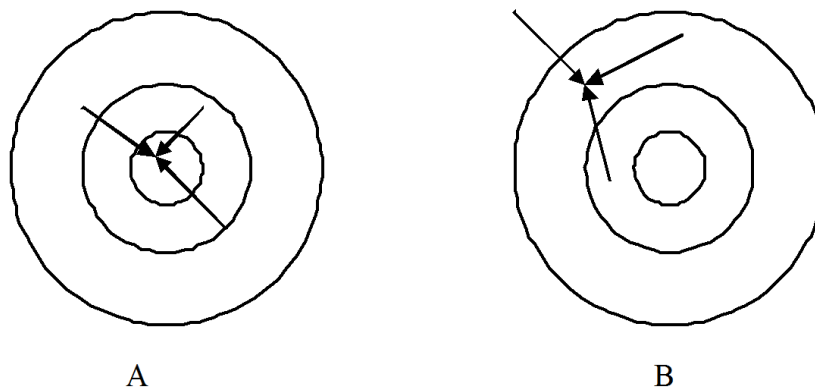
$$\text{deviation} = d = |\text{average value} - \text{observed value}| \quad (\text{EQ 1.3})$$

Precision is frequently described by the percent deviation:

$$\% \text{ deviation} = \frac{\text{observed value} - \text{average value}}{\text{average value}} \times 100 \% \quad (\text{EQ 1.4})$$

Unfortunately, precision cannot give much information regarding the accuracy of a measurement. A common illustration for these terms is a “bull’s-eye” target. Good accuracy means several arrows close to or in the middle of the target. Good precision means all the arrows are clustered in the same region of the target. Good precision does not guarantee good accuracy; all of the arrows can be grouped close together yet far from the center of the target. However, good precision often lends confidence to the experimentalist since it would appear that all measurements are consistently good in the absence of any obvious systematic errors.

FIGURE 1.1



Although, both sets of arrows represent a set of precisely thrown arrows, only picture A would be considered accurate and precise, while picture B would be considered precise, but not accurate.

How can the best possible results be obtained during an experiment?

- Perform experiments as precisely as possible to minimize random error.
- Analyze each of the measurements to identify possible sources of systematic error and minimize them.
- Determine the result using several entirely independent methods of measurements and compare. If these independent methods give the same final results it is a good indication of accuracy.

Treatment of Errors

Since a series of measurements will produce random errors, some positive and some negative values, the true value is best estimated by finding the **mean** value (\bar{x}). The mean is often called the average value and is found by summing all the values and dividing by the number of measurements:

$$\bar{x} = \frac{\sum M_n}{n} \quad \text{(EQ 1.5)}$$

where M is the individual value and n is the total number of measurements

Closely related is the **median** value which is the value that has an equal number of measurements above and below the mean. Consider this set of percent chlorine data in a sodium chloride sample. The balance is good to four significant figures and five observations were taken:

TABLE 1.1

Trial #	Observed Value for Percent Chlorine
1	60.50
2	60.41
3	60.53
4	60.54
5	60.52
Mean	60.50
Median	60.52

Some questions may come to mind: Why wasn't the same value obtained for each trial? What value should have been obtained for the percent chlorine? One way to analyze the distribution of values is to report the spread or range which is defined as the difference between the highest and lowest values.

$$\text{range} = 60.54 - 60.41 = 0.13 \quad \text{(EQ 1.6)}$$

The range is not particularly useful since it does not indicate anything about the distribution of data points about the mean value. The mean or average value is:

$$\bar{x} = \frac{60.50 + 60.41 + 60.53 + 60.54 + 60.52}{5} = \frac{302.50}{5} = 60.500 \quad \text{(EQ 1.7)}$$

The median is found to be 60.52%. The true value for the percent chlorine in sodium chloride can be calculated:

$$\%Cl = \frac{35.45 \frac{g}{mol}}{35.45 \frac{g}{mol} + 22.99 \frac{g}{mol}} \times 100 \% = 60.66\%Cl \quad (\text{EQ 1.8})$$

Therefore, the true or calculated value is 60.66%. Then the absolute error for each measurement can be determined for each trial as shown for trial 1:

$$\text{Absolute error} = |60.66\% - 60.500\%| = 0.16\% \text{ for trial 1} \quad (\text{EQ 1.9})$$

The deviation for each measurement from the average can also be determined:

$$\text{Deviation} = |60.500\% - 60.50\%| = 0.00\% \text{ for trial 1} \quad (\text{EQ 1.10})$$

Tabulating these results:

TABLE 1.2

Trial #	Observed Value for Percent Chlorine	Absolute Error	Deviation
1	60.50	0.16	0.00
2	60.41	0.25	0.09
3	60.53	0.13	0.03
4	60.54	0.12	0.04
5	60.52	0.14	0.02
Average	60.50	0.16	0.04

Using the same data set, the deviation and absolute deviation can be tabulated for each value as shown in Table 1.1 on page 4. Notice that except for rounding errors, the mean deviation is nearly zero as one would expect if the errors in measurement were randomly distributed above and below the mean. The only significant information in this example is the average of the absolute deviation or simply the **average deviation**, \bar{d} .

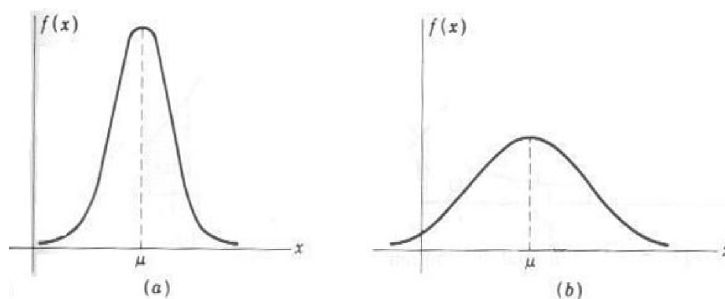
$$\bar{d} = \frac{\sum M_n - \bar{x}}{n} = \frac{0.00 + 0.09 + 0.03 + 0.04 + 0.02}{5} = 0.04 \text{ as seen in Table 1.2.} \quad (\text{EQ 1.11})$$

Notice that in this data the average deviation, a measure of the precision, is less than the average error. This indicates that there is some systematic error in the experiment resulting in inaccurate data. This example demonstrates how a student might be misled into believing their data was accurate based on good precision. Unfortunately, systematic error can not be described using any clean mathematical theories; So it is often ignored although, it is frequently found to be orders of magnitude larger than the random errors. In fact, many published papers have later been shown to be incorrect by amounts far greater than the claimed limits of error.

Given the fact that it is very difficult to identify and quantify all sources of systematic error statistical methods of analyzing random error are used as an indication of the error found in experimental data.

Although random errors cannot be corrected for, they can be treated statistically in an attempt to establish the reliability of the measurement. The analysis is based on the "normal" error curve.

FIGURE 1.2



The curve shows the relative frequency of deviation that can be expected to be found if a large number of measurements are made. The curve allows determinations about the magnitude of indeterminate errors to be made. Some of the main points of these curves are:

- The curves are symmetric about the midpoint, which is the arithmetic mean. Therefore, positive and negative deviations are equally likely.
- The curves rise to a maximum at the midpoint, indicating that small deviations occur more often than large deviations. In fact, if a large deviation is observed a systematic error is most likely involved.
- The shape of the curve is dependent on the inherent precision of the measurements. Sloppy or crude instrumentation give a high frequency of large deviations, as in curve (b). Refined measurements with improved precision show large deviations to be improbable, as in curve (a).

For reasons that will not be discussed here, the standard deviation is preferred over average deviation because it can be interpreted statistically. **Standard deviation** is the measure of the size of the random error in a set of data. The standard deviation gives information about the shape of the error curve that is associated with a set of experimental measurements. In order to measure the exact, theoretical value of the standard deviation of a measurement, the measurement must be taken many times. Therefore, the equation of standard deviation is technically only an approximation of the true standard deviation of a particular measurement. This estimation of the standard deviation, σ , is given as:

$$\sigma = \sqrt{\frac{\sum d^2}{n-1}} = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}} \quad (\text{EQ 1.12})$$

Returning to our example the standard deviation of the percent chlorine data can be determined. First the deviation squared is calculated as shown in Table 1.3 on page 6.

TABLE 1.3

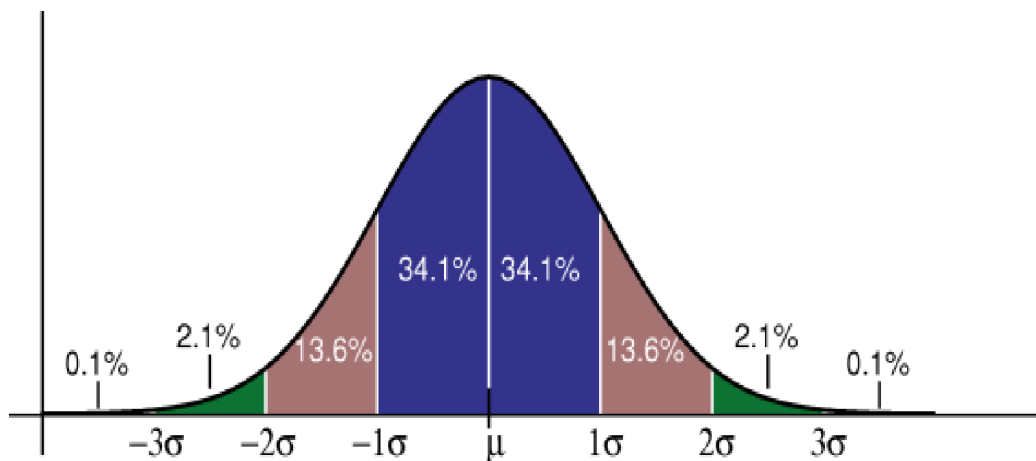
Trial #	Observed Value for Percent Chlorine	Deviation, d	d ²
1	60.50	0.00	0.00
2	60.41	0.09	0.0081
3	60.53	0.03	0.0009
4	60.54	0.04	0.0016
5	60.52	0.02	0.0004
Sum			0.011

The standard deviation is calculated to be:

$$\sigma = \sqrt{\frac{0.011}{5-1}} = 0.052 \quad (\text{EQ 1.13})$$

The standard deviation tells a lot about the error curve. A small value for sigma corresponds to a sharp, steeply rising curve, where deviations are close to zero. On the flip side, a broad, squat curve indicates that large deviations are highly probable.

FIGURE 1.3



The shaded area bound by $-\sigma$ and σ is proportional to the probability of an observation with a deviation within one unit of σ of the arithmetic mean (located at the midpoint of the curve). This shaded area represents about two-thirds of the total area, or more exactly 68.4% of the total area under the curve. This means that if a large number of measurements are made about two-thirds should fall within $\bar{x} - \sigma$ to $\bar{x} + \sigma$ or $\bar{x} \pm \sigma$ (i.e. the average plus or minus the standard deviation). So, about one-third of the trials should fall outside of these boundaries and hence, would show a larger deviation or be classified as “good”. Actually, $\pm 2\sigma$ covers most of the area under the curve or about 95%. This means that 95% of the trials fall within $\pm 2\sigma$ from the arithmetic mean, $\bar{x} - 2\sigma$ to $\bar{x} + 2\sigma$ or $\bar{x} \pm 2\sigma$. Therefore, these values would be classified as “fair.” This leaves about 5% of the measurements out of this range. In other words, about one-twentieth of the measurements will have a deviation of greater than $\pm 2\sigma$. Those falling within 3σ are classified as “poor.” Keep in mind the probability of where a measurement falls is valid when dealing with a large number of observations.

Looking at the percent chlorine data, the mean value is within a range of $60.500 \pm 0.052\%$. So, four out of five (80%) measurements are within one standard deviation 60.448% to 60.552% and all of the measurements are within two standard deviations 60.396% to 60.604% . Therefore, the measurements in this experiment have good accuracy since more than 68.4% fall within one standard deviation. Similarly, four of five measurements fall within one standard deviation of the median value. So, the measurements also have good precision.

In other words, the standard deviation indicates the distribution of values about the mean. To say this another way, the standard deviation is an indication of the precision involved with a certain set of measurements.

Procedure Part A: Glassware

For each piece of glassware, the volume will be determined by weighing the amount of DI water in each sample and then using the density to calculate the volume. For example, a beaker filled with water to the 50 mL mark contains approximately 50 mL of liquid. By weighing the beaker and its water, then subtracting the empty beaker weight, the actual mass of the water sample is known. The density of water is then used to calculate the true volume of that sample. Which piece of glassware do you expect to be the most accurate? The most precise?

Part I: Beaker Calibration

Use a 100 or 150 mL beaker that has a calibration line at the 50 mL point. Use the beaker in your drawer, not your partner's beaker. The aim is to determine the accuracy of your beaker so you know the reproducible volume of liquid that is delivered with your beaker. Check out a clean beaker from the stockroom if you do not have one that is suitable for this experiment. Wash your beaker and rinse with DI water. Do not dry the inside of your beaker. Dry the outside then follow the instructions below. Record your data in your laboratory notebook.

1. Fill the beaker to the 50 mL mark as carefully as possible. Adjust the level using an eye dropper if needed. What is the uncertainty of the beaker measurement?
2. Weigh the beaker and its contents. Do not use an analytical balance. Zero the balance first and continue to use the same balance for each measurement throughout this part of the experiment. What is the uncertainty of the balance?
3. Pour the water out of the beaker until it stops draining, then weigh the empty beaker (remember to use a glass stir rod, "glass-to-glass-to-glass" to ensure that as much of the liquid is transferred as possible). This is your tare weight. Do not dry out any remaining drops of water before it is weighed. This procedure will measure the volume of water delivered by the beaker, not the actual volume that it holds.
4. Repeat steps 1 – 3 for two more trials.
5. Determine the mass of water delivered by your beaker for each trial. This is simply done by subtracting the tare weight from the weight of the beaker plus the water.

Part II: Graduated Cylinder Calibration

Use a 10 mL graduated cylinder from your equipment drawer. Wash your glassware and rinse with DI water. As before, do not dry the inside of the cylinder; dry the outside. You will also need a plastic bottle with cap that can hold approximately 125 mL of liquid. Follow the steps below and record the data in your notebook.

1. Fill a clean 250 mL beaker with approximately 200 mL DI water. Record the temperature of the water. Use this water for the six trials that you will do in this part of the experiment.
2. Weigh the plastic bottle and its cap on an appropriate balance. The bottle should be empty but does not have to be completely dry. This is your tare weight for the plastic bottle.
3. Fill the graduated cylinder to the 10.0 mL mark. Make sure the meniscus is just even with the 10.0 mL mark. Use an eye dropper to adjust final volume if needed. What is the uncertainty of the graduated cylinder?
4. Pour the contents of the graduated cylinder into the plastic bottle ("glass-to-glass-to-glass"). Some drops of water will adhere to the inside of the cylinder which is fine. Remember, you want to determine the deliverable volume, not the actual volume. Place the cap on the plastic bottle and record the weight. What is the uncertainty of the balance?
5. Transfer another 10.0 mL of water from the graduated cylinder to the plastic bottle like you did in steps 3 and 4. Do not empty the water in the plastic bottle from the first transfer. You will add

each sample to the bottle in consecutive trials. By the end of this exercise, the bottle will be quite full.

6. Repeat steps 3, 4 and 5 until you have a total of seven measurements.
7. Add another column to the right of your data table and fill it with the mass of the water delivered in each transfer. You will need this value later when interpreting your results.

Part III: Pipet Calibration

Before the pipet can be used, it must be clean so that it drains freely (i.e wash three times with soapy water, rinse three time with tap water, rinse three times with D.I. water, and if necessary rinse three times with your solution.). After cleaning, practice with the pipet before you start the procedure. Use DI water to practice until you have mastered the skill needed to deliver an aliquot from the pipet. This exercise is similar to the procedure for the graduated cylinder except you will use the 10 mL pipet to deliver your samples into a small plastic bottle that has a 50 mL capacity. Follow the steps below and record your data in your notebook.

1. Obtain the tare weight of your plastic bottle on an appropriate balance. As before, the bottle does not have to be completely dry on the inside.
2. Fill the pipet to the 10 mL mark and deliver the contents to the plastic bottle. What is the uncertainty of the pipet?
3. Weigh the bottle plus its contents. What is the uncertainty of the balance?
4. Repeat steps 2 and 3 until you have data for four trials. Remember- don't empty the bottle between trials.

Calculations and Results



Remember to convert your masses to volumes since the beaker, graduated cylinder, and pipet are used to measure volumes and not masses.

Part I: Beaker Calibration

1. Calculate the mean and standard deviation for the mass of water contained in the beaker.
 - a. What does the standard deviation tell you about the precision of the beaker? Classify the precision as good, fair, or poor. Refer to Figure 1.3 on page 7 and the subsequent text. Remember that you will use your data to support your choice in your discussion.
2. Assuming that the density of water is 1.0 g/mL, what is the most likely volume contained in your beaker when filled to the 50 mL mark (i.e the "true value" for the volume)?
 - a. What is the percent error with respect to the volume? What does the percent error tell you about the accuracy of your measurements? Classify the accuracy as good, fair, or poor. Remember that you will use your data to support your choices in your discussion.

Part II: Graduated Cylinder

1. Calculate the mean and standard deviation for the mass of water contained in the cylinder.
2. Find the density of water at the temperature you recorded in the *Handbook of Chemistry and Physics*. Use this density to convert the mean value of the mass of water and its standard deviation to the corresponding volume.

- a. What does the standard deviation tell you about the precision of the beaker? Classify the precision as before. You will use your data to support your choices in your discussion.
3. What is the percent error? What does the percent error tell you about the accuracy of your measurements? Classify the accuracy as good, fair, or poor as you did before.

Part III: Volumetric Pipet

1. Do the same calculations as listed above for the graduated cylinder.
2. Classify the accuracy and precision of the volumetric pipet as good, fair or poor. Remember that you will use your data to support your choices in your discussion. .



NOTE: Your results and calculations section should include a table like the one below to summarize your major data.

TABLE 1.4 Analysis of Volume Instruments

Instrument	Uncertainty	Average Volume	Standard Deviation	Precision (good, fair, poor)	True Value	%error	Accuracy (good, fair, poor)
beaker							
graduated cylinder							
pipet							

Part B: Measuring the Density of Coke and Diet Coke



Remember that the instrument was calibrated previously. Use that volume in your calculations.

Objective

Determine the density of each soft drink using 10 mL samples. From your results in Part A, you need to decide which piece of glassware is the best choice for measuring the density of each. .

Procedure

The student should develop and follow a procedure similar to that used in Part A. You should do a minimum of three trials on each soda.

Results

Report the mean density and standard deviation for each soft drink. Show your calculations.

References

Masterton and Slowinski: *Elementary mathematical preparation for General Chemistry*. Saunders Publishing, 1974.

Shoemaker, Garland, and Steinfeld: *Experiments in Physical Chemistry*. McGraw-Hill, 1974.

Kratchvil, H.: *Chemical Analysis*. Barnes and Noble, 1969.

Post Lab Questions

1. What factors did you consider in choosing the particular piece of glassware for Part B of the experiment? Include comments on the accuracy and precision of your glassware choice.
2. Is the density of the two soft drinks the same, greater or less than that of water? Suggest reasons for your answer (hint- examine the contents label on the aluminum cans).
3. Compare the density of Coke with the density of Diet Coke. Are they the same or different? Explain your answer.

