

Gas Chromatographic Determination of the Composition of Expired Air and Atmospheric Air Mixtures

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ABSTRACT

Gas chromatography is a widely used analytical chemistry method for determining the composition of vaporizable mixtures, such as to determine the concentration of carbon dioxide in the air to study climate change, or to carefully measure the composition of pharmaceutical drugs. The method was used to determine the molar fractions of four major gases—carbon dioxide, CO_2 (g), oxygen, O_2 (g), nitrogen, N_2 (g), and water vapor, H_2O (g)—in samples of laboratory air and exhaled (expired) breath. In general, the standard deviations of the calculated mole fractions for different gas components were low, but the accuracy of the lab compared to literature values was variable: the percent error for some components of the analysis of atmospheric air was as high as 4900% for one component, while the maximum percent error for the exhaled breath sample was 7.6%. However, there were large potential errors, such as poor injection technique, that may have been the reason for the poor accuracy. If the gross errors could be corrected, this method could be used to better understand the composition of ambient air and of the human respiratory system.

EXPERIMENTAL METHODS

A Gow-Mac 400 gas chromatograph was used to generate traces for three different gas mixtures: a standard gas mixture (with known molar concentrations) and two solutions with an unknown composition: laboratory air and exhaled breath (of Prof. Topper). Because the area under the peak in a trace is proportional to the number of moles of the gas corresponding to the peak, the traces were used to determine the number of moles, and subsequently the mole fractions, of the component gases of the two mixtures with unknown concentration. The nitrogen, oxygen, and carbon dioxide peaks of the traces were analyzed. The traces of the unknown mixture were used to generate calibration curves of area versus calculated number of moles. These calibration curves were used to determine the number of moles of the three gases. A separate calculation was performed to estimate the amount of water vapor present in the samples, because the gas chromatograph setup could not detect it, and was factored into the final mole fraction calculation. The procedure followed was based on the procedure stated in “Gas Chromatographic Determination Of The Composition of Vapor Mixtures,” from *The Official Cooper Union General Chemistry Laboratory Guide* (1). The discussion behind the methods used are explained in more detail in the discussion section.

Rather than drawing standard gas samples from a polyurethane bag, they were obtained by injecting a syringe into a specialized pressurized container that automatically filled the syringe. Before the injection of any sample, the syringe was purged by partially filling and emptying with the gas sample. After the syringes were purged, they were filled slightly past the injection volume and emptied to the correct volume just before injection, in order to prevent contamination. The injection volumes used for the standard sample calibration curves were 3mL, 3mL, 4mL, and 5mL, and the injection volumes for the other samples were 4mL. Four samples of the standard solution were tested for the calibration curve; five samples of exhaled breath were tested; and four samples (three ordinary, and one spiked with carbon dioxide) of laboratory air were tested. The “spiked” laboratory air was an exercise not included in the official laboratory guide; it involved taking a sample of laboratory air very close to a sublimating chunk of solid carbon dioxide, giving a trace similar to that of laboratory air with a prominent peak for carbon dioxide. This provides a qualitative retention time for carbon dioxide, because a carbon dioxide peak would be otherwise unnoticeable in a trace of laboratory air.

During injection, most often the syringe was not pressed down as firmly and quickly as would be optimal. Several issues arose from this: first, occasionally the pressure of the gas from inside the injection port pushed back on the syringe and caused it to slightly refill. The speed of the injection may not have been entirely consistent, which may have caused broadening of the peaks—this gives an explanation of why there was some overlap between the peak for the initial rush of air and the peak for carbon dioxide (see Figures 1, 5, and 6), which may lead to gross

error during calculations of the area under the carbon dioxide peak. This slow injection may also have contributed to the very large initial peak

The flow rate for the first sample was slightly lower than the laboratory guide-recommended rate of 60-65mL/min, so it was increased to fit in that range. All of the following samples used the increased flow rate. This should not have any effect on the area under the peaks, but it does change the retention time of the gas. The retention time for the gases in this mixture should be ignored when used to identify gases by their respective retention times (see Table 3).

There was some random fluctuation up to 0.1mV on the readings on the standard gas traces. The source of this fluctuation was not found, but the fluctuation was not observed in the samples of mixtures of unknown composition.

For the third sample of the exhaled breath, the experimenter injecting the volume was switched. The goal was to inject the gas more quickly than the other experimenter to avoid the broadening of the peaks. However, the carbon dioxide peak for this was fairly smaller than the other peaks for the exhaled breath samples (see Table 5 and Figure 6 for the CO₂ area for sample 3).

RESULTS

The molar composition of the standard gas was identified from the standard (reference) gas sample can. The molar compositions can be found in Table 1.

Table 1. Compositions of Standard Gas

	CO ₂	CO*	CH ₄ *	O ₂	N ₂
Mole Fraction (%)	15	7	4.5	4	69.5

The laboratory and gas chromatograph conditions during the injections of the standard gas are listed in Table 2. The pressure, temperature, and relative humidity were measured with a digital sensor. The detector current was displayed on the gas chromatograph (on a digital display). The flow rate of the gas was determined with a bubble meter (see A.1.5. for calculation of flow rate).

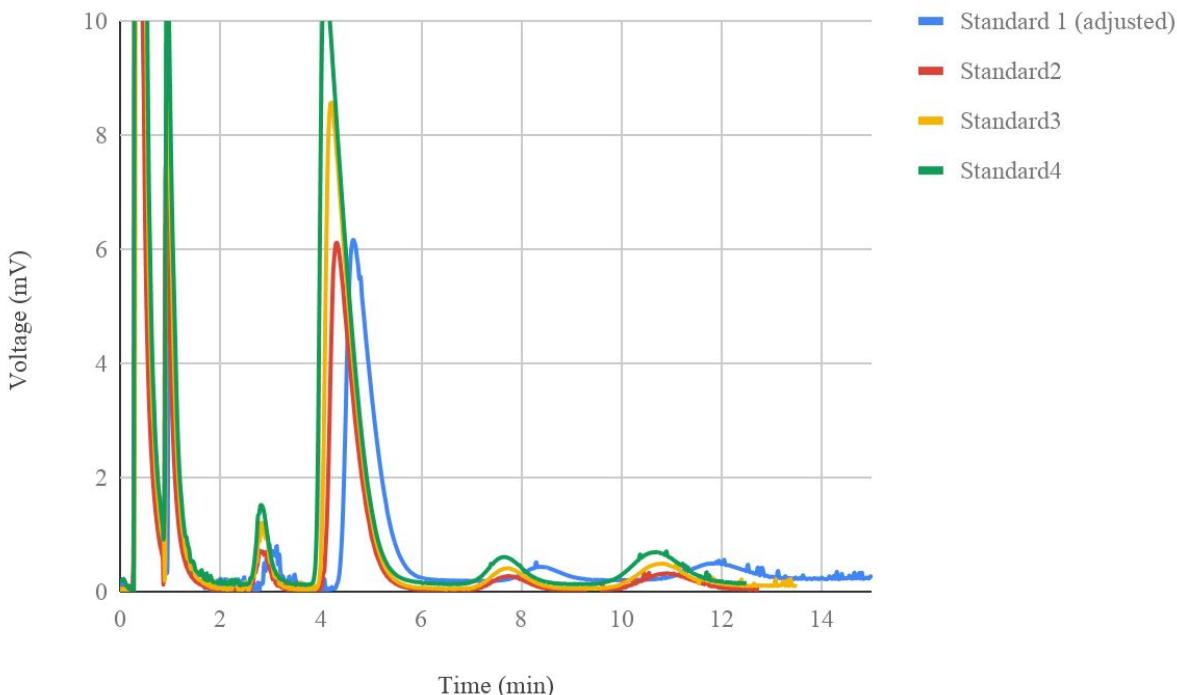
Table 2. Standard Gas Injection Conditions

	Ambient Pressure (in. Hg)	Ambient Temperature (K)	He Flow Rate (mL/min)	Detector Current (mA)	Relative Humidity (%)
Sample 1 (3mL)	29.88	297.65	57.6*	100.	29
Sample 2 (3mL)	29.88	297.65	60.6	100.	29
Sample 3 (4mL)	29.88	297.65	60.6	100.	29
Sample 4 (5mL)	29.88	298.15	60.6	100.	29

Traces of the standard samples can be found in Figure 1. Note that there are peaks for carbon monoxide and methane, but these are not analyzed in this experiment (this experiment focuses on carbon dioxide, oxygen, and nitrogen gases, as well as calculations for the amount of water vapor). The graph of the trace shows expected results, with consistent peaks throughout each sample: the first peak is the rush of air from the injection; the second peak is carbon dioxide; the third peak is oxygen; the fourth peak is nitrogen; and the last two peaks are carbon monoxide and methane. The peak of the 5mL injection is higher than the peaks for the 4mL injection, which are in turn higher than the peaks for the 3mL injections, as expected.

Except for sample 1, the peaks all roughly line up. (Sample 1 had a slightly slower flow rate; see experimental methods). However, because the identity of the gases is still apparent from the trace, its data is still used in the calibration curves.

Figure 1. Standard Gas Samples Trace



To generate a calibration curve, two pieces of data about each component gas were calculated: the area under the peak of the component gas, and the number of moles of the component gas. The area under the peaks of standard gas may be determined using the trapezoidal rule (calculation outlined in A.1.2). The moles of each component gas were calculated using the mole fraction of the gas in the standard gas mixture and the ideal gas law (see calculation in A.1.3).

The retention time of each component is calculated by subtracting the time of the start of the initial rush of air from the time of the start of the component's peak. See A.1.5. for the corresponding equation.

A summary of the areas, moles, and retention times of each peak for each standard gas sample are summarized in Table 3.

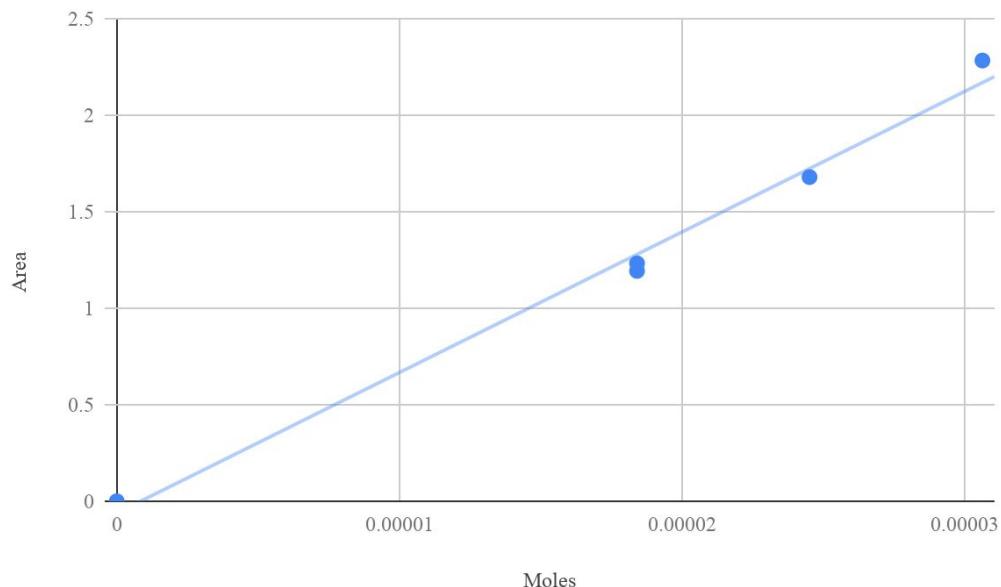
Table 3. Areas and Calculated Molar Compositions of Standard Gas Injection Samples

	CO ₂	O ₂	N ₂	Total
Sample 1 (3mL)				
Moles	0.0000184	0.00000491	0.0000853	0.000123
Volume (L)				0.0030
Retention Time (min)*	0.722	2.425	4.100	
Area of Peak	1.19	0.236	3.94	
Sample 2 (3mL)				
Moles	0.0000184	0.00000491	0.0000853	0.000123
Volume (L)				0.0030
Retention Time (min)	0.625	2.375	3.700	
Area of Peak	1.23	0.244	3.49	
Sample 3 (4mL)				
Moles	0.0000245	0.00000654	0.000114	0.000164
Volume (L)				0.0040
Retention Time (min)	0.625	2.375	3.650	
Area of Peak	1.68	0.367	5.16	
Sample 4 (5mL)				
Moles	0.0000306	0.00000816	0.000142	0.000204
Volume (L)				0.0050
Retention Time (min)	0.625	2.375	3.600	
Area of Peak	2.28	0.501	6.95	

* The retention time for this sample is not helpful because of the different flow rate for this sample— see the Experimental Methods for a brief discussion on this.

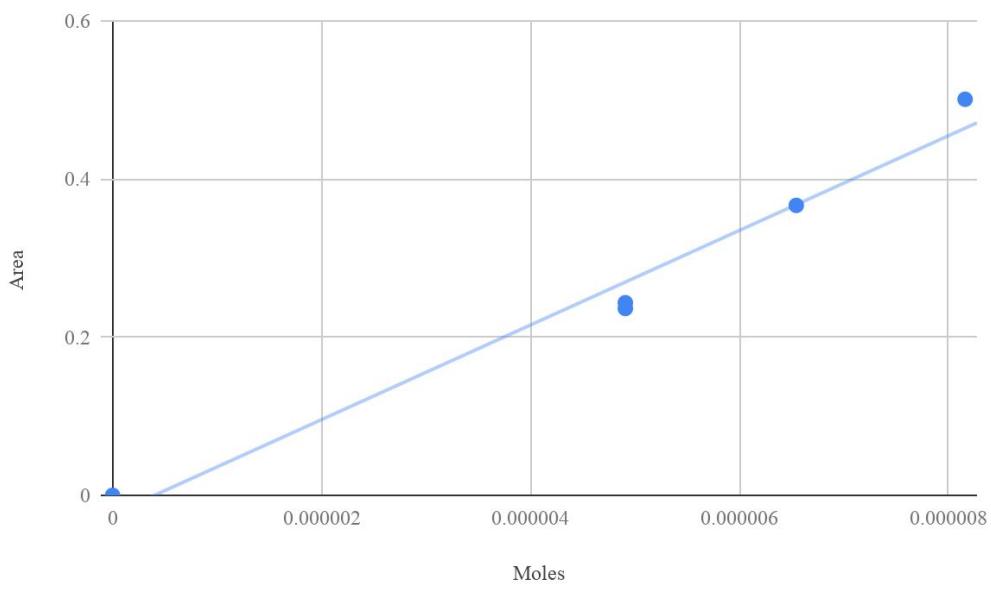
A plot of the area under the component peak as a function of number of moles of the component gives the calibration curve for a component. Figures 2, 3, and 4 show the calibration curves for CO₂, O₂, and N₂, respectively. The best fit lines and R² values are also shown. (Note that the point (0, 0) was included as a valid point on the curve; see the Discussion.

Figure 2. Standard Gas CO₂ Calibration Curve



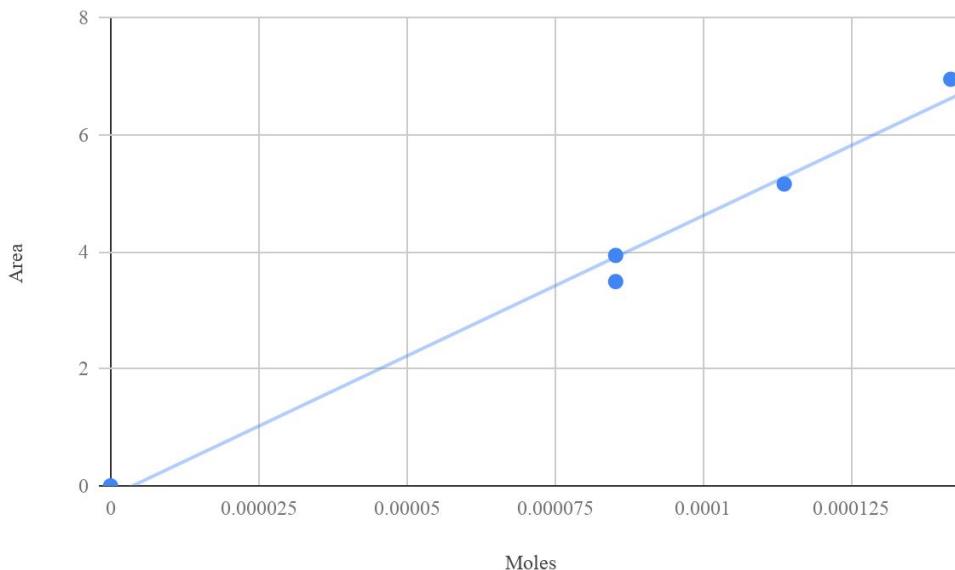
Best-Fit Line Equation: $A = 72876n - 0.0614$; R²: 0.99

Figure 3. Standard Gas O₂ Calibration Curve



Best-Fit Line Equation: $A = 59861n - 0.0239$; R²: 0.973

Figure 4. Standard Gas N₂ Calibration Curve



$$\text{Best-Fit Line Equation: } A = 47939n - 0.178 ; R^2: 0.987$$

Because the coefficient of determination of each calibration curve is fairly high (all are greater than 0.973), and the y-intercept of each graph is close to zero (y-intercepts lie between -0.178 and 0), the calibration curves are likely fairly reliable. The best-fit lines for these calibration curves will be inverted (see A.1.3) for use in calculating the number of moles of a component gas in a sample from the area under a peak on its trace.

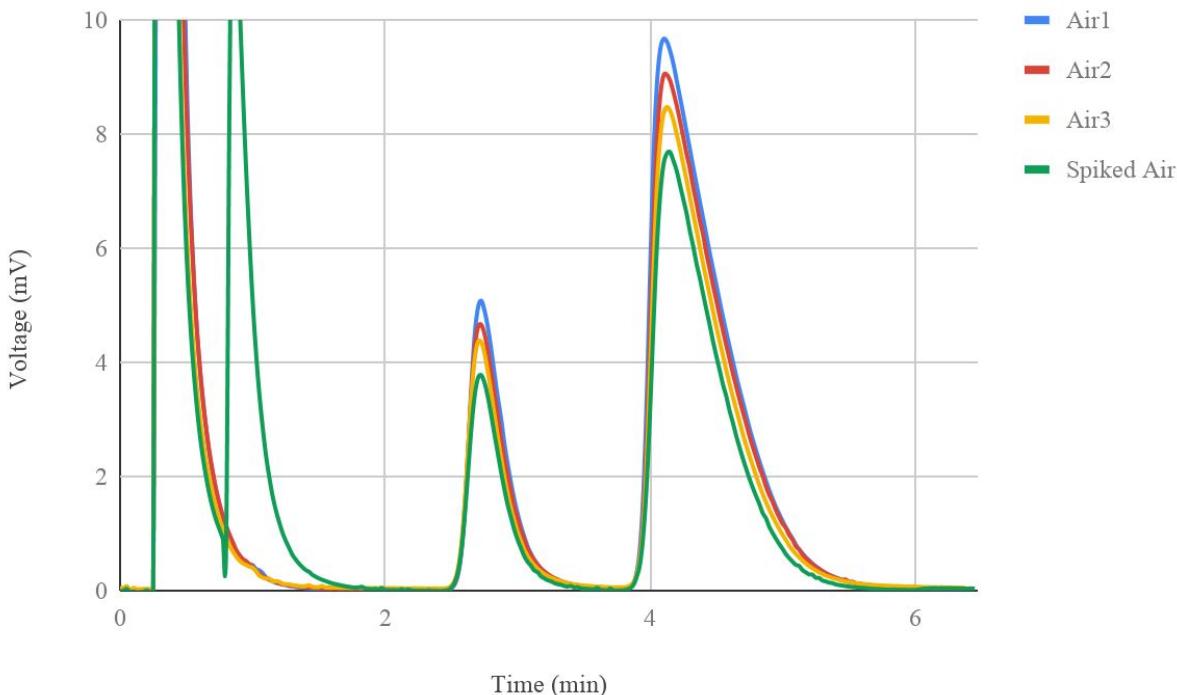
The laboratory conditions while taking the exhaled breath and laboratory air samples are displayed in Table 4. There was no change in any of the conditions between any of the sample trials, so they are consolidated into one table.

Table 4. Conditions for Exhaled Breath and Laboratory Air Samples

Injection Volume (L)	0.0040
He Flow Rate (mL/min)	60.6
Pressure (in. Hg)	29.88
Temperature (K)	298.15
Relative Humidity (%)	29

A trace of the laboratory air samples is shown in Figure 5.

Figure 5. Laboratory Air Samples Trace



The retention time of each component was calculated the same way as for the standard samples in Table 3. Peak area was found using the trapezoidal rule (see A.1.2.). The number of moles of gas were found using the inverse of the best-fit line of the corresponding component calibration curve (see A.1.3.). The mole fraction is calculated by dividing the number of moles by the total number of moles in the gas (see A.1.4.); note that this includes the calculated moles of water. The number of moles of water were calculated in A.1.1.

The sample with the spiked laboratory air was used to determine the retention time of CO₂, but its data was not used to calculate the component mole fractions.

The average retention times, peak area, and moles for each component time are displayed in Table 5. Also displayed are the calculated mole fraction of each component for every sample. The mole fraction takes into account the number of moles of water.

Table 5. Retention Time and Composition of Laboratory Air

	CO ₂	O ₂	N ₂	H ₂ O
Mean retention time (min.)	0.600	2.250	3.625	
Mean peak area	0.187	1.48	5.54	
Mean moles	0.00000253	0.0000251	0.000119	0.00000148
Mole Fraction	Sample 1	0.00537	0.171	0.814
	Sample 2	0.0228	0.168	0.800
	Sample 3	0.0242	0.168	0.797
Mean Mole Fraction	0.0171	0.169	0.804	0.00997

Figure 6 shows the traces of the exhaled breath samples, similar to Table 5. Table 6 shows the retention time and composition of exhaled breath, similar to Table 5.

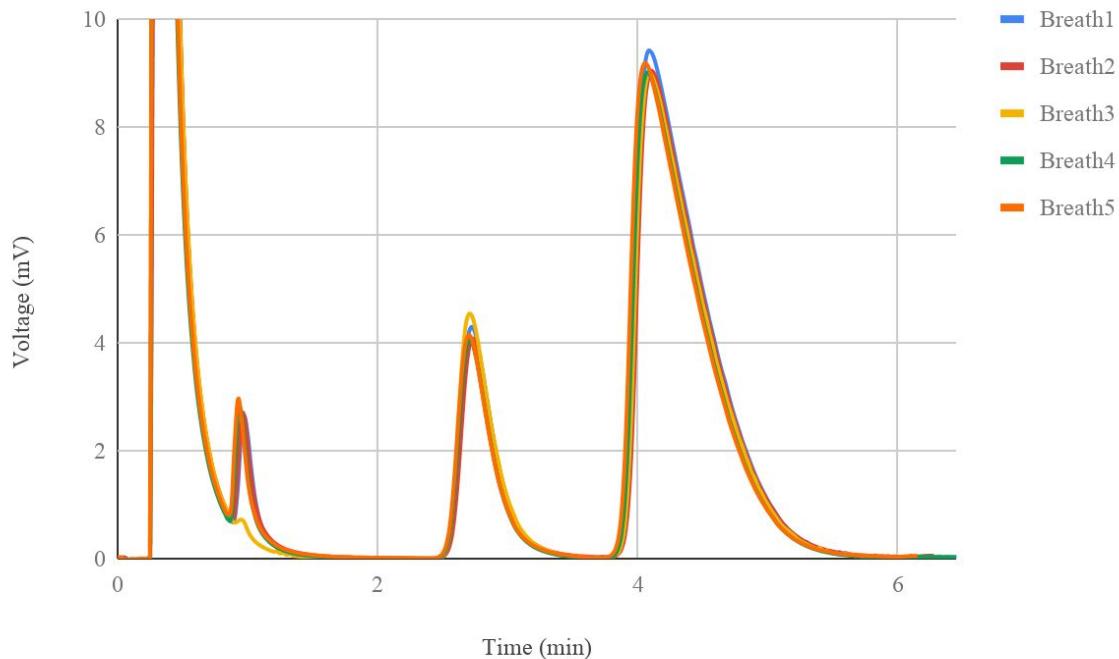
Figure 6. Exhaled Breath Samples Trace

Table 6. Retention Time and Composition of Exhaled Breath

		CO ₂	O ₂	N ₂	H ₂ O
Mean retention time (min.)		0.600	2.250	3.550	
Mean peak area		0.370	1.304	5.524	
Mean moles		0.00000592	0.0000222	0.000119	0.0000101
Mole Fraction	Sample 1	0.0405	0.138	0.759	
	Sample 2	0.0432	0.138	0.755	
	Sample 3	0.0190	0.157	0.759	
	Sample 4	0.0423	0.137	0.755	
	Sample 5	0.0432	0.138	0.755	
Mean Mole Fraction		0.0377	0.141	0.757	0.0642

Table 7 compares the calculated mole fractions with literature mole fractions. The literature mole fractions and references are stated in Appendix 3.

Table 7. Comparison of Calculated Mole Fractions to Literature Values

	Laboratory Air		Exhaled Breath	
	Calculated Mole Fraction	Literature Mole Fraction	Calculated Mole Fraction	Literature Mole Fraction
CO ₂	0.0171	0.0003	0.0377	0.036
O ₂	0.169	0.2085	0.141	0.153
N ₂	0.804	0.7862	0.757	0.749
H ₂ O	0.00997	0.0005	0.064	0.062

DISCUSSION

Much of the insight on the discussion of the experimental method was based off of content from *Fundamentals of Analytical Chemistry* (2).

The studied gases were nitrogen gas, oxygen gas, carbon dioxide gas, and water vapor. While significant amounts of methane and carbon monoxide gas were present in the standard gas mixture, these are ignored in the calculations. Because these four gases comprise more than 99% of air (see Appendix 3), the mole fraction of each component gas in the entire sample of gas is estimated to be its mole fraction out of the total number of moles of these four gases.

The expectation is that the compositions of the two mixtures of unknown composition (exhaled breath and laboratory air) should have similar concentrations of nitrogen gas, because it is not involved in metabolic processes. However, since oxygen gas is used up in respiration, and because water vapor and carbon dioxide are formed, it is expected that the concentration of water vapor and carbon dioxide will be higher and that the concentration of oxygen will be lower in the exhaled breath sample than in the atmospheric air sample. (If the concentrations of other gases, such as methane or carbon monoxide, were studied, the result would be similar to nitrogen because they are also not involved in metabolic processes).

The specific gas chromatography column used does not detect water vapor. This will cause a systematic error to the results, because the mole fraction of water will be too low (if it is not detected, its mole fraction is 0%) and the mole fractions of the other gases will be too high (because the number of moles of water vapor are not considered in the total number of moles). In samples with a higher concentration of water vapor (i.e., the samples of exhaled breath), the error is more significant.

The correction is performed by determining the amount of water in the sample. The partial pressure of water can be found using the relative humidity of the sample (the relative humidity of the laboratory air was measured with a digital sensor; the relative humidity of the exhaled breath is estimated to be 100%) and the vapor pressure of water at the ambient temperature. The partial pressure of water vapor, volume of the injection, and ambient temperature can be used to calculate the number of moles of water vapor in the injection. These calculations are found in A.1.1. This amount of water can be added onto the calculated number of moles of the other gas components, and the relative humidity was calculated out of this corrected total number of moles of gas. This calculation is described in A.1.4.

In the calibration curves, an extra point at (0mol, 0mV) was added to increase the strength of the correlation. This point makes sense because an 0mol of gas should correspond with a 0mV reading.

In Tables 3, 5, and 6, the retention time of a component gas is calculated by subtracting the start of the component gas peak from the start of the initial gas peak. The start of the peak was chosen because that is when the component gas begins to reach the detector—the spread of the peak is dependent on how quickly the sample is injected.

In Tables 3, 5, and 6, the area under the peak is calculated using the trapezoidal rule (see A.1.2.). The units for the area are $mV \cdot min$. This unit is irrelevant because only the fact that the area is proportional to the number of moles of gas is important, and hence is not included in the tables.

As expressed in the experimental methods section, there was the potential for a large gross error due to poor injection technique, causing broad bands that had some overlap. The main overlap was between the peaks of the initial rush of air and the peak for the carbon dioxide gas. The calculated area of the CO₂ may therefore have contained some of the area of the peak of the initial air, making a systematically high value for the CO₂.

There were many assumptions made in the calculations. For example, the ideal gas law was used to calculate number of moles of gas from pressure, volume, and temperature measurements, but the behavior of real gases (especially H₂O) is not ideal. However, because of the small volumes, the correction factors using the Van der Waals equation are likely negligible compared to other errors caused by technique. This may cause some random error compared to the literature values.

Another assumption made was that laboratory air is very close to the literature atmospheric air, and that Prof. Topper's expired breath is close to the literature expired air compositions. It is unknown in which conditions the literature values were obtained, and it is unknown how the composition in the laboratory and Prof. Topper's breath compares to the average atmospheric and breath values. It is only known that Prof. Topper attempted to augment the CO₂ levels in his breath's sample by breathing in and out multiple times quickly before creating the sample. This may be the cause of some random error in contrast to the literature values.

Another potential error is that the calculated amount of water vapor in the air was calculating using the vapor pressure of water at body temperature (310.15K), but the sample had cooled down to the temperature of the surrounding air (298.15K) by the time the sample was used. Some of the water may have condensed, leaving in the gas mixture a lower amount of water vapor than calculated, causing a systematically high estimate.

A major error is that there was overlap between the first peak (of the initial air rush) and the second peak (for carbon dioxide). This means that the calculated area for carbon dioxide is systematically high, because some of that area is from gas in the first peak. While this was not a major problem in the standard gas and in the breath sample, where the concentrations of CO₂ are relatively large compared to the overlap from the first peak, there was a massive error in the calculated carbon dioxide mole fraction in the sample of atmospheric air. In this sample, the atmospheric air has very little carbon dioxide (0.03% as opposed to 15% in the standard sample), so a tiny overlap has a very large relative effect on the calculation of the carbon dioxide peak.

The errors, ranked from most to least significant, are the overlap between peaks, bad injection technique, assuming the ideal behavior of gases (i.e., using the ideal gas law), the calculation of water the fluctuation in the detector voltage output and other laboratory equipment precision errors.

Because there was a long sequence of dependent calculations, it is possible that there was a propagation of uncertainty from early calculations to the final calculated mole fraction. Any error in the calibration curve would have resulted in error in the calculation of the number of moles of a component gas, and therefore the overall mole fraction. An error in the calculation of the water pressure and number of moles of water would have affected the mole fraction. There is also the propagation of uncertainty from the small fluctuations inherent to the gas chromatograph (see Figure 1). However, there is nothing to suggest that any of these error calculations were systematic and would cause an overall systematic bias: the calibration curves had a high coefficient of determination and y-intercepts with small magnitudes, as expected, and there was no pattern in the fluctuations of the gas chromatograph reading. Because the general variance in the data were small (see Table 8), it is likely that any propagation of error was not very significant.

The calculated percentages of error (see Table 8) indicate that the data taken for the ambient air were much more accurate than those for the laboratory air. For the ambient air, all of the percent errors were under 10%. The laboratory had percent errors that far exceeded 10%, with a maximum of 4900% for carbon dioxide because of the overlap mentioned above. These large values are probably a result of the previously mentioned gross errors affecting these sample collections, creating significantly greater variances among the collected data.

CONCLUSIONS

The experimentally determined mole fractions for the mole fractions of gases had a distribution more similar to the literature values for the exhaled breath samples than for the laboratory air samples. The 90% confidence intervals for the exhaled breath was determined to be 0.037 ± 0.009 for carbon dioxide, 0.141 ± 0.008 for oxygen, 0.757 ± 0.002 for nitrogen, and 0.064 ± 0.001 for water. The confidence interval just barely miss (within ± 0.005) the literature values for all of the components, which are 0.036, 0.153, 0.749, and 0.062, respectively. The molar fraction values for the laboratory air was determined to be 0.02 ± 0.01 for carbon dioxide, 0.169 ± 0.003 for oxygen, 0.81 ± 0.01 for nitrogen, and 0.0097 ± 0.0005 for water. The carbon dioxide and water confidence intervals greatly fail to capture the literature values of 0.0003 and 0.0005, respectively, but the oxygen and nitrogen confidence intervals were close to (but still missed) the the literature values of 0.2085 and 0.7862, respectively. The wide range of accuracies indicates that this method is not entirely reliable; however, there were a number of potential gross errors which may have contributed to much of this error.

A potential improvement to the procedure is to encourage a slower flow rate, which will allow the gases more time to separate and reduce the overlap between different peaks. This may also counter some of the band broadening that may be caused when a sample is injected too slowly, such as that from some of the first samples in this report. The largest percent error for any mole fraction was for carbon dioxide in the air sample, where its peak was the smallest and the overlap from the initial air rush peak caused a massive error, so a method of reducing overlap would most likely have the greatest beneficial result on the accuracy of this method.

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Jonathan Lam was responsible for authoring the Experimental Methods, Results, Discussion, Acknowledgements, Appendix I, and Appendix II sections of this laboratory report, and served as editor for the sections written by Paul Cucchiara.

Paul Cucchiara was responsible for authoring the Abstract, Experimental Methods, Results, Conclusion, References, and Appendix III sections of this laboratory report, and served as editor for the sections written by Jonathan Lam.

Sun Hung Zhao was consulted for some of the considerations in the Discussion section.

The format of this laboratory report is based off of the “Laboratory Report” section of The Official Cooper Union General Chemistry Laboratory Guide, 19th edition, by Marcus Lay et al.

REFERENCES

- [1] Lay, M.; Newmark, A.; Topper, A.; Vichchulada, P.; Wiener, S. *The Official Cooper Union General Chemistry Guide*; Department of Chemistry: New York, NY, 2017; pp 33-42.
- [2] Kimball, J. W. Kimball's Biology Pages. <http://www.biology-pages.info/> (accessed Dec 10, 2018).

APPENDIX I

CALCULATION METHODS AND REPRESENTATIVE CALCULATIONS

A.1.1. Correction for Water Vapor

The gas chromatograph column used is not able to detect water vapor. A correction is necessary to adjust the mole fractions of the gases to take into account the humidity of the sample.

Relative humidity is defined in Equation 1. In the sample of breath (at metabolic temperature), the relative humidity is roughly 100%. The relative humidity of the laboratory air was measured using a digital sensor.

$$\text{Equation 1. } RH (\%) = \frac{P_{H_2O}}{P_{vap}} \times 100\%$$

where P_{H_2O} is the partial pressure of water and P_{vap} is the vapor pressure of water at the sample's temperature.

The vapor pressure of water can be calculated from temperature. An estimate is given in Equation 2.

$$\text{Equation 2. } P_{vap} = \exp(77.345 + 0.0057T - 7235T^{-1}) \div T^{8.2}$$

Equation 1 can be rewritten in the following form to solve for the partial pressure of water if relative humidity and vapor pressure are known, which will be used to calculate the number of moles of water vapor in the air.

$$\text{Equation 1a. } P_{H_2O} = \frac{RH}{100\%} \times P_{vap}$$

The ideal gas law is used to estimate the number of moles of water in the sample using Equation 3.

$$\text{Equation 3. (Ideal Gas Law) } n_{H_2O} = \frac{P_{H_2O}V}{RT}$$

where V and T are the volume and temperature of the injection, respectively.

A representative calculation of number of moles of water is shown below, using Equations 1a, 2, and 3. The calculation is that of the number of moles of H_2O in the laboratory air. The laboratory temperature is 298.15K, the pressure is 101185Pa, and the (injection) volume is 4.0mL.

$$P_{vap} = \exp(77.345 + 0.0057(298.15K) - 7235(298.15K)^{-1}) \div (298.15K)^{8.2} = 3158Pa$$

$$P_{H_2O} = \frac{29\%}{100\%} \times 3158Pa = 916Pa$$

$$n_{H_2O} = \frac{(916Pa)(0.040L)}{(8314Pa \times L \times mol^{-1} \times K^{-1})(298.15K)} = 0.00000148mol$$

A.1.2. Calculation of Area Under Peak

The area under a peak on a chromatogram trace is proportional to the number of moles of the corresponding gas (the gas with the same retention time as the peak). Therefore, the number of moles may be calculated from the area if a known number of moles produces a known area. This calibration was carried out using the standard gas solution.

To calculate the area under a peak, an approximate upper and lower limit for the peak were chosen by observation of the graph to include as much of the peak without overlap with other peaks. (Overlap was only an issue with the CO₂ peak — see the Discussion.) Then, the trapezoidal rule (Equation 4) was performed to determine the area under one peak.

Equation 4 (Trapezoidal Rule).
$$A = \sum_{k=a}^{b-1} \left(\frac{1}{2}(V_k + V_{k+1})\Delta t \right)$$

where a is the lower limit for retention time, b is the upper limit for retention time, V_n is the detector voltage at the n retention time, and Δt is the interval between two consecutive detector readings.

A representative calculation for the CO₂ peak of the exhale sample 1 is illustrated below.

$$A = \sum_{k=36}^{54} \left(\frac{1}{2}(V_k + V_{k+1})(0.025min) \right) = 0.0178875 + 0.0261375 + \dots + 0.0024875 = 0.418025$$

A.1.3. Standard Gas Calibration Curve and Mole Calculation

The number of moles of each gas in the standard gas samples were estimated from the injection volumes of the samples using the ideal gas law (similar to equation 3) and the mole fractions of each gas.

Equation 5:
$$n_{gas} = \chi_{gas} \times \frac{PV}{RT}$$

where n_{gas} is the number of moles of one gas, χ_{gas} is the mole fraction of the gas, and P , V , and T are the pressure, (injection) volume, and temperature, respectively, of the sample.

The area under the peak of the each gas versus the number of moles of the corresponding gas (calculated from Equation 5) for each major gas (CO_2 , O_2 , and N_2) are plotted as a calibration curve. For each gas, a least-squares linear regression is performed (using the Google Sheets spreadsheet program) to produce a function mapping areas to moles.

The function is then inverted to create a function mapping moles to areas. This inverse function is used to calculate the number of moles of the corresponding gas in a sample given its area (see A.1.2.)

A representative calculation is shown below for the number of moles of carbon dioxide, using the inverse best-fit calibration curve for carbon dioxide.

Calibration curve: $A = 72876n - 0.0614$

Inverse calibration curve: $n_{\text{gas}} = \frac{A+0.0614}{72876}$

$$n_{\text{CO}_2} = \frac{0.418+0.0614}{72876} = 0.00000658 \text{ mol}$$

A.1.4. Mole Fraction Calculation with Correction

The mole fraction of the solution is the ratio of the number of moles of one gas to the total number of gases. The total number of moles includes the calculated number of moles of water vapor (see A.1.2.) using Equation 6.

Equation 6. $\chi_{\text{gas}} = \frac{n_{\text{gas}}}{n_{\text{total}}}$

A representative calculation is shown below for the mole fraction of carbon dioxide in the first breath sample.

$$\chi_{\text{gas}} = \frac{0.000162}{0.00000658} = 0.0405$$

A.1.5. Miscellaneous Calculations

The bubble meter was used to determine flow rate. The flow rate is the quotient of the volume of air by the amount of time it takes for a bubble to travel through that volume.

Equation 7. $FR = \frac{V}{t}$

The retention time of a component gas is the difference between the beginning of the component gas's peak and the beginning of the peak of the initial gas rush. An explanation of this reasoning is described in the Discussion.

Equation 8. $RT = (\text{time of start of component gas peak}) - (\text{time of start of initial gas peak})$

APPENDIX II

COMPUTATION OF STATISTICAL MEASURES OF PRECISION

Statistical measures were calculated for each of the calculated mole fractions of a component gas for each of the two gas mixtures with unknown compositions. The calculations for the statistical measures for the CO₂ gas in exhaled air are shown below as a representative sample.

The calculations for the mean (\bar{x}), sample standard deviation (s), standard error (s_m), variance (s^2), and relative standard deviation of the calculated mole fraction values are shown below. Because the data points are roughly spread uniformly over a small range and not heavily skewed, the mean will be used to represent the center and the standard deviation will be used to estimate the range (as opposed to the median and IQR). The data analyzed here is from Table 6.

$$n = 3$$

$$\bar{x} = \frac{1}{n} \sum_{k=1}^n (\text{calculated } \chi)_k = 0.0376$$
$$s = \sqrt{\frac{1}{n-1} \sum_{k=1}^n ((\text{calculated } \chi)_k - (\text{mean } \chi))^2} = 0.0105$$
$$s_m = \frac{s}{\sqrt{n}} = 0.00468$$
$$s^2 = 0.000110$$
$$\text{rel. std. dev. (ppt)} = 1000 \times \frac{s}{\bar{x}} = 278$$

The calculation of a 90% confidence interval of the mole fractions is shown below.

$$90\% \text{ confidence level } t_{n-1} = t_2 = 2.92$$
$$\text{uncertainty (u)} = t_{n-1} \times \frac{s}{\sqrt{n}} = 0.00999$$
$$90\% \text{ confidence interval} = 0.04 \pm 0.01$$

The percent error is calculated using the literature value from Table 8 (Appendix III).

$$\% \text{ Error} = \frac{|0.0376 - 0.036|}{0.036} \times 100\% = 4.5\%$$

The intermediate calculation results are displayed rounded, but all calculations are all only rounded at the end.

A summary of all of the statistical measures, for the mole fractions of the three gases, for the two different gas mixture samples, is displayed in Table 8.

Table 8. Summary of Statistical Values for Mole Fraction Calculations

		Atmospheric Air			
		CO ₂	O ₂	N ₂	H ₂ O
<i>n</i>	3	3	3	3	3
\bar{x}	0.0151	0.169	0.806	0.00974	
<i>s</i>	0.00889	0.00180	0.00736	0.000290	
<i>s_m</i>	0.00513	0.00104	0.00425	0.000167	
<i>s²</i>	0.0000791	0.00000322	0.0000541	0.0000000838	
<i>rel. std. dev. (ppt)</i>	589	10.597	9.129	29.73	
<i>90% confidence interval</i>	0.02 ± 0.01	0.169 ± 0.003	0.81 ± 0.01	0.0097 ± 0.0005	
<i>% Error</i>	4900%	19%	2.5%	1800%	
Exhaled					
		CO ₂	O ₂	N ₂	H ₂ O
<i>n</i>	5	5	5	5	5
\bar{x}	0.0376	0.141	0.757	0.0643	
<i>s</i>	0.0105	0.00850	0.00226	0.00137	
<i>s_m</i>	0.00468	0.00380	0.00101	0.000611	
<i>s²</i>	0.000110	0.0000722	0.00000511	0.00000187	
<i>rel. std. dev. (ppt)</i>	278	60.1	2.99	21.3	
<i>90% confidence interval</i>	0.037 ± 0.009	0.141 ± 0.008	0.757 ± 0.002	0.064 ± 0.001	
<i>% Error</i>	4.5%	7.6%	1.0%	3.7%	

APPENDIX III

GAS MIXTURE LITERATURE VALUES

In Table 9, a list of literature values for the percentage by volume of CO₂, O₂, and NO₂ are shown. The values were obtained from [2].

Table 9. Gas Mixture Literature Values

	Mole Fraction	
	Atmospheric Air	Expired Air
CO ₂	0.0003	0.036
O ₂	0.2085	0.153
N ₂	0.7862	0.749
H ₂ O	0.0005	0.062

Gravimetric Determination of Chloride in Unknown Chloride Mixture by Precipitation with Silver Nitrate

Jonathan Lam and Paul Cucchiara

The Cooper Union
for the Advancement of Science and Art

CH-111 Section C
Professor Robert Q. Topper
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ABSTRACT

Gravimetric analysis is an analytical procedure commonly used to determine the mass of substances in mixtures, such as lactose in milk products and nicotine in pesticides (2).

Gravimetric analysis was used to determine the mass percent composition of chloride ions in an unknown mixture (#1801) of chloride salts, by precipitation with silver nitrate, AgNO_3 (aq), to form silver chloride, AgCl (s), to be filtered and weighed. Various methods were used to mitigate possible sources of systematic error, such as photodecomposition of the silver chloride, reaction with atmospheric anions, and peptization. The average calculated experimental mass percent of chloride ions in the unknown mixture was 52.06%, and the true mass percent of chloride in the unknown is calculated to be in the interval between 48% and 56% with a 90% confidence level.

EXPERIMENTAL METHODS

[Exp. 1] A precipitation gravimetric determination is performed on an unknown mixture of a soluble chloride mixture. A solution of the unknown is reacted with a solution of silver nitrate to form silver chloride precipitate, and the mass of the precipitate can be measured to determine the amount of chloride in the unknown sample. The specific procedure followed was based on the procedure stated in “The Gravimetric Determination of Chloride in a Soluble Unknown,” from *The Official Cooper Union General Chemistry Laboratory Guide* (1). The discussion behind the methods used, such as keeping the solution slightly acidic and rinsing with a dilute acidic solution, are explained in more detail in the discussion section. The following is a summary of the tasks completed.

[Exp. 2] Three clean Gooch crucibles with filter mats were dried in an oven for a week, and their final masses were recorded. The masses of three samples of the dry unknown compound #1801 were measured by difference and dissolved into a mildly-acidic solution of nitric acid (see Dis. 5). A small excess of silver nitrate was added to a solution of the unknown chloride mixture (see Eq. 1 for the calculated minimum silver nitrate required) to ensure complete precipitation of the chloride, and the solution was digested until no additional precipitation was observed when a few drops of silver nitrate were added; this process was repeated for each sample. After sitting in a dark cabinet for a week, the solutions were filtered, through the filtration apparatus, into their respective crucibles. After the second and following filtrations, the filtrate was tested for the presence of silver ions by adding drops of concentrated hydrochloric acid (HCl) and re-filtered if any turbidity was observed. The crucibles were then dried in the oven and their masses taken after one interval of one hour and two intervals of 30 minutes, and the final mass was recorded as the dry mass.

[Exp. 3] The laboratory guide stated to continue the drying-weighing cycle for the crucible and filter paper, and the crucible with filter paper and precipitate, until the mass is constant. Due to time restrictions, the mass of the dried crucible and filter paper left in the oven for a week was assumed to be dry weight, and the mass of the crucibles with precipitate after three weighings was assumed to be the dry weight, but this is a possible source of gross error. Care was taken to only digest one solution at a time and perform one filtration at a time to minimize light exposure of the silver chloride precipitate (see Dis. 6). During the digestion, a sheet of paper was held up to shade the solution as a further attempt to mitigate photodecomposition. During the filtration, the rubber policeman to move the precipitate in sample 3 was not cleaned properly, and there is the chance for possible contamination. Also during the filtration, the first filtrate for sample 2 was extremely cloudy. After the first weighing of the mass of sample 1, the crucible was tipped onto its side briefly while in the dessicator, and the mass from the second weighing of sample 1 was approximately 20mg lower than the first, which is a possible source of gross error.

RESULTS

The mass of the dry crucible and filter mat, and the mass of the dry precipitate, crucible, and filter mat are the final weighings after multiple dryings to completion (see Exp. 3 for specifics on the drying).

Table 1. Experimental mass measurement data

Unknown chloride sample number: 1801

	Sample 1	Sample 2	Sample 3
Mass of dry crucible and filter mat (g)	18.8399	18.9965	18.0009
Mass of dry unknown sample (g)	0.1325	0.1011	0.1161
Mass of dry precipitate, crucible, and filter mat (g)	19.1068	19.2104	18.2544

The mass of the chloride ions (Cl^-) in a sample is calculated by a stoichiometry calculation from the mass of the precipitate (see Eq. 2), and the percent mass composition of the chloride ions is the quotient of the mass of the chloride ion and the mass of the unknown sample (see Eq. 3).

Table 2. Calculated mass percent composition of chloride in unknown

	Sample 1	Sample 2	Sample 3
Percent chloride (%)	49.83	52.34	54.01

A descriptive statistical analysis was performed on these data points (see St. 1), and a summary is displayed below:

Table 3. Statistical summary of percent composition

Sample mean	Sample standard deviation	90% confidence interval for the mean
$52.06\% \pm 1.22\%$	2.11%	$52\% \pm 4\%$

The sample mean of the percent chloride was 52.06% with a standard error of 1.22% and a standard deviation of 2.11%. The distribution of the three points was roughly uniform, and a

Q-test (see St. 2) did not predict any statistically unreliable data points. The confidence interval indicates that there is a 90% chance that the actual percent composition of chloride in the unknown is in between 48% and 56%.

DISCUSSION

Much of the insight on the discussion of the experimental method and systematic error was based off content from *Fundamentals of Analytical Chemistry* (2).

[Dis. 1] The double-replacement reaction between silver nitrate and the unknown chloride mixture forms a colloidal suspension of silver chloride in water. A colloidal suspension is a form of heterogeneous mixture, in which one particle forms microscopic, insoluble particles inside another. In order to be able to separate the colloid from the water, the particles must be coagulated first to maximize the size of the silver chloride particles, which maximizes the amount of particles being caught by the filter mat. If the colloidal suspension is not coagulated or a significant portion is not coagulated, the calculated percent chloride will be systematically too low because some of the precipitate will have been lost through the filter mat and not weighed. Secondly, larger particles of precipitate are more pure than fine particles of precipitate, which allows for a more accurate weighing of the precipitate.

[Dis. 2] A colloidal suspension is kept stable because of the formation of an electric double layer. In an excess of silver, a primary adsorption layer of positively-charged silver ions, and a secondary adsorption layer of oppositely-charged nitrate ions, create an overall-negative shell. The negative charge of all of the colloidal particles prevents the particles from colliding and keeps the suspension stable. Coagulation occurs by keeping an excess of silver nitrate electrolyte and heating the solution, which decreases the width of the double-layer and increasing the kinetic energy of the particles, allowing colloid particles to approach each other more closely and increasing the chance for coagulation. The solution should be heated almost to boiling to maximize kinetic energy but avoid the mechanical disruption caused by boiling bubbles that may separate large colloidal particles—this process of heating is called digestion.

[Dis. 3] The likely sources of systematic and random error, from most to least, are: the peptization of silver chloride, the formation of silver carbonate precipitate, AgCO_3 (s), the photodecomposition of silver chloride, and the tolerance of normal equipment operation. Each of these possible sources of error are discussed in more detail below.

[Dis. 4] A possible source of systematic error is the peptization of the silver chloride precipitate. Peptization is the process of breaking down large, coagulated chunks of precipitate into a stable, dispersed colloidal form, and is unwanted for this experiment. If peptization occurs, the calculated percent chloride will be systematically low, because the particles of silver chloride that have reverted to microscopic particle sizes may not be filtered and their masses not included in the mass of the precipitate. It may happen if the electrolyte concentration is decreased, which increases the width of the electric double-layer and causes colloidal particles to separate again.

This is mitigated by using a wash solution of mildly-concentrated nitric acid to maintain the electrolyte concentration instead of using deionized water, when possible, to move the precipitate from the beaker to the filtering crucible. There appeared to be some peptization in sample 2 (see Exp. 3), in which the filtrate was very cloudy, which is likely due to using too much deionized water to wash out the precipitate. As a result, it is possible that the calculated percent chloride for sample 2 is too low.

[Dis. 5] Another possible source of systematic error is the formation of silver carbonate precipitate, by the reaction of silver with carbonate ions formed when environmental carbon dioxide, CO_2 (g), dissolves in the solution. This would cause a systematic increase in the calculated percent chloride ions, because the unwanted mass of silver carbonate would be added to the mass of the desired silver chloride precipitate. This effect is reduced by keeping a low concentration of nitric acid in the solution to react with the carbonate ions to produce soluble carbonic acid.

[Dis. 6] Silver chloride undergoes photodecomposition. The effect of photodecomposition should be negligible without prolonged, direct exposure to sunlight. Silver chloride photodecomposes into elemental silver and chlorine gas. If dry, the calculated percent chloride will be systematically low, because the mass of the chlorine gas from the photodecomposed silver chloride will not be included in the weighing of the precipitate. When in solution, there may be an additional reaction involving that produces soluble chlorate ions that will be lost during the filtration process, also causing less silver chloride to be formed and also a loss of mass of the precipitate, resulting in a systematically low calculated percent chloride.

[Dis. 7] The only precise measurements were taken with an analytical balance, which has a tolerance of approximately 0.0002g (0.2mg). The other measurements were approximate and would not be a source of error. Because the tolerance of the analytical balance is so small, the random error associated with the equipment is negligible.

[Dis. 8] Possible sources of gross error are discussed in Exp. 3. If the mass of the crucibles and filter paper assumed to be dry were not actually dry, the difference between the mass of crucibles with precipitate and the mass of the crucibles without precipitate would be smaller, which would cause the calculated mass of percent chloride to be too low. If the mass of the crucibles, filter paper, and precipitate assumed to be dry were not actually dry, the reverse would be true and the calculated mass of percent chloride would be too high. If some precipitate was lost when the crucible for sample 1 was tipped over, the calculated percent chloride was too low.

[Dis. 9] Because the true percent composition of the chloride is not known, nothing is certain about the accuracy of the gravimetric analysis method.

CONCLUSIONS

The mean experimental percent composition of chloride from the gravimetric analysis of the silver chloride precipitate was 52.06%. A confidence interval of the true percent composition of chloride in the sample was $52\% \pm 4\%$. A small standard deviation of the data points indicates that this method of determining percent composition is precise. However, due to the many possible sources of systematic error (see Dis. 4-6) and gross error (see Dis. 8), the calculated percent chloride determined by this method is likely not very accurate.

This experiment will be immediately followed with another determination of the percent composition of the same unknown solution by means of titration with ion exchange and back-titration, and the two experiments will be compared in terms of precision, accuracy, and the amount of resources necessary.

Improvements to the lab procedure for future investigations to mitigate the sources of error would include the creation of a precipitate that does not photodecompose as silver chloride does (see Dis. 6) and drying at a hotter temperature than 110°C or for longer periods than those stated in the laboratory manual to ensure complete drying of the crucible with and without the precipitate (see Dis. 8).

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Paul Cucchiara was responsible for authoring the Abstract, Results, Conclusions, and References sections of this laboratory report, and served as editor for the sections written by Jonathan Lam.

Andrew Kim reviewed this report and provided comments.

The scientific journal article “Infrared Spectroscopy of Water Cluster Anions, $(H_2O)_{n=3-24}$ in the HOH Bending Region: Persistence of the Double H-Bond Acceptor (AA) Water Molecule in the Excess Electron Binding Site of the Class I Isomers” was consulted for the style of this laboratory report (citation below).

Roscioli, Joseph R., Hammer, Nathan I., and Johnson, M. A. Infrared Spectroscopy of Water Cluster Anions, $(H_2O)_{n=3-24}$ in the HOH Bending Region: Persistence of the Double H-Bond Acceptor (AA) Water Molecule in the Excess Electron Binding Site of the Class I Isomers. *The Journal of Physical Chemistry Letters*. **2006**, 110, 7517-7520.

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APPENDIX I

SAMPLE (REPRESENTATIVE) CALCULATION

The calculation for the volume of AgNO₃ necessary to dissolve 0.1g NaCl is:

$$\text{[Eq. 1]} \quad 0.1\text{g NaCl} \times \frac{\text{mol NaCl}}{58.443\text{g NaCl}} \times \frac{\text{mol AgNO}_3}{\text{mol NaCl}} \times \frac{L \text{ 0.2M AgNO}_3}{0.2\text{mol AgNO}_3} \times \frac{1000\text{mL AgNO}_3}{L \text{AgNO}_3} = 9\text{mL 0.2M AgNO}_3$$

(molar masses were calculated from elemental molar masses found in *Fundamentals of Analytical Chemistry* (2))

This value indicates the minimum AgNO₃ that must be added to the unknown solution so that the unknown chlorides completely react. In the experiment, an excess of approximately 5mL (approximately 14mL total of AgNO₃) was added to each solution to ensure the chlorides completely react.

The mass of chloride ion in a sample is calculated from the mass of filtered precipitate in a stoichiometric calculation. The mass of the precipitate is the difference between the final, dry mass of the precipitate in the crucible with the filter paper, and the mass of the crucible and the filter paper.

$$\text{[Eq. 2]} \quad m_{Cl^-} = (m_f - m_i) \times \frac{\text{mol AgCl}}{143.321\text{g AgCl}} \times \frac{\text{mol Cl}^-}{\text{mol AgCl}} \times \frac{35.453\text{g Cl}^-}{\text{mol Cl}^-}$$

The mass percent composition of chloride in the unknown can be determined by dividing this calculated chloride ion mass by the dry mass of the unknown samples.

$$52\% \pm 4\% \quad \% Cl^- = \frac{m_{Cl^-}}{m_{\text{unknown}}}$$

The calculation for the percent composition of chloride in sample 1 is shown below as a representative calculation (see table 1):

$$m_{Cl^-} = (19.1068\text{g} - 18.8399\text{g}) \times \frac{\text{mol AgCl}}{143.321\text{g AgCl}} \times \frac{\text{mol Cl}^-}{\text{mol AgCl}} \times \frac{35.453\text{g Cl}^-}{\text{mol Cl}^-} = 0.06602\text{g Cl}^-$$
$$\% Cl^- = \frac{0.06602\text{g Cl}^-}{0.1325\text{g unknown}} = 0.4983 \times 100\% = 49.83\%$$

APPENDIX II

COMPUTATION OF STATISTICAL MEASURES OF PRECISION

[St. 1] The calculations for the mean (\bar{x}), standard deviation (s), standard error (s_m), variance (s^2), and relative standard deviation of the percent composition of chloride in the unknown are shown below. Because the data points are roughly spread uniformly over a small range and not heavily skewed, the mean will be used to represent the center and the standard deviation will be used to estimate the range (as opposed to median and IQR). The data shown below were obtained from table 2.

$$n = 3$$

$$\bar{x} = \frac{1}{3}(49.83\% + 52.34\% + 54.01\%) = 52.06\%$$

$$s = \sqrt{\frac{1}{2}((49.83\% - 52.06\%)^2 + (52.34\% - 52.06\%)^2 + (54.01\% - 52.06\%)^2)} = 2.11\%$$

$$s_m = \frac{2.11\%}{\sqrt{3}} = 1.22\%$$

$$s^2 = (4.43\%)^2$$

$$rel. std. dev. (ppt) = 1000 \times \frac{2.11\%}{52.06\%} = 40.5$$

The calculation of a 90% confidence interval for the mean percent chloride is shown below.

$$90\% \text{ confidence level } t_3 = 2.920$$

$$uncertainty (u) = 2.920 \times \frac{2.11\%}{\sqrt{3}} = 3.55\%$$

$$90\% \text{ confidence interval} = 52\% \pm 4\%$$

[St. 2] Although the three experimental values are roughly equally spaced out, a Q test is performed below at a 90% confidence level.

$$range = 54.01\% - 49.83\% = 4.18\%$$

$$90\% \text{ confidence } Q_{crit_3} = 0.94$$

$$Q_{54.01\%} = \frac{|54.01\% - 52.34\%|}{4.18\%} = 0.400$$

$$Q_{49.83\%} = \frac{|49.83\% - 52.34\%|}{4.18\%} = 0.600$$

The Q-values for the extreme point do not exceed Q_{crit} , so it is not statistically justified to remove any data points. None of the data points are impossible, so no data points will be discarded.

Determination of Percent Chloride in an Unknown Chloride Mixture by Ion Exchange and Back-Titration

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The Cooper Union
for the Advancement of Science and Art

CH-111 Section C
Professor Robert Q. Topper
October 29th, 2018

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ABSTRACT

Ion exchange is a process in which ions bonded to an exchange media are replaced with different ions that come into contact with the exchange media. This method is useful for replacing interfering ions with non-interfering ones as well as for concentrating ions from dilute solutions, and is commonly used in water softeners. The percent composition of chloride in the unknown chloride mixture 1801 was determined using ion exchange with hydroxide ions, and then measuring the hydroxide ion concentration by over-titration with potassium hydrogen phthalate, $\text{KHC}_8\text{H}_4\text{O}_4$ (aq) (abbreviated to KHP), and back-titrated with sodium hydroxide, NaOH (aq). The average calculated experimental mass percent of chloride ions in the unknown mixture was 34.3%, and a true value to be in between 25% and 43% at the confidence level of 90%. The results and methods were compared with those from an earlier experiment determining the percent chloride of the same chloride using gravimetric analysis. The data gathered in this experiment may affect which methods are chosen to determine the percent compositions of other compounds in future experiments.

EXPERIMENTAL METHODS

A column was filled with Amberlite IRA 910 ion-exchange resin, and saturated with hydroxide ions (from a sodium hydroxide solution). Three samples of a solution of unknown mixture of chloride were drained through the column, each displacing hydroxide ions that were over-titrated with standardized potassium hydrogen phthalate and back-titrated with standardized sodium hydroxide. The specific procedure followed was based on the procedure stated in “Determination Of Percent Chloride By Ion Exchange and Back-Titration,” from *The Official Cooper Union General Chemistry Laboratory Guide* (1). The discussion behind the methods used, such as keeping the solution slightly acidic and rinsing with a dilute acidic solution, are explained in more detail in the discussion section. Below is a summary of the tasks completed.

A 0.1M sodium hydroxide solution was prepared, and four samples were standardized by titration with potassium hydrogen phthalate. A column with an inbuilt filter was filled with approximately 35mL of Amberlite IRA 910 resin and saturated with hydroxide ions by washing with stock sodium hydroxide. Four samples of solution with an exact, known concentration of the unknown chloride mixture were prepared. Each sample unknown solution was drained through the column and eluted with multiple bed volumes of deionized water. The eluent solution was then over-titrated with potassium hydrogen phthalate and back-titrated with the sodium hydroxide solution standardized in the beginning of the experimental procedure.

Four samples of the sodium hydroxide solution were standardized and four samples of the unknown chloride solution were analyzed by forward-titration and back-titration instead of three (from the lab manual procedure). A column with an inbuilt filter was used instead of a buret prepared with a glass wool filter. Due to a misunderstanding of the laboratory guide, rather than preparing one solution of unknown mixture and using 10.00mL aliquots as samples, one solution was prepared for sample 1 and another sample was prepared for samples 2 through 4; this is not, however, a source for error, as the process is identical for the different solutions. A gross error in the experimental procedure from the laboratory guide is that there is no instruction to mix the bottle before use in week three, after two weeks of being left to sit; this may cause an uneven concentration in the bottle and an unpredictable result on the overall calculation of percent chloride. Another potential source of error is that the basic eluent was over-titrated by far more than 3mL of titrant in samples 1 and 2, which may magnify error in reading the buret during the first titration. These errors are discussed in greater detail in the discussion section.

RESULTS

The standardization of the roughly 0.1M sodium hydroxide solution was performed using a solution of potassium hydrogen phthalate of known mass as the analyte and the prepared solution of sodium hydroxide as the titrant. The measured masses of potassium hydrogen phthalate and the volume of sodium hydroxide solution used to titrate the analyte are shown below.

Table 1. Masses of dry KHP and volume of NaOH necessary for titration

	Sample 1	Sample 2	Sample 3	Sample 4
Mass of dry KHP (g)	0.5022	0.4743	0.5009	0.4975
Volume of NaOH to titrate KHP (mL)	23.11	21.90	23.20	22.50

The values from Table 1 were used to calculate the concentration of each standardized solution (Eq. 5), and mean and standard deviation of these solution concentrations were found (A.II.I). These values are displayed below.

Table 2. Calculated standardized NaOH concentrations and statistical summary

Sample 1	Sample 2	Sample 3	Sample 4
0.1064M	0.1061M	0.1057M	0.1083M
Mean	0.1066M		
Standard Deviation	0.001141M		

The measurements from the forward over-titration and back-titration of the solutions of the unknown chlorides are shown below. The unknown sample is the same as that in the gravimetric analysis (3).

Table 3. Mass of unknown chloride sample and volumes of titrant
for over-titration with KHP and back-titration with NaOH

	Sample 1	Sample 2	Sample 3	Sample 4
Mass of unknown (g)	0.3235*	0.3954	0.3954	0.3954
Volume KHP to overtitrated OH ⁻ ions (mL)	8.11	13.18	5.55	4.85
Volume NaOH to back-titrate over-titrated KHP (mL)	28.1	44.9	17.71	14.34

* The chloride solution in sample 1 was different from the chloride solutions in samples 2, 3, and 4. See experimental section for more details.

The measurements from Table 3 were used to calculate the percent mass composition of chloride in the unknown samples (Eq. 6-8), displayed below. A statistical summary of these percent compositions is also displayed below (see A.II.II).

Table 4. Calculated percent mass composition of chloride and statistical summary

Sample 1	Sample 2	Sample 3	Sample 4
27.2%	43.49%	29.8%	36.9%
Sample mean		$34.3\% \pm 3.68\%$	
Sample standard deviation		7.35%	
90% confidence interval for the mean		$34\% \pm 9\%$	

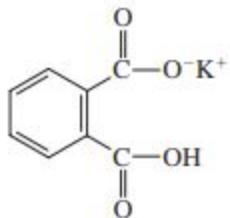
The sample mean of the calculated percent mass composition of chloride in the unknown was $34.3\% \pm 3.68\%$, and the sample standard deviation was 7.35%. The Q-test (see A.II.II) did not predict any statistically-unreliable data points, so no data was discarded. The confidence interval indicates that the actual percent composition of chloride in the unknown is between 25% and 43% at a 90% confidence.

DISCUSSION

Much of the insight on the discussion of the experimental method was based off of content from *Fundamentals of Analytical Chemistry* (2).

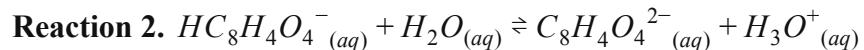
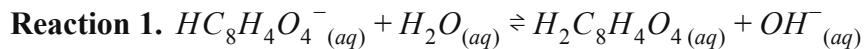
While the concentration of the prepared sodium hydroxide solution may have been calculated from the mass of the sodium hydroxide pellets used and the volume of the solution, a standardization of the solution was an important first step in the experimental methods to ensure accuracy of the solution's concentration. Sodium hydroxide is highly hygroscopic, and measuring the mass may include the mass of some water on the surface of the pellets.

Potassium hydrogen phthalate, commonly abbreviated KHP, was used to standardize the prepared sodium hydroxide solution and over-titrate the eluent. It has a molecular mass of 204.222g/mol (molar masses calculated from elemental molar masses found in *Fundamentals of Analytical Chemistry* (2)). An image of the structure of KHP is displayed below.



(Image courtesy of *Fundamentals of Analytical Chemistry* (2))

0.5g of potassium hydrogen phthalate is dissolved in 50mL of solution. The pH of this solution is 3.35 (see A.I.I. Eq. 3). Hydrogen phthalate is the weak monoprotic acid formed after the dissociation of phthalic acid. It is amphoteric, able to undergo either of the following hydrolysis reactions:



The net ionic equation of the reaction between hydrogen phthalate and sodium hydroxide is shown below. The pH at the equilibrium point is 9.0 (see A.I.I. Eq. 4).



An over-titration using potassium hydrogen phthalate titrant followed by a back-titration using sodium hydroxide titrant was used because of the difficulty of determining the endpoint of the forward titration. Using the phenolphthalein indicator, it is easier to notice the endpoint of the

titration when the color changes from colorless to pink (acid to base) than from pink to colorless (base to acid). Because the forward titration is of the latter type, a back-titration is used to determine exactly how much excess potassium hydrogen phthalate was reacted in the forward titration. Another reason for over-titration was to keep the stored solution in an acidic solution between weeks 2 and 3 of the experimental procedure; if the collected eluent solution (containing the sodium hydroxide ions that had been exchanged with chloride ions) was left basic, the sodium hydroxide ions would react with the glass of the container and with the carbon dioxide in the air, which would yield inaccurate results for a forward titration conducted the following week.

The likely sources of systematic and random error are, ranked in decreasing order of influence on the results, are: not mixing the sodium hydroxide solution before use in the third week, greatly over-titrating the eluent, and the tolerance of normal equipment operation. These are discussed further below.

The sodium hydroxide solution prepared and standardized in the first week was used in the third week. After sitting in a cabinet for two weeks, it is possible that a vertical gradient of sodium hydroxide concentration formed due to the differences in densities between sodium hydroxide and water. This most likely led to a lower-concentration aliquot near the top of the sodium hydroxide solution to be used during the back-titration. A lower concentration of sodium hydroxide would require more to be used as a titrant, which systematically increases the calculation of percent mass composition of chloride.

A gross error that may have greatly influenced the results is in the over-titration of the basic eluent solution. From the calculation in Eq. 7, only a few millimoles of potassium hydrogen phthalate (corresponding to roughly 1mL of 0.4001M potassium hydrogen phthalate) were necessary to titrate the eluent. The excess titrant in the first two samples greatly exceeded the 3mL volume stated by the laboratory manual: there was roughly 7mL and 12mL of extra titrant used in samples 1 and 2, respectively. In the second titration, 44.9mL of sodium hydroxide were needed to back-titrate this excess, over three times the amount necessary in sample 4 (Table 3). Because of the large ratio of concentrations of potassium hydrogen phthalate to sodium hydroxide solutions used in the titrations (0.4001M potassium hydrogen phthalate and 0.1066M sodium hydroxide; roughly 4:1), small errors in the measurements of the volumes in the forward titration with the more concentrated potassium hydrogen phthalate will be amplified into larger errors in the final calculation. This likely contributed to the result from sample 2 being the farthest from the mean.

Precise measurements were taken with the analytical balance to measure the mass of compounds, which have a tolerance of approximately 0.0002g (0.2mg) for the mass of potassium hydrogen

phthalate and mass of unknown solution. Precise measurements were also taken with burets, which have a tolerance of approximately 0.05mL, for the volume of sodium hydroxide during the standardization, potassium hydrogen phthalate during the forward titration, and sodium hydroxide during the back-titration. However, these errors associated with the equipment are small and should not have a major impact on the results.

When compared to the results of the *Gravimetric Determination of Chloride in Unknown Chloride Mixture by Precipitation with Silver Nitrate* (3), the calculated percent mass composition determined doesn't show consistent results. The results are summarized in the table below; see Eq. 6-8 for the calculations of percent mass composition from this lab, and A.II.II. Both analyzed the unknown 1801 chlorine mixture.

Table 6. Summary of percent mass composition of chloride and statistical measures by precipitation gravimetric analysis and ion exchange and titration

	Gravimetric analysis			Ion exchange and titration			
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3	Sample 4
%Cl ⁻	49.83%	52.34%	54.01%	27.2%	43.49%	29.8%	36.9%
Mean %Cl ⁻	$52.06\% \pm 1.22\%$			$34.3\% \pm 3.68\%$			
St. dev.	2.11%			7.35%			
Confidence Interval (90% level)	$52\% \pm 4\%$			$34\% \pm 9\%$			

The calculated values in the first experiment were much more consistent than those of this experiment. Even though there were fewer samples, the standard deviation of the results from the first experiment is 2.11%, less than one-third of the standard deviation from this experiment (7.352%). The range is more extreme as well—in the gravimetric analysis, the range was less than 5%, while the range of the calculated percent chloride values in this experiment was roughly 16%. The smaller spread of the results of the gravimetric analysis indicates that it is the more reliable experiment.

Because the true percent mass composition of chloride in the unknown is unknown, nothing can be said for certain about the accuracy of these two tests. The 90% confidence intervals do not overlap, so the two experiments' results do not agree on a mean value for the percent chloride (to 90% confidence). However, the more erratic results of this experiment likely cause data obtained

from the gravimetric analysis to be more reliable and preferred over the results from this experiment.

In addition to the decreased precision of this experiment's results, the more advanced equipment and more complex experimental procedure in this experiment makes the gravimetric analysis preferable. The previous experiment only required three precise measurements, all using one piece of equipment (the analytical balance), while this experiment required two precise mass measurements and six precise volume measurements, requiring a buret and column as extra equipment. While this experiment did not have the same source of error of photosensitivity of the chemicals (as did the silver compounds in the gravimetric analysis), there was the potential source of error of leaving bases in glass containers or when exposed to air for long periods of time, and the potential source of error of having a standardized solution of sodium hydroxide settle over two weeks so that its concentration became uneven.

CONCLUSIONS

The calculated mean percent mass composition of chloride in the unknown mixture was 34.3% with a standard deviation of 7.35%. A 90% confidence interval of the true mean percent chloride in the mixture is $34\% \pm 9\%$. The range of the calculated percent masses , as well as the standard deviation, are both high, indicating that this method is not very precise. While accuracy of the experiment cannot be determined absolutely, the large spread of the data indicate poor reliability of this experimental method.

The results and procedure were compared to that of gravimetric analysis (3), which analyzed percent chloride of the same unknown mixture. It was concluded that because of the increased simplicity and precision of the earlier experiment, its method is preferred over the current one. The results from the two experiments did not agree with each other (the 90% confidence interval for the gravimetric analysis was $52\% \pm 4\%$, not overlapping the confidence interval from this procedure); the higher precision of the gravimetric analysis suggest that it is more likely to represent the true value than the ion exchange approach.

There were several flaws with this procedure. An error in the given procedure is that it does not mention to stir the sodium hydroxide before use; this is fixed by a simple addition to the laboratory guide, or if the solution is prepared right before use, both of which ensure homogeneity of the solution. Secondly, to fix the gross error of over-titrating by more than the recommended amount, the amount of potassium hydrogen phthalate necessary to titrate the eluent should be calculated before the titration to have a better idea of the true amount necessary so that the slow color change from pink to colorless is noticed.

ACKNOWLEDGEMENTS

The Cooper Union for the Advancement of Science and Art provided the laboratory and safety equipment, as well as the chemicals used in this experiment.

Jonathan Lam was responsible for authoring the Results, References, Acknowledgements, and Appendices sections of this laboratory report, and served as editor for the sections written by Paul Cucchiara.

Paul Cucchiara was responsible for authoring the Abstract, Experimental Methods, Discussion, and Conclusion sections of this laboratory report, and served as editor for the sections written by Jonathan Lam.

Andrew Kim reviewed this report and provided comments. Sun Hung Zhao was consulted for help with the calculation of the pH of the equilibrium point for the titration between potassium hydrogen phthalate and sodium hydroxide.

REFERENCES

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- [2] Skoog, D. A.; West, D. M.; Holler, F. J.; Crouch, S. R. *Fundamentals of Analytical Chemistry*; Brooks/Cole, Cengage Learning: Belmont, CA., 2014; pp 387, 857, A-8.
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APPENDIX I

SAMPLE (REPRESENTATIVE) CALCULATIONS

A.I.I. Calculations for Concentration from Standardization

The estimated mass of sodium hydroxide necessary to create 500mL of 0.1M sodium hydroxide solution, and the estimated mass of potassium phthalate necessary to titrate 25mL of the 0.1M sodium hydroxide, were calculated using equations 1 and 2, respectively. These values were used as approximate values for the mass of sodium hydroxide pellets and potassium phthalate used to make the standardized sodium hydroxide solution.

$$[\text{Eq. 1}] \quad 500\text{mL } 0.1\text{M NaOH} \times \frac{1\text{L}}{1000\text{mL}} \times \frac{0.1\text{mol NaOH}}{\text{L}} \times \frac{39.997\text{g NaOH}}{\text{mol NaOH}} = 2\text{g NaOH}$$

$$[\text{Eq. 2}] \quad 25\text{mL } 0.1\text{NaOH} \times \frac{\text{L}}{1000\text{mL}} \times \frac{0.1\text{mol NaOH}}{\text{L}} \times \frac{\text{mol KHP}}{\text{mol NaOH}} \times \frac{204.222\text{g KHP}}{\text{mol KHP}} = 0.5\text{g KHP}$$

(molar masses were calculated from elemental molar masses found in *Fundamentals of Analytical Chemistry* (2))

The pH of the potassium hydrogen phthalate used to standardize the sodium hydroxide is calculated below using an ICE table. The K_a value is given as the second acid dissociation constant of o-phthalic acid in *Fundamentals of Analytical Chemistry* (2).

$$[\text{Eq. 3}] \quad [\text{HC}_8\text{H}_4\text{O}_4^-] = \frac{0.5\text{g} \times \frac{\text{mol KHC}_8\text{H}_4\text{O}_4}{204.222\text{g}}}{0.050\text{L}} = 0.049\text{M}$$

Table 7. ICE table for dissociation of hydrogen phthalate

	$\text{HC}_8\text{H}_4\text{O}_4^-$ (aq)	H_2O (l)	$\text{C}_8\text{H}_4\text{O}_4^{2-}$ (aq)	H^+ (aq)
Initial	0.049M	N/A	0	0
Change	-x	N/A	+x	+x
Equilibrium	0.049M-x	N/A	x	x

$$K_a = \frac{[\text{H}^+][\text{C}_8\text{H}_4\text{O}_4^{2-}]}{[\text{HC}_8\text{H}_4\text{O}_4^-] - x} \approx \frac{x^2}{[\text{HC}_8\text{H}_4\text{O}_4^-]} = 3.91 \times 10^{-6}$$

$$pH = -\log([\text{H}^+])$$

$$x = [\text{H}^+] = [\text{C}_8\text{H}_4\text{O}_4^{2-}] = \sqrt{K_a \times [\text{HC}_8\text{H}_4\text{O}_4^-]}$$

$$pH = -\log(\sqrt{3.91 \times 10^{-6} \times 0.049\text{M}}) = 3.4$$

The pH of the potassium hydrogen phthalate at the equilibrium point during the titration with sodium hydroxide is shown calculated below using an ICE table. The direction of the reaction is flipped from how it is shown in reaction 3 so that the value for K_b can easily be used.

$$[\text{Eq. 4}] \text{ Volume NaOH} = 0.5 \text{ g } K\text{C}_8\text{H}_4\text{O}_4 \times \frac{\text{mol KHC}_8\text{H}_4\text{O}_4}{204.222 \text{ g}} \times \frac{\text{mol NaOH}}{\text{mol KHC}_8\text{H}_4\text{O}_4} \times \frac{L}{0.1 \text{ mol NaOH}} = 0.0245 \text{ L}$$

$$\text{Total volume solution} = 0.050 \text{ L (KHP)} + 0.0245 \text{ L (NaOH)} = 0.0745 \text{ L}$$

At equivalence point, $[C_8H_4O_4^{2-}] = \text{moles of titrated } HC_8H_4O_4^- = [HC_8H_4O_4^-]$

$$[C_8H_4O_4^{2-}] = [HC_8H_4O_4^-] = \frac{0.5 \text{ g } HC_8H_4O_4^- \times \frac{\text{mol HC}_8\text{H}_4\text{O}_4^-}{204.222 \text{ g}}}{0.0745 \text{ L}} = 0.03287 \text{ M}$$

Table 8. ICE table for reaction between hydrogen phthalate and hydroxide

	$C_8H_4O_4^{2-}$ (aq)	H_2O (l)	$HC_8H_4O_4^-$ (aq)	OH^- (aq)
Initial	0.03287	N/A	0	0
Change	-x	N/A	+x	+x
Equilibrium	$0.03287 - x$	N/A	x	x

$$K_b = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{3.91 \times 10^{-6}} = 2.56 \times 10^{-8}$$

$$K_b = \frac{[HC_8H_4O_4^-][OH^-]}{[C_8H_4O_4^{2-}] - x} \approx \frac{x^2}{[C_8H_4O_4^{2-}]} = 2.56 \times 10^{-8}$$

$$x = [OH^-] = [HC_8H_4O_4^-] = \sqrt{K_b \times [C_8H_4O_4^{2-}]}$$

$$pH = 14 - pOH = 14 - (-\log(\sqrt{2.56 \times 10^{-8} \times 0.03287 \text{ M}})) = 9.0$$

(Only the final result was rounded. Intermediate are displayed rounded arbitrarily for simplicity).

The concentration of the roughly-0.1M sodium hydroxide was calculated from the standardization with KHP using the following calculation.

$$[\text{Eq. 5}] \text{ Concentration NaOH (M)} = \frac{\text{mol NaOH}}{L} = \frac{\text{mass KHP} \times \frac{\text{mol KHP}}{204.222 \text{ g KHP}} \times \frac{\text{mol NaOH}}{\text{mol KHP}}}{(\text{final volume NaOH} - \text{initial volume NaOH})}$$

The calculation for the concentration of the sodium hydroxide solution calculated from the standardization of sample 1 is shown below as a representative calculation. The source of this data can be found in Table 1.

$$(\text{Sample standardization 1}) \text{ Concentration of Sample 1} = \frac{0.5022 \text{ g} \times \frac{\text{mol KHP}}{204.222 \text{ g KHP}} \times \frac{\text{mol NaOH}}{\text{mol KHP}}}{0.02931 \text{ L} - 0.00620 \text{ L}} = 0.1064 \text{ M}$$

A.I.II. Calculations for Percent Mass Chloride

The amount of excess potassium hydrogen phthalate was calculated from the volume of the standardized sodium hydroxide solution used in the back-titration. The molarity of the

standardized solution used in the equation below is the average of the calculated concentrations of the standardized

[Eq. 6] Excess KHP (mol) = (final volume NaOH - initial volume NaOH)

$$\times \frac{0.1066\text{ mol NaOH}}{L} \times \frac{\text{excess mol KHP}}{\text{mol NaOH}}$$

The excess moles of potassium hydrogen phthalate can be used to calculate the amount of potassium hydrogen phthalate that reacted during the forward titration by subtraction:

[Eq. 7] Reacted KHP (mol) = ((total volume KHP) $\times \frac{0.4001\text{ mol KHP}}{L}$) - excess mol KHP

The mass percent chloride of the unknown can be calculated via stoichiometry using this value. The value is multiplied by ten at the end because only one-tenth of the volume of the solutions of the unknown chloride (and thus one-tenth of the measured mass of the unknown) was used in each forward titration.

[Eq. 8] %Cl⁻ = (reacted KHP) $\times \frac{\text{mol OH}^-}{\text{mol KHP}} \times \frac{\text{mol Cl}^-}{\text{mol OH}^-} \times \frac{35.45\text{ g Cl}^-}{\text{mol Cl}^-} \div (\text{mass unknown}) \times 10 \times 100\%$

(molar masses were calculated from elemental molar masses found in *Fundamentals of Analytical Chemistry* (2))

The calculation for the percent mass composition of chloride for sample 1 of the unknown solution is shown below as a representative sample. The source of this data can be found in Table 3. This incorporates Eq. 6 through Eq. 8.

(Sample unknown chloride solution 1)

$$\text{Excess KHP} = (0.03410L - 0.00600L) \times \frac{0.1066\text{ M NaOH}}{L} \times \frac{\text{mol excess KHP}}{\text{mol NaOH}} = 0.002995\text{ mol}$$

$$\text{Reacted KHP} = ((0.01616L - 0.00805L) \times \frac{0.4001\text{ mol KHP}}{L}) - 0.002995\text{ mol KHP} = 0.000249\text{ mol}$$

$$\% \text{Cl}^- = 0.000249\text{ mol KHP} \times \frac{\text{mol OH}^-}{\text{mol KHP}} \times \frac{\text{mol Cl}^-}{\text{mol OH}^-} \times \frac{35.45\text{ g Cl}^-}{\text{mol Cl}^-} \div 0.3235\text{ g} \times 10 \times 100\% = 27.2\%$$

APPENDIX II

COMPUTATION OF STATISTICAL MEASURES OF PRECISION

A.II.I. Statistics of Concentrations from Standardization

The calculations for the mean (\bar{x}), standard deviation (s), standard error (s_m), variance (s^2), and relative standard deviation of the calculated concentration of the standardized sodium hydroxide solution are shown below. Because the data points are roughly spread uniformly over a small range and not heavily skewed, the mean will be used to represent the center and the standard deviation will be used to estimate the range (as opposed to median and IQR). The data shown below were obtained from table 2.

$$n = 4$$

$$\bar{x} = \frac{1}{4}(0.1064M + 0.1061M + 0.1057M + 0.1083M) = 0.1066M$$

$$s = \sqrt{\frac{(0.1064M - 0.1066M)^2 + (0.1061M - 0.1066M)^2 + (0.1057M - 0.1066M)^2 + (0.1083M - 0.1066M)^2}{3}} = 0.001141M$$

A.II.II. Statistics for Percent Mass Chlorides

The calculations for the mean (\bar{x}), standard deviation (s), standard error (s_m), variance (s^2), and relative standard deviation of the calculated percent mass composition of chloride ions in the unknown chloride mixture are shown below. Because the data points are roughly spread uniformly over a small range and not heavily skewed, the mean will be used to represent the center and the standard deviation will be used to estimate the range (as opposed to median and IQR). The data shown below were obtained from table 4.

$$n = 4$$

$$\bar{x} = \frac{1}{4}(27.2\% + 43.49\% + 29.8\% + 36.9\%) = 34.3\%$$

$$s = \sqrt{\frac{(27.2\% - 34.3\%)^2 + (43.49\% - 34.3\%)^2 + (29.8\% - 34.3\%)^2 + (36.9\% - 34.3\%)^2}{3}} = 7.35\%$$

$$s_m = \frac{7.35\%}{\sqrt{4}} = 3.68\%$$

$$s^2 = (7.35\%)^2 = 0.541\%^2$$

$$rel. std. dev. (ppt) = 1000 \times \frac{7.35\%}{34.3\%} = 214$$

The calculation of a 90% confidence interval for the standardized is shown below.

$$90\% \text{ confidence level } t_4 = 2.353$$

$$uncertainty (u) = 2.353 \times \frac{7.35\%}{\sqrt{4}} = 8.65\%$$

$$90\% \text{ confidence interval} = 34\% \pm 9\%$$

A Q test is performed below at a 90% confidence level.

$$range = 43.49\% - 27.2\% = 16.3\%$$

$$90\% \text{ confidence } Q_{crit_4} = 0.76$$

$$Q_{43.49\%} = \frac{|43.49\% - 34.3\%|}{16.3\%} = 0.562 < Q_{crit}$$

$$Q_{27.20\%} = \frac{|27.2\% - 34.3\%|}{16.3\%} = 0.438 < Q_{crit}$$

The Q-values for the extrema do not exceed Q_{crit} , so it is not statistically justified to remove any data points. None of the data points are impossible, so no data points will be discarded. The possible sources of error leading to the large standard deviation are discussed in the discussion.

RESEARCH NOTEBOOK

NAME ?

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Determination of Lead Chloride by Ion Exchange and Back-Titration	6
Spectrophotometric Determination of the Identity of an Unknown Indicator	11
Gas Chromatographic Determination of the Composition of Vapor Mixtures	17

TITLE The Gravimetric Determination of Chloride in a Soluble Unknown
BOOK NO. _____

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Procedure

1. Wash crucibles with distilled water.
2. Heat up crucible in dryer until mass is constant.
3. When crucible mass is constant mass, record as dry mass of crucible.
4. Add filter mats into every crucible.
5. Put crucibles in watchglasses-covered beakers.
6. Heat crucibles in oven at 110°C for at least one hour.
7. Let crucible cool in a slightly open desiccator, and then measure its mass.
8. If its mass has not changed, record masses of crucibles.
9. Get a sample of the unknown from the oven, and let cool in a desiccator.
10. Obtain Using the method of weighing by difference, measure out approximately 0.1 g of the unknown into three clean beakers.
11. Prepare approximately 30mL of solution by adding 2-3mL of 6M HNO_3 was been added to 30mL of water.
12. Pour approximately 10mL of the acidic solution into each beaker with the unknown.

Week 2

13. Add 0.2M AgNO_3 slowly to sample solutions until AgCl is observed to coagulate.
14. Add 3-5 mL of AgNO_3 to each solution; and add separate stirring rods.
15. Heat almost to boiling, then allow digestion for 10 minutes.
16. Add a few drops of AgNO_3 and test for completeness of precipitation.
17. Let beakers cool. Cover with parafilm, and then store in dark place.

Week 3

18. Prepare 250mL of HNO_3 wash solution and add 1mL 6M HNO_3 .
19. Decant each sample's extra (supernatant) liquid through a crucible.
20. Wash precipitate (in beaker) several times with HNO_3 wash solution.
21. Decant washings into crucible. Transfer AgCl to crucible using deionized water and a rubber policeman.
22. Keep washing until no turbidity (cloudiness) is observed when a few drops of KCl are added.
23. Let each precipitate be dried in the oven at 110°C for at least 1 hr.
24. Repeat cooling-heating cycles for drying like cooling the initial crucibles.

Chemical SDS Information HNO_3 , 6M

- ✓ May cause headache, shortness of breath, irritation for any exposure. Exposure to eyes may cause blindness. May cause ulcerations of skin, redness, pain, gastrointestinal pain, nausea, and vomiting (if ingested).

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(HNO₃ Safety Information, continued)

- wear protective equipment and ensure adequate ventilation
- For safe handling, prevent formation of aerosols, follow good hygiene practice
- ✓ Keep away from flame or sources of ignition.

AgNO₃ : 0.2M

Health: Very dangerous after skin contact or ingestion. Contact with eye may result in damage to corneas or blindness. Ingestion will cause gastritis, irritation or respiratory irritation, resulting in burning feeling, coughing or sneezing. Can cause permanent damage to eyes, lungs, skin, and/or stomach on contact.

Safety: Non-flammable. Oxidizing and corrosive.

Handling: Keep container dry, and away from sources of ignition. Do not add to water. Store in light-resistant containers. Keep in cool, well-ventilated storage.

Concentrated HCl : HCl

Health: HCl is very hazardous on contact with skin (corrosive, irritant), severe contact with eyes, or ingestion. HCl is slightly hazardous when inhaled. Vapor may damage membranous tissues. Exposure can cause redness, itching of eyes and breathing when inhaled. Eye exposure may cause death.

Safety: Non-flammable. Non-combustible. Corrosive and poisonous, with respiratory irritation.

Handling: Keep locked up in dry container. Never add water to HCl. Keep away from oxidizing agents and metals.

NaCl (white part of unknown chloride solution)

Health: Fatal if ingested when in contact with skin, eyes, lungs (inhalation) or ingestion. No acute health effects.

Safety: Non-flammable. Non-combustible. Non-corrosive. Emits toxic fumes when heated - decomposition.

Handling: Keep locked up in a cool, dry place. Do not ingest or breathe dust.

Calculations

How much of 0.2M AgNO₃ needed to dissolve 0.0g NaCl.

$$\frac{0.0\text{ g NaCl}}{58.44 \text{ g NaCl}} \times \frac{\text{mol NaCl}}{\text{mol NaCl}} \times \frac{\text{mol AgNO}_3}{\text{mol NaCl}} \times \frac{L \text{ 0.2M AgNO}_3}{0.2\text{ mol AgNO}_3} \times \frac{1000\text{ mL 0.2M AgNO}_3}{L \text{ 0.2M AgNO}_3}$$

$$= \frac{0.0\text{ g}}{58.44 \text{ g}} \times \frac{1}{1} \times \frac{1}{1} \times \frac{0.2\text{ mol}}{0.2\text{ mol}} \times \frac{1000\text{ mL}}{1} = 1.71\text{ mL 0.2M AgNO}_3$$

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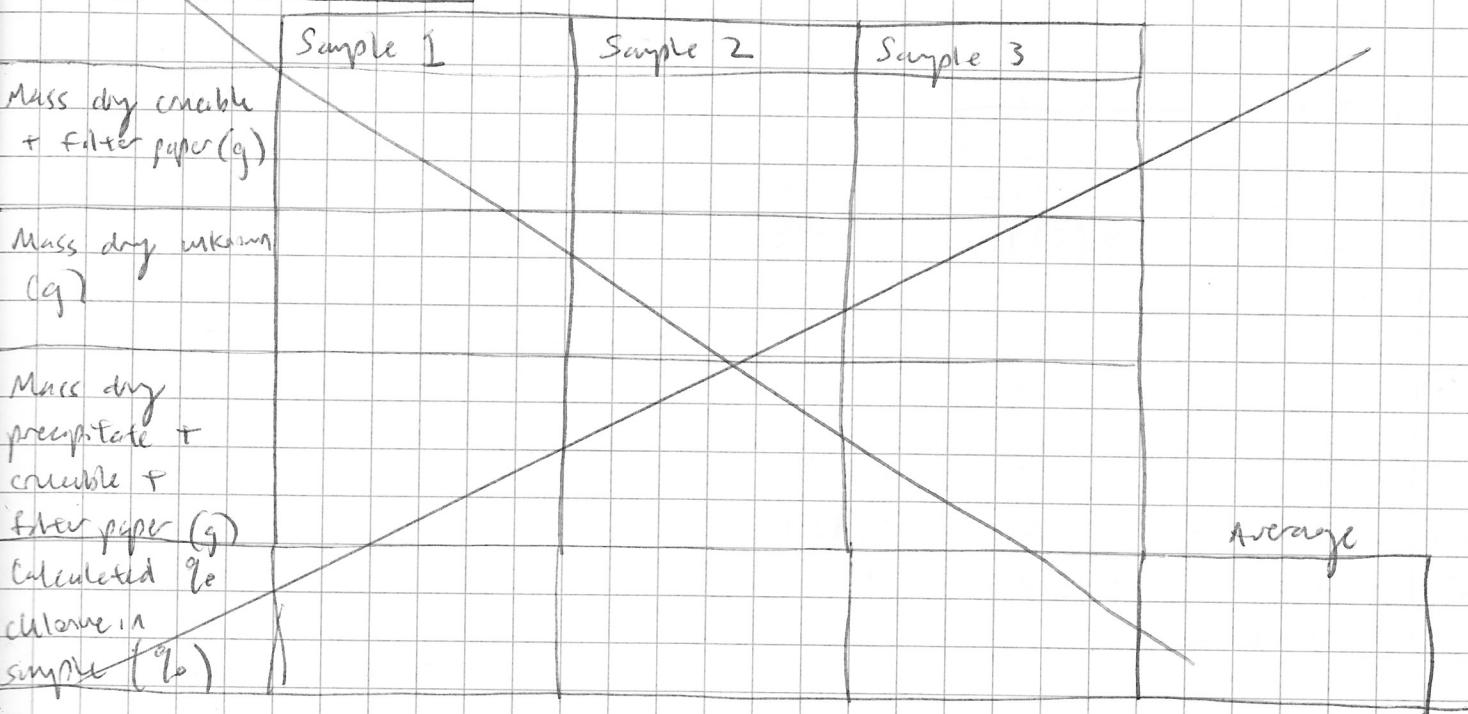
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Project No.

TITLE The Gravimetric Determination of Chloride in a Soluble Chloride Book No.

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80/80

Data CollectionUnknown:Discussion Questions

- a) A colloidal suspension is a form of heterogeneous mixture with very small particles, such that it does not separate when left alone.
- b) Coagulation is necessary to get maximize the size of the AgCl precipitate particles so that the majority are caught by the filter paper.
- c) Coagulation is accomplished by adding Ag^+ ions (as AgNO_3) and heating the colloidal suspension almost to boiling (digestion).
- 2a) Colloidal ions may be introduced if any O_2 from the atmosphere enters the solution.
- b) If carbonate ions form Ag_2CO_3 precipitate, the mass of the ~~chloride~~^{total} precipitate would increase and the % Cl^- would also increase. This would be a systematic overestimation of the % Cl^- .
- c) ~~Excess~~ HNO_3 acid is added to react with any excess CO_3^{2-} ions. to prevent
- 3a) Peptization is the reverting of a coagulated colloid to a dispersed state.
- b) It would cause some of the AgCl to disperse lowering the calculated % Cl^- .
- c) Heating the solution with Nitric acid prevents peptization.
4. The major source of the silver ion is the silver nitrate.
5. a) % Cl^- would be too low, as some would form HClO_4^- and evaporate.
- b) % Cl^- would be too low, as some would form $\text{Cl}_2(g)$ and not be included in the mass.

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Data Collection

Unknown #: 1801

		Sample 1 18.8425	Sample 2. 18.9989	Sample 3 18.9949
Mass dry concrete + filter paper (g)	Trial 1	12.5787 ± 0.005g	18.9971	18.9949
	Trial 2	18.8430	18.9971	18.9926
	Trial 3	18.8442	18.9969	18.9948
	Trial 4	18.8399	18.9965	18.9909
Mass dry unknown (g)		0.1325g	0.1011g	0.1161g
Mass dry precipitate + concrete + filter paper (g)	Trial 1	19.1288	19.2104	18.2536
	Trial 2	19.1070	19.2104	18.2532
	Trial 3	19.1068		18.2544
	Trial 4			

To Page _____

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Project No.

2

Book No.

TITLE The Determination of Percent Chloride by Ion Exchange and

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Procedure week 1

- Measure the mass of one NaOH pellet in a tared watchglass
- Calculate the # of pellets necessary to get correct mass for approximately 0.1 NaOH
- Put pellets in large clean beaker using NaOH spatula
- Add 500mL deionized water
- Store solution in 500mL plastic bottle
- Obtain KHP from over, and place in clean dry beaker
- Measure ~~to~~ the mass of three samples of KHP on the analytical balances by weighing by difference
- Dissolve the KHP in approximately 50mL of ~~water~~ deionized water
- Add some drops of phenolphthalein
- Put a ~~plastic~~ white sheet of paper under the beaker, put a stirring bar in the beaker.
- Rinse barrel with detergent solution followed by tap water, and drain through the valve.
- Rinse with a few mL of deionized water.
- Rinse with a few mL of NaOH stock solution.
- Fill the barrel with NaOH solution above the level of the zero calibration mark.
- Drain some solution so no air is trapped in the barrel.
- Titrate KHP until pink color for half a minute. Repeat for other KHP solutions.

Week 2:

- Obtain a 50mL buret and ~~not~~ clean very well. Make it ^{sure} is free draining at water level
- Put a small glass wool plug in with clean tongs. A long glass rod may be used to gently nudge it to the bottom.
- Test buret by setting it up and making sure water can flow.
- Obtain about 75mL of ion exchange ~~resin~~ resin and carefully pour into a ~~100mL~~ beaker ~~or~~ or a 125mL Erlenmeyer flask using a funnel. Make sure it stays wet at all times.
- Use a plastic funnel to pour the slurry of resin and water into the buret. Top off to avoid uneven packing.
- Add 35mL of NaOH solution at ~~3.5~~ mL/min, 5-10mL at a time.
- Wash in at least 52.5 mL of deionized water. Test pH to make sure
- Measure the mass of a sample by difference by pouring liquid into a clean ~~100mL~~ volumetric flask. It should be between 0.20g and 0.50g. Use deionized water to wash down any additional solid.
- Prepare 100mL of solution by rinsing the tube until it becomes homogeneous.

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TITLE The Determination of Percent Chloride by Ion Exchange and Back Titration

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Procedure (contd.)

- ~~Fill~~ a 10mL pipette with the unknown, and use it to add exactly 10.00mL of the unknown solution to the top of the column. The tip of the pipette should be dried using a Kim wipe.
- Pipette 10.00mL of unknown onto the top of the column.
- Keep adding deionized water at the rate of 3mL/min for 70mL of deionized water.
- Repeat for other two samples of unknown solution.
- Add 2-3 drops of phenolphthalein to a solution.
- Fill a buret with 0.410M KHP. ~~Addition~~
- Add enough KHP to make the solution colorless, and then add 3 additional mL. The total volume of KHP added is recorded.
- Add 2-3 drops of CCl₄ and ~~seal~~ with Parafilm before storing.
- Do the same extraction with the other two samples.

Week 3

- Repeat week 1 titration procedure. Measure the exact amount of standardized NaOH used. Each sample of overtitrated unknown KHP will be titrated.

SDS InformationAmbertite IRA 910

~~Health~~ May cause eye and skin irritation. Wash with soap and water. Use dry chemicals in case of fire. Do not pour down the drain. Keep away from dust. Keep in a well-ventilated place free of dust.

Sodium Hydroxide (NaOH)

Flush with water if it comes in contact with skin or eyes. Strong corrosive agent and irritant. May cause lung damage if inhaled. Neutralize before cleaning up. Do not add water. Keep in a cool place with adequate ventilation.

Carbon Tetrafluoride (CCl₄)

Flush with lots of water if it comes in contact with skin or eyes. Irritant of skin, eyes. Carcinogenic, ~~teratogenic~~, and mutagenic. Toxic to vital organs. Store with proper ventilation.

Potassium hydrogen phthalate (KHC₈H₄O₄)

May cause eye, skin, digestive tract, respiratory tract irritation. Flush with water for at least 15 minutes if in contact with skin or eyes. Weak acid. Avoid strong oxidizing agents and excess heat. Use adequate ventilation. Store in a tightly closed container.

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Phenolphthalein

May cause skin, eyes, digestive system, respiratory tract irritation. May cause fever, hypertension if ingested. May be carcinogenic. Flush with water for at least 15 minutes if on skin or clothes. Avoid dusty conditions. Use only in a chemical fume hood. Do not let this chemical enter the environment. Keep away from strong oxidizing agents and heat. Store in a tightly-closed container in a cool, dry place.

Glass Wool

Irritant for skin and eye contact. Carcinogen. Toxic to lungs and mucous membranes. Wash with water on skin or eye contact. Non-flammable, keep locked tightly in a container.

Calculations

1. # grams of NaOH to prepare 500mL 0.1M NaOH solution:

$$500\text{mL } 0.1\text{M NaOH} \times \frac{1\text{L}}{1000\text{ mL}} \times \frac{0.1\text{ mol}}{1\text{ L}} = 0.05\text{ mol NaOH}$$

$$0.05\text{ mol NaOH} \times \frac{39.997\text{ g NaOH}}{\text{mol NaOH}} = 2\text{ g NaOH}$$

2. # grams KHP necessary to titrate 25mL 0.1M NaOH

$$25\text{mL } 0.1\text{M NaOH} \times \frac{L}{1000\text{mL}} \times \frac{0.1\text{ mol NaOH}}{L} \times \frac{\text{mol KHP}}{\text{mol NaOH}} \times \frac{204.22\text{ g KHP}}{\text{mol KHP}}$$

$$= 0.5\text{ g KHP}$$

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TITLE The Determination of Protein Chloride by Ion Exchange and Backtitration
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Data CollectionStandardization of NaOH solution:

mass of NaOH pellet (g): 2.2115 g

actual # pellets necessary: 10

Total mass pellets: 2.2091 g

	Sample 1	Sample 2	Sample 3	Sample 4
Mass of dry KHP (g)	0.5022 g	0.4793	0.5009 g	0.4997
Volume NaOH added to KHP (mL)	16.08 mL	3.60 mL	1.80 mL	Initial Volume 11.50
-Titrate KHP (mL)	23.125.00 mL	25.50 mL	25.00 mL	Final Volume 37.00

Overtitration and Backtitration of Unknown:

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Mass of unknown (g)	0.5022 g	0.4743 g	0.5009 g	0.3957 g	Initial Volume
Total volume KHP to overtitrated OH- ions	8.05	0.998 g	0.3957	8.92 mL	Final Volume
Volume NaOH to back-titrate overtitrated KHP	16.06	22.10 mL	22.45 mL	28.00 mL	Initial Volume
	6.00 mL	4.30 mL	8.20 mL	19.20 mL	Final Volume
	34.10 mL				25.91 mL

X

Discarded

Calculations

$$\text{Concentration NaOH} = \frac{\text{mass KHP/g}}{204.22 \text{ g KHP}} \times \frac{\text{mol KHP}}{\text{mol NaOH}} \times \frac{1}{(\text{final - initial volume NaOH}) \times \frac{L}{1000 \text{ mL}}}$$

	Sample 1	Sample 2	Sample 3	Sample 4	Average
Concentration NaOH (mol)	0.1064	0.1061	0.1057	0.1083	0.1066

Noteswell 30 mL mol delivered after- discarded sample 2 b/c stopped or slow for a week- not clean stirring rod- spilled a little NaOH- mag of expand not entirely stable

- didn't shake mag
 - brief stopcock let sit and stirring
 - too much in overtitration
 - too much in backtitration in sample 3
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Calculations

$$\text{mL NaOH for back titration} \times \frac{0.1066 \text{ mol NaOH}}{\cancel{0.1066 \text{ mL NaOH}}} \times \frac{\text{mol KHP}}{\text{mol NaOH}} \times \frac{\cancel{0.400 \text{ mol KHP}}}{0.400 \text{ mol KHP}} = \text{excess mol KHP}$$

$$(\text{total mol KHP for neutralization} - \text{excess mol KHP}) \times \frac{\text{mL KHP for titration}}{\text{mL KHP}} = \text{mL KHP for titration}$$

$$\text{KHP for titration} \times \frac{0.400 \text{ mol KHP}}{\cancel{0.400 \text{ mL}}} \times \frac{\text{mol } \text{O}\text{H}^-}{\text{mol KHP}} \times \frac{\text{mol Cl}^-}{\text{mol } \text{O}\text{H}^-} = \text{mol Cl}^-$$

$$\% \text{ chloride} = \text{mol Cl}^- \times \frac{35.45 \text{ g Cl}^-}{\text{mol Cl}^-} \times \frac{1}{\text{mass unknown}} \times 100$$

Overall calculation:

$$\% \text{ chloride} = \left(\frac{\text{total mL KHP} - \left(\text{mL NaOH} \times \frac{0.1066 \text{ mol NaOH}}{1000 \text{ mL NaOH}} \times \frac{\text{mol KHP}}{\text{mol NaOH}} \times \frac{1000 \text{ mL KHP}}{0.400 \text{ mol KHP}} \right)}{\text{total mL KHP}} \times \frac{0.400 \text{ mol KHP}}{1000 \text{ mL}} \times \frac{\text{mol } \text{O}\text{H}^-}{\text{mol KHP}} \times \frac{\text{mol Cl}^-}{\text{mol } \text{O}\text{H}^-} \right) \times \frac{35.45 \text{ g Cl}^-}{\text{mol Cl}^-} \times \frac{100}{\text{mass}}$$

$$\text{For soln 1: } \left((8.1 \text{ mL} - (28.1 \text{ mL} \times \frac{0.1066 \text{ mol}}{1000 \text{ mL}} \times \frac{\text{mol KHP}}{\text{mol NaOH}} \times \frac{1000 \text{ mL KHP}}{0.400 \text{ mol KHP}})) \times \frac{0.400 \text{ mol KHP}}{1000 \text{ mL}} \times \frac{\text{mol } \text{O}\text{H}^-}{\text{mol KHP}} \times \frac{\text{mol Cl}^-}{\text{mol } \text{O}\text{H}^-} \right) \times \frac{35.45 \text{ g Cl}^-}{\text{mol Cl}^-} \times \frac{100}{\text{mass}}$$

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TITLE Spectrophotometric Determination of the Identity of an Unknown ^{Indicator}

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Procedure

- Obtain sample and record sample # of indicator unknown and record sample #1.
- Perform a two-point calibration at pH meter (see laboratory for details).
- 4) Clean probe of pH meter, place in one buffer solution, change slope to 100%, and wait for temperature to equalize ($\approx 2\text{ min.}$). Then, change the "standardize" knob until the correct pH value is displayed. Adjust temperature knob.
- 4) Clean probe with deionized water, and repeat above procedure in other buffer solution. This time, the slope knob should be adjusted and the "standardize" knob should be adjusted to display the correct pH value.
- Dilute 20 drops (1mL) of sample in approximately 25mL 1M acetic acid in a clean 100mL beaker. Repeat in a second beaker (to be used for color comparison).
- Place white sheet of paper under ~~stirrer~~ beaker on stirrer (for contrast). Place beaker (with stir bar) on stirrer. Stir.
- Add 0.1M NaOH drop-wise. Record color vs. pH for dilutions in pH.
- Add 5mL of KH_2PO_4 solution (roughly) to acetic beaker. Add 1M NaCl , while stirring, to the KH_2PO_4 until the pH reaches roughly 2 units above the high end⁺ of the effective pH range of the indicator. Pour into a volumetric flask.
- Add 300mL of indicator sample by volumetric pipet. Add deionized water to the volumetric flask until it reaches 100mL (the final amount with a small pipet), and mix well.
- Store in a dry or lined 250mL Erlenmeyer flask with a rubber stopper.
- Repeat last three steps to produce two more buffered solutions: one with a pH two units below the effective pH range of the indicator, and the other at the middle of the effective pH range.
- Recalibrate the pH meter to include the range of pH's. (using 2.00, 3.00, and 10.00 pH buffered standard solutions), and measure the pH of each solution.
- Add one drop of CaCl_2 to each flask (preservative).
- Calibrate the spectrometer and obtain "nothing" currents.
- Measure and record the absorbance of each solution as a function of the wavelength from 350 to 650nm at 25nm intervals. Determine the two optimal wavelengths (use smaller (5nm) increments near the absorption maxima).
- ~~Perform a serial dilution~~ Prepare solutions with concentrations 0.8 times, 0.6, and 0.4, and 0.2 times that of the low-pH ~~start~~ buffered indicator solution, using a graduated cylinder.
- Measure the absorbance of each of these in a cuvette (use the same one) at the optimal wavelength for the ~~higher~~ low-pH solution.
- Repeat last two steps with high-pH buffered solutions.

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Safety, Health, and Handling1M $\text{HCl}_2\text{H}_3\text{O}_2$ (acetic acid)

Harmful for skin, eyes, and in case of ingestion and inhalation. Corrosive to skin and eyes or other membranes. Toxic to liver and in case of prolonged exposure. Flammable and corrosive. Keep away from heat and source of combustion. Keep in cool, well-ventilated area, in a tightly-sealed grounded container.

1M NaOH (sodium hydroxide)

Extremely hazardous to skin and eyes. Do not inhale or ingest. Rinse immediately with copious amounts of water if contact. Allow victim well-ventilated area if inhaled. Not flammable ~~or~~ corrosive. Corrosive to some metals. Provide ventilation for containers. Do not store near extreme heat, food, oxidizing agents. Store cool and well-ventilated.

2dM KH_2PO_4 (potassium dihydrogen phosphate)

Harmful when it contact with eyes, when inhaled, or when ingested. Mild irritant in case of skin contact. Non-flammable and non-corrosive in presence of glass. Keep in a cool, well-ventilated area.

1.0M HCl (hydrochloric acid)

Very hazardous on contact with skin (corrosive, irritant, permeator.), eyes or ingestion. Slightly hazardous when inhaled. Vapor may damage mucous membranes & lungs. Over-exposure may cause death. Non-flammable and non-combustible. Corrosive and very dangerous to personal. Never add water and ^{always} use protective equipment. Keep locked up in dry container. Keep away from oxidizing agent and metals.

 CCl_4 (carbon tetrachloride)

Very hazardous in contact with skin, eyes, ingestion and inhalation. Contact, permeation, carcinogenic. Toxic to kidneys, lungs, nervous system, liver, mucous membranes. Non-flammable. Keep locked up. wear protective clothing, respiratory equipment if needed, gloves.

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TITLE Spectrophotometric Determination of an Unknown Indicator

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DataUnknown Indicator Sample # 1815

Table 1: color vs. pH

pH	color	pH	color	pH	color	pH	color	pH	color
2.3	yellow	3.8	dark red-	5.3		6.8		8.3	
2.4	yellow	3.9	violet	5.4		6.9		8.4	
2.5	yellow	4.0	dark	5.5		7.0		8.5	
2.6	yellow	4.1	violet	5.6		7.1		8.6	
2.7	yellow	4.2	dark-violet	5.7		7.2		8.7	
2.8	yellow	4.3	violet	5.8		7.3		8.8	
2.9	yellow	4.4	violet	5.9		7.4		8.9	
3.0	yellow	4.5	violet	6.0		7.5		9.0	
3.1	(unwritten)	4.6	violet	6.1		7.6		9.1	
3.2	green-yellow	4.7	violet	6.2		7.7		9.2	
3.3	yellow-green	4.8	violet	6.3		7.8		9.3	
3.4	light green	4.9	violet	6.4		7.9		9.4	
3.5	green	5.0	violet	6.5		8.0		9.5	
3.6	dark yellow-green	5.1	violet	6.6		8.1		9.6	
3.7	dark yellow-green	5.2		6.7		8.2		9.7	

Table 2. pH of buffered solutions

Solution	pH
low pH	1.90
medium pH	3.95
high pH	6.25

Approximate pH effective range of indicator (from Table 1)

High pH: _____

Low pH: _____

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Data Transmittance and

Table 3. Absorbance of Buffered Solutions

Wavelength (nm)	Transmittance			Absorbance		
	Low pH	Int. pH	High pH	Low pH	Int. pH	High pH
350				0.106	0.091	0.087
375				0.148	0.142	0.148
400				0.255	0.187	0.090
425				0.367	0.233	0.026
450				0.371	0.246	0.044
475				0.250	0.189	0.086
500				0.125	0.146	0.181
525				0.042	0.161	0.351
550				0.010	0.264	0.65
575				0.006	0.439	1.076
600				0.005	0.521	1.213
625				0.002	0.090	0.185
650				0.001	0.006	0.016

Last entries are 0.002A

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TITLE Spatophotometric Determination of an Unknown Indicator

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Data

Table 4: Transmittance and Absorbance of Different Concentrations

(Concentration % of buffer concentration)	Transmittance		Absorbance	
	Low pH	High pH	Low pH	High pH
100%			0.326	1.409
89%			0.304	1.090
60%			0.230	0.825
40%			0.153	0.537
20%			0.072	0.262

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TITLE Gas Chromatographic Determination of the Composition of Viper Mixtures
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10/1/90

Procedure

Setup:

- Check which chromatograph model is being used (350 or 400).
- Make sure chromatograph is on, the He is running, and that current is ~~set~~ turned off (should be performed by lab. faculty).
- Use bubble flow meter to ~~check~~ measure carrier gas rate through each column. Flow rate should be 60-65 mL for optimal. (i.e., try to get flow rate close to 1 mL per second). Record flow rate for every column.
- Turn on chart recorder (to make sure chromatograph is grounded properly).
- Double check He is flowing. Disconnect bubble meter. Turn detector on, and set current to 100mA (make sure not to let above about 110mA)
- Connect ~~to~~ netbook. Login: student password: edson(N).
- Connect LabQuest to netbook via USB
- Change "Instrumentation Amp. Filt" ~~to~~ to 0-20mV option. Connect to CH1 of the LabQuest
- Open the Legger Lite program (go to Experiment \rightarrow Setup screens \rightarrow LD menu). Make sure the Inst. Amp. is displayed. Close setup.
- Check to see if instrument reading is relatively stable. (if not, consult teacher.) Choose Experiment \rightarrow Zero. (Should be around 100mV now)
- Select Experiment \rightarrow Data Collection. Choose the following options:
 - ↳ Mode: Time-based
 - ↳ Length: 15 min.
 - ↳ Sampling Rate: 40 samples/min.
- Double click y-axis, scale to manual (Top = 10mV, Bottom = ~~0~~ 0mV)
- Save experimental setup file to USB as "GCMethod".

Data Collection: (see Operating Notes (next page) for more reminders about data collection)

- \rightarrow Student 1 injects sample into input port B of gas chromatograph (see notes on operation)
- \rightarrow Student 2 presses "Collect" on legger lite
- Do not touch setup until data collection period is complete (unless absolutely ^{testing sample} sure all ^{samples} have completely passed through, in which case it may be ended early.)
- When complete, Click File \rightarrow Export As \rightarrow CSV
- Identify peaks on graph by locations, shapes, and retention times. Compare with standard chromatogram and identify components.
- Open "Your latest run".

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Procedure, cont'd.Post-lab shutdown:

- Turn in (capped) syringe to professor
- Shut down computer
- Turn main "power" / "current" switch off.
- Turn "current" dial off.

Notes on Optimizing Operating Parameters and General Operations

- The column is only connected to the B input port
- There must ALWAYS be He passing through the detector.
- Do not touch the gas cylinder or valves.
- Be careful with syringes and do not touch the injection port.
- Fill syringe from polyethylene sample bags.
 - ↳ Gently inject it to avoid sample loss
 - ↳ Quickly inject it to avoid broad base reduce band broadening.
- Write down operating conditions for every trial
- Make sure the syringe and needle have been purged before injecting the next sample
- Three or more injections should be used to optimize flow rate and injection size
- At least three volume sizes of standard gas should be injected to establish the calibration curve for that component of the mixture.

SDS DataOxygen gas, (O₂(g))

Oxidizer: may cause or intensify fire. Protect from sunlight. Store in a well-ventilated place. Contact with rapidly expanding gas may cause burns or fractures. No effects at ^{very} low pressure and temperatures. Take care when gas is under pressure.

Helium gas, (He(g))

May displace oxygen and cause rapid suffocation. Keep tightly and safely sealed under pressure. Protect from sunlight. Store in cool and well-ventilated place. Use equipment rated for cylinder pressure. Get medical attention if health effects persist or are severe. It may be dangerous to give mouth-to-mouth resuscitation without proper training.

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SDS Data, cont'd.

Carbon dioxide ($\text{CO}_2(\text{g})$)

If under pressure, may explode when heated. May displace oxygen and cause rapid suffocation (asphyxiate). May increase respiration and heart rate. Use equipment rated for cylinder pressure. Store it in an upright container. Use outdoors or in a well-ventilated place. Flush contaminated skin or eyes with plenty of water. Get medical assistance if symptoms persist or are severe. Dangerous carbon monoxide when decomposed.

Nitrogen gas ($\text{N}_2(\text{g})$)

Dangerous if under pressure. May displace oxygen and cause rapid suffocation. Protect from sunlight. Store in a well-ventilated place. Flush contaminated skin or eyes with plenty of water. If medical symptoms persist or are severe, get medical assistance. Contact with rapidly expanding gases may cause frostbite or burn on skin and eyes. Decomposition produces harmful nitrogen oxides.

Dry Ice ($\text{CO}_2(\text{s})$)

OK to use

May displace O_2 and cause rapid suffocation. May increase respiration and heart rate. May cause frostbite. In contact with skin or eyes, remove thoroughly with water and remove contaminated clothing. May cause eye irritation. Store placed in dry, cool, well-ventilated area. Keep weight in sealed containers.

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Data Collection

Most of the data will be collected on the LabQuest Mini. The data will be 600 data points of detector reading (mV) versus time (s).

Conditions during standardization teststandard

Table 1: Unknown Sample Conditions

Sample	Flow Rate (mL/min)	Detector Current (mV)	Ambient Temperature (°C)	Ambient pressure (cm Hg)	Injection volume (mL)
1 Standard	57.58 mL /min	100	24.5 °C	29.88 m. Hg	3 mL
2 Standard	67.06 mL /min	100	"	"	3 mL
3 Standard	"	"	"	"	4.0 mL

Table 2: Unknown Sample Conditions

Sample	Flow Rate (mL/min)	Detector Current (mV)	Ambient Temperature (°C)	Ambient Pressure (atm)	Injection Volume (mL)
1 Amorphous	60.06 mL /min	100	25.0 °C	28.8 m. Hg	4.0 mL
2 "	"	"	"	"	"
3 "	"	"	"	"	"
4 Breath	"	"	"	"	"
5 "	"	"	"	"	"
6 "	"	"	"	"	"
7 "	"	"	"	"	"
8 Amorphous water soluble	"	"	"	"	"
9 Beam	"	"	"	"	"

Humidity was 29%.

Standard 1 and sample 6 ~~were~~ had mistakes

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TITLE Gas Chromatograph Determination

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Discussion Questions

- 1). The breath most likely has higher CO_2 concentration and lower O_2 concentration.
The concentration of N_2 is likely very similar in lab air and breath.

~~$p = 1.00 \text{ atm}$ and 34.4°C is 1.16 g .~~

~~$M_{\text{air}} = \frac{28.97}{22.4} = (0.781 \times \frac{28.0}{22.4}) + (0.210 \times \frac{32.0}{22.4})$~~

$$X_{\text{N}_2} = 0.781$$

$$X_{\text{O}_2} = 0.210$$

$$\text{mass percent N}_2 = \frac{0.781 \text{ mol} \times 28.0 \frac{\text{g}}{\text{mol}}}{28.6 \frac{\text{g}}{\text{mol}}} = 0.66 \quad 0.765$$

$$\text{mass percent O}_2 = \frac{0.210 \text{ mol} \times 32.0 \frac{\text{g}}{\text{mol}}}{28.6 \frac{\text{g}}{\text{mol}}} = 0.235$$

2.)

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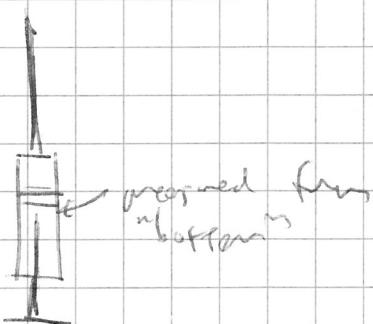
Testing Day Notes

- Flow rate: right to show, like to quicker
- chromatograph Chromatograph ft 1 (400)

Measurement Day Notes

Flow rate A: 10.515 for 10 ml

Flow rate B: 10.475 " "

~~10.475~~

Flow rate: $\frac{10 \text{ ml}}{10.475 \text{ sec}} \times \frac{60 \text{ sec}}{\text{min}} = 57.58 \text{ ml/min}$

At the tip of nozzle

New flow rates $\frac{10 \text{ ml}}{9.995 \text{ sec}} \times \frac{60 \text{ sec}}{\text{min}} = 60.06 \text{ ml/min}$

B: 9.995
A: 9.725

Shift baseline for samples 3, 4 (zero)
experienced over; part of pushing

Bend on needle

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TITLE Gas Chromatogram Determination

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Discussion Questions

1. The breath likely has a higher concentration of O_2 and a lower concentration of O_2 than the surrounding air. The N_2 concentration ~~must~~^(laboratory) should be very similar. The breath should also have higher levels of H_2O gas vapor.

Q1. Density of dry air at 1.00 atm and $34.4^\circ C$ is $1.16 \frac{g}{L}$

Assuming behavior is ideal: $PV = nRT$

$$\text{Volume of 1 mol of dry air: } V = \frac{nRT}{P} = \left(1\text{ mol}\right) \left(\frac{0.08205 \text{ L atm}}{\text{mol K}}\right) \left(\frac{34.4\text{ K} + 273.15}{1.00 \text{ atm}}\right) \\ = 25.2 \text{ L}$$

$$\text{Molar mass dry air} @ 34.4^\circ C = \frac{1.16 \text{ g}}{25.2 \text{ L}} \times \frac{25.2 \text{ L}}{\text{mol}} = \frac{29.3 \text{ g}}{\text{mol}}$$

Assuming air is comprised only of N_2 and O_2 :

Let $x = \frac{\text{mole g of } N_2}{\text{mole g of air}}$,

$y = \frac{\text{mole g of } O_2}{\text{mole g of air}}$,

$$x + y = 100\%$$

$$M_{N_2}x + M_{O_2}y = M_{\text{air}} \Rightarrow M_{N_2}x + M_{O_2}(1-x) = M_{\text{air}}$$

$$\Rightarrow M_{N_2}x + M_{O_2} - M_{O_2}x = M_{\text{air}} \Rightarrow x(M_{N_2} - M_{O_2}) = M_{\text{air}} - M_{O_2}$$

$$\Rightarrow x = \frac{M_{\text{air}} - M_{O_2}}{M_{N_2} - M_{O_2}} = \frac{29.3 \frac{1}{\text{mol}} - 31.998 \frac{1}{\text{mol}}}{28.014 \frac{1}{\text{mol}} - 31.998 \frac{1}{\text{mol}}} = 0.677 \quad 0.684 \quad (\text{mole fraction } N_2)$$

$$y = 1 - x = 1 - 0.677 = 0.323 \quad (\text{mole fraction } O_2)$$

$$\text{Mass fraction } N_2 = \frac{18.014 \frac{g}{\text{mol}} \times 0.677}{29.3 \frac{g}{\text{mol}}} = 0.641 \quad 0.654$$

$$\text{Mass fraction } O_2 = \frac{31.998 \frac{g}{\text{mol}} \times 0.323}{29.3 \frac{g}{\text{mol}}} = 0.355 \quad 0.346$$

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A2

(systematic)

- a) This will introduce an error in the results because the GC does not detect some of the gas (water vapor) in the sample, the amounts of gas measured will be systematically low.
- b) Samples with more water vapor will be more greatly affected. Specifically, the sample of breath will be affected more than the (relatively) dry laboratory air.
- c) The partial pressure of water vapor can be calculated from the relative humidity (equation given) and vapor pressure of water (calculated from temperature). This can be subtracted from the total atmospheric pressure to obtain the partial pressure of the dry air — this can be used normally in the equation to calculate the moles of each gases.

$$\text{i.e.: } RH = 100\% \left(\frac{P_{\text{water}}}{P_{\text{vap}}} \right) \Rightarrow P_{\text{water}} = \frac{RH}{100\%} P_{\text{vap}}$$

$$P_{\text{dry}} = P_{\text{atm}} - P_{\text{water}}$$

P_{dry} = P_{atm} — P_{water}
 actual pressure of measured gases (because GC doesn't detect H_2O).

Calculations from Mendle

$$\text{a) moles } H_2O \text{ in liter of humid air } T = 21.5^\circ K + 273.15^\circ K = 294.65^\circ K$$

$$P_{\text{water}} = \frac{RH}{100\%} P_{\text{vap}} = \frac{RH}{100\%} e^{\frac{47.06}{77.345 + 0.0057T} - 7235T^{-1}} =$$

$$\frac{0.470}{(294.65^\circ K)^{8.2}} e^{77.345 + 0.0057(294.65^\circ K) - 7235(294.65^\circ K)^{-1}} = 1200 \text{ Pa}$$

$$P = 29.56 \text{ in. Hg} \times \frac{3386.39 \text{ Pa}}{\text{in. Hg}} = 100100 \text{ Pa} \quad (\text{not used in this section})$$

$$V = 1 \text{ L (exact)}$$

$$n = \frac{PV}{RT} = \frac{1200 \text{ Pa} \times 1 \text{ L}}{(8314.4598 \frac{\text{J}}{\text{mol} \cdot \text{K}})(294.65^\circ K)} = 4.91 \times 10^{-4} \text{ mol } H_2O \text{ in a Liter of humid air}$$

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E Gas Chromatographic Determination

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2, contd

$$P_{\text{atm}} = 100,100 \text{ Pa} \quad (\text{calculated earlier})$$

mole %:

$$\text{N}_2: 78.08\%$$

$$\text{O}_2: 20.95\%$$

$$\text{Ar}: 0.93\%$$

$$\text{CO}_2: 0.04\%$$

(by ~~Henry's~~ ^{Dalton's} Law of Partial pressures, these are also the partial pressure fractions of the gases)

$$P_{\text{gas}} = (\text{mole \%}) P_{\text{atm}}$$

$$\text{and } n = \frac{PV}{RT} = \frac{P_{\text{gas}} V}{RT} = \frac{(\text{mole \%})(P_{\text{atm}}) V}{RT}$$

$$\text{moles N}_2: \frac{(0.7808)(100100 \text{ Pa})(1 \text{ L})}{(8314.4598 \frac{\text{L Pa}}{\text{mol K}})(294.65 \text{ K})} = 0.03190 \text{ mol N}_2$$

$$\text{moles O}_2: \frac{(0.2095)(100100 \text{ Pa})(1 \text{ L})}{(8314.4598 \frac{\text{L Pa}}{\text{mol K}})(294.65 \text{ K})} = 0.008560 \text{ mol O}_2$$

$$\text{moles Ar: } \frac{(0.0093)(100100 \text{ Pa})(1 \text{ L})}{(8314.4598)(294.65 \text{ K})} = 0.00038 \text{ mol Ar}$$

$$\text{moles CO}_2: \frac{(0.0004)(100100 \text{ Pa})(1 \text{ L})}{(8314.4598 \frac{\text{L Pa}}{\text{mol K}})(294.65 \text{ K})} = 0.0002 \text{ mol CO}_2$$

$$P_{\text{dry}} = P_{\text{atm}} - P_{\text{water}} = 100100 \text{ Pa} - 1200 \text{ Pa} = 98900 \text{ Pa} = \underline{\underline{98900 \text{ Pa}}}$$

now partial pressures are out of P_{dry} instead of P_{atm} ($P_{\text{gas}} = (\text{mole \%}) P_{\text{dry}}$)

$$P_{H_2O} = 1200 \text{ Pa} \quad (\text{from calc})$$

$$P_{N_2} = (0.7808)(98900 \text{ Pa}) = 77200 \text{ Pa}$$

$$P_{O_2} = (0.2095)(98900 \text{ Pa}) = 20700 \text{ Pa}$$

$$P_{Ar} = (0.0093)(98900 \text{ Pa}) = \underline{\underline{919 \text{ Pa}}} = 920 \text{ Pa}$$

$$P_{CO_2} = (0.0004)(98900 \text{ Pa}) = 40 \text{ Pa}$$

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O₂ cont'd8c) cont'd

Because partial pressure is proportional to mole fraction,
 mole fraction ~~can be~~ is equal to fraction of partial pressure to total pressure.

$$\text{i.e., mole fraction } g_i = \frac{P_{gas}}{P_{total}}$$

$$P_{total} = 100100 \text{ Pa}$$

$$\text{mole fraction H}_2\text{O} = \frac{1200 \text{ Pa}}{100100 \text{ Pa}} = 0.0120$$

$$\text{mole fraction N}_2 = \frac{71200 \text{ Pa}}{100100 \text{ Pa}} = 0.711$$

$$\text{mole fraction O}_2 = \frac{20700 \text{ Pa}}{100100 \text{ Pa}} = 0.207$$

$$\text{mole fraction Ar} = \frac{920 \text{ Pa}}{100100 \text{ Pa}} = 0.0092$$

$$\text{mole fraction C}_2\text{H}_5\text{OH} = \frac{40 \text{ Pa}}{100100 \text{ Pa}} = 0.0004$$

(The mole fractions of the four "dry air" gases are slightly lower because of the addition of the H₂O vapor).

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$$\begin{aligned}
 2e) \text{ New moles of air} &= n_{N_2} + n_{O_2} + n_{Ar} + n_{CO_2} + n_{H_2O} \\
 &= 0.03190 \text{ mol} + 0.008630 \text{ mol} + 0.00038 \text{ mol} + 0.0002 \text{ mol} + 0.00049 \text{ mol} \\
 &= 0.04144 \text{ mol}
 \end{aligned}$$

Mole Percentages:

$$\chi_{N_2} = \frac{0.03190 \text{ mol}}{0.04144 \text{ mol}} = 0.7698$$

$$\chi_{O_2} = \frac{0.008630 \text{ mol}}{0.04144 \text{ mol}} = 0.2087$$

$$\chi_{Ar} = \frac{0.00038 \text{ mol}}{0.04144 \text{ mol}} = 0.0092$$

$$\chi_{CO_2} = \frac{0.00002 \text{ mol}}{0.04144 \text{ mol}} = \cancel{0.0005} - 0.0003$$

$$\chi_{H_2O} = \frac{0.000491 \text{ mol}}{0.04144 \text{ mol}} = 0.0118$$

$$\begin{aligned}
 \text{New volume: } V &= \frac{nRT}{P} = \frac{(0.04144 \text{ mol})(8314.4598 \frac{\text{J}}{\text{mol K}})(294.65 \text{ K})}{(100100 \text{ Pa})} \\
 &\approx 1.014 \text{ L}
 \end{aligned}$$

Partial Pressures:

$$P_{N_2} = 100100 \text{ Pa} \times 0.7698 = 77050 \text{ Pa}$$

$$P_{O_2} = (100100 \text{ Pa})(0.2087) = 20890 \text{ Pa}$$

$$P_{Ar} = (100100 \text{ Pa})(0.0092) = 920 \text{ Pa}$$

$$P_{CO_2} = (100100 \text{ Pa})(0.0003) = 40 \text{ Pa}$$

$$P_{H_2O} = (100100 \text{ Pa})(0.0118) = 1180 \text{ Pa}$$

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Identification of an Unknown Indicator by Spectrophotometry Using Two pK_a Calculation Methods

Jonathan Lam and Paul Cucchiara

The Cooper Union
for the Advancement of Science and Art

CH-111 Section C
Professor Robert Q. Topper
November 19th, 2018

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ABSTRACT

Each substance transmits and absorbs a fixed amount of light at a certain wavelength; when plotting absorbance as a function of wavelength, the substance's absorption spectrum is obtained. Spectrophotometry is a specific form of electromagnetic spectroscopy used to determine the identity of substances by measuring their absorption spectra using a spectrophotometer. Spectrophotometry was used to generate absorption spectra for three buffered solutions of the unknown indicator #1815 at different pH levels, as well as to generate Beer's law plots of absorbance versus concentration at peak wavelength values of the indicator. The absorption spectra and the Beer's law plot were used to calculate the pK_a of the indicator by two different calculation methods (one using absorption directly, and the other focusing on concentrations), which was then used to determine the identity of the indicator. Method 2 was deemed more reliable, and it produced a calculated pK_a value of 4.13. The properties of the indicator closely matched the literature values of the bromophenol blue indicator, which has a literature pK_a value of 4.10. Because the standard deviation of the experiment was so low and the calculated pK_a value was so close to the literature value, this spectrophotometry procedure (and pK_a calculation method 2) could be used to identify different substances by their absorbance.

EXPERIMENTAL METHODS

Spectrophotometry was used to determine the identity of an unknown pH indicator. Absorption spectra of three buffered solutions at different pH levels (one below the effective pH range, one in the effective pH range, and one over the effective pH range) were measured using a spectrophotometer and plotted. Optimal wavelengths from the absorption spectra were used to measure the absorbance of different concentrations of the low and high pH buffered solutions to form a Beer's law plot. The absorption spectra and Beer's law plot were then used to estimate the pK_a of the unknown indicator by two calculation methods. The procedure followed was based on the procedure stated in "Spectrophotometric Determination of the Identity of an Unknown Indicator," from *The Official Cooper Union General Chemistry Laboratory Guide* (1). The discussion behind the methods used are explained in more detail in the discussion section.

The indicator was put in acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$ (aq), solution, and its pH was raised by adding sodium hydroxide, NaOH (aq), until the color stopped changing, in order to determine the effective pH range of the indicator. Buffered solutions at a pH of roughly 2 pH units below and above the effective pH range bounds, and a buffered solution in the middle of the pH range, were created to a known concentration. The pH measurements were taken using the Fisher Scientific AB150 pH meter. The pH meter was calibrated before use using an automatic 3-point calibration built into the AB150 pH meter, automatically recognizing the pH 4, pH 7, and pH 10 standard buffer solutions; it was not re-calibrated before measuring the pH of the three prepared buffered solutions because the digital 3-point automatic calibration is more robust than the 2-point, manual calibration outlined in the laboratory manual. Absorption spectra of each of the three buffered solutions were recorded at mostly consistent intervals from 350nm to 650nm wavelengths, and with measurements clustered more closely near the peaks. Optimal wavelengths for the two species (low pH and high pH) were identified. The low pH and high pH solutions were diluted to several concentrations, and a Beer's law plot was obtained by measuring the absorbance of both solutions at their respective optimal wavelengths. The spectrophotometer used was the Thermo Spectronic Genesys 20.

A potential gross error is that, due to inexperience with the pH meter, the tip of the pH meter was not always submerged in the provided equipment buffer solution or in a solution to be measured. Another potential source of error is that the cuvettes were not exactly matched. When filling the four cuvettes with water and measuring the absorbances (to check that the cuvettes were matched), one cuvette had an absorbance value 0.002 higher than the others. Other possible sources of gross error are the formation of bubbles in the cuvettes, the analysis of cuvettes that were not rotated equally in the spectrophotometer, the analysis of cuvettes that are not completely dry, and touching cuvettes with gloves in the region of the cuvette that was analyzed spectrophotometrically. Due to lack of experience with the spectrometer, the cuvettes were

touched with (gloved) hands below the analysis point several times at the beginning of the procedure, especially when washing the cuvettes. A best attempt was made at clearing any glove residue off by washing and drying with Kimwipes. Solutions with noticeable bubbles were discarded, but it is possible that small bubbles too small to notice, but large enough to affect the spectrophotometer reading, were left behind. These potential sources of error are discussed in greater detail in the discussion.

RESULTS

The effective pH range was determined by placing the indicator in a solution with an initial pH of 2.4, and increasing the pH by adding sodium hydroxide until the full color change is observed. The complete recorded data of color versus pH is in Appendix III, Table 7. The effective pH range (and the associated colors of the bounds of the effective pH range) is displayed in Table 1.

Table 1. Effective pH Range and Colors

	pH	Color
Low end of effective range	3.2	yellow
High end of effective range	4.2	violet

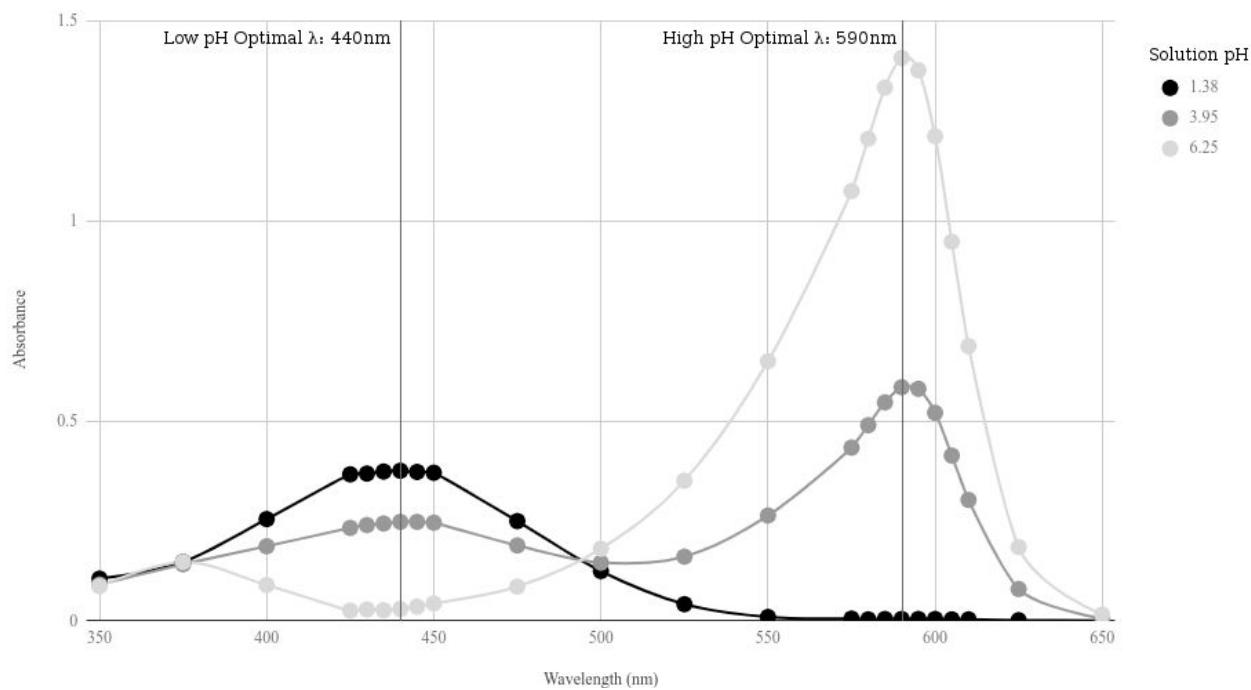
The pH values of the three prepared buffered indicator solutions are displayed in Table 2. The low pH solution was created to be roughly 2 pH units below the low bound of the effective pH range, the high pH solution was created to be roughly 2 pH units above the high bound of the effective pH range, and the pH of the intermediate pH solution was placed in the effective pH range.

Table 2. pH and Optimum Wavelength of Buffered Indicator Solutions

	pH	Color	Optimum Wavelength (nm)
Low pH	1.38	yellow	440
Intermediate pH	3.95	dark violet/red	—
High pH	6.25	violet	590

The absorption spectra of each solution was measured and graphed in Figure 1. The peak values for the low and high pH solutions are indicated on the graphs and recorded in Table 2. These absorption spectra data can be found in textual form in Appendix III, Table 8.

Figure 1: Absorption Spectra of Three pH Indicator Buffered Solutions



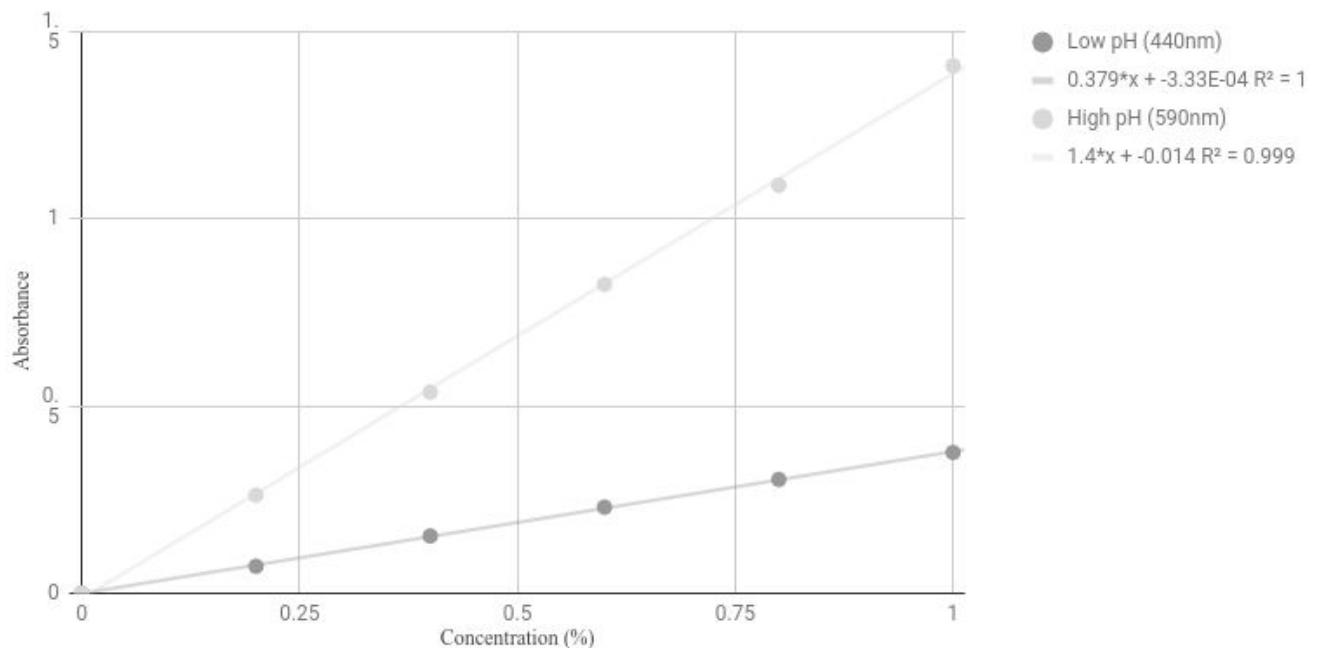
The measured Beer's law data (absorbance versus concentration) of the low and high pH solutions at their optimal wavelengths are displayed in Table 3. The 100% concentration value is the absorbance value from the absorption spectra of the two solutions at their optimal wavelengths. The 0% concentration is an added theoretical point used to strengthen the correlation, because a zero concentration should have zero absorbance.

Table 3. Absorbance vs. Concentration at Optimum Wavelengths for Low and High pH

Concentration (%)	Absorbance	
	Low pH (440nm)	High pH (590nm)
0	0	0
20	0.072	0.262
40	0.153	0.537
60	0.230	0.825
80	0.304	1.090
100	0.376	1.409

The data from Table 3 is displayed graphically in Figure 2. The coefficient of determination (r^2 value) for both linear regressions is very high (1.00 and 0.999 for the low pH and high pH solutions, respectively). The coefficient of determination represents the percent of the variation in the absorbance that is explained by the variation in concentration; the 1.00 and 0.999 mean that roughly 100% and 99% of the variation in absorbance is caused by a variation in concentration, or that there is a very strong linear correlation. By Beer's law, the absorbance should be proportional to concentration, so this is expected.

Figure 2. Absorbance vs. Concentration at Optimum Wavelengths for Low and High pH



The proportionality constant for the relationship between absorbance and concentration for the high and low pH solutions is the slope of the corresponding trendlines on Figure 2. Because both absorptivity (a) and length of light path (b) are constant for each substance, the proportionality constant is $a_{\text{substance}} \lambda b$, where substance is HIn or In⁻ at a specific wavelength. These slopes correspond to the values $a_{\text{HIn}}^{440\text{nm}} b$ (slope of low pH Beer's law graph at low pH optimum wavelength) and $a_{\text{In}^-}^{590\text{nm}} b$ (slope of high pH Beer's law graph at high pH optimum wavelength). These values are stated in Table 4 and used in method 2.

The other two values listed in Table 4 are approximations for the ab products of the non-dominant indicator species at the optimal values. Because the concentrations are so small, a reasonable approximation for these ab values are the absorbance values of the non-optimal solution at the specified wavelength. For example, the approximation for $a_{\text{HIn}}^{590\text{nm}} b$ is 0.030, the absorbance of HIn at 590nm.

Table 4. Beer's Law Absorptivity-Length of Light Path (ab) Products

	Wavelength	
	440nm	590nm
$a_{HI_n} b$	0.379	0.005
$a_{In^-} b$	0.030	1.402

A summary of the pK_a value determined from the two methods are stated in Table 5. It is apparent that the mean pK_a calculated from method 1 is the same as the mean value calculated by method 2 (to the appropriate number of significant figures). These values are obtained from the calculations in A.1.2. And A.1.3., and the mean value for method 1 is obtained from Appendix 2.

Table 5. Summary of pK_a Values

	pK_a
Experimentally determined (method 1 mean)	4.13
Experimentally determined (method 2)	4.13
Literature value	4.10

Statistical measures for the determined pK_a values are displayed in Table 6. While method 1 calculated a pK_a value at every wavelength, method 2 only resulted in 1 pK_a calculation; therefore, method 1 involves a mean, standard error, and standard deviation for the pK_a , while method 2 does not have either. The statistics are obtained in Appendix 2.

Table 6: Methods 1 and 2 Statistical Measures

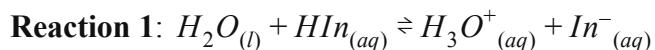
	Mean	Standard Deviation	% Error
Method 1	4.13 ± 0.0107	0.0477	0.8%
Method 2	—	—	0.6%

For method 1, the standard error and standard deviation of the data were very small (0.0107 and 0.0477, respectively). Both methods calculated very similar pK_a values, which had very small percent error values (< 1%). This suggests that the error in the experiment was very small, and that the results (from either method) were very reliable.

DISCUSSION

Much of the insight on the discussion of the experimental method was based off of content from *Fundamentals of Analytical Chemistry* (2).

pH indicators are compounds that can form a weak acid, notated generically as HIn, and a weak (conjugate) base, notated In⁻ (1). These two forms of the indicator have different colors; when the ratio of the two shifts, the color of the indicator changes. The net ionic reaction for the hydrolysis of the indicator acid is shown below.



The acid dissociation constant (K_a) of the indicator acid is the dimensionless product of the concentrations of the products divided by the concentration of the indicator acid. The pK_a of the acid can be calculated using the pH of the solution and the ratio of the concentration of In⁻ to the concentration of HIn, using the Henderson-Hasselbalch equation (see A.1.1. Equation 1); this is useful because of the pH of the solutions are known and the ratio of the concentration of In⁻ to the concentration of HIn can be approximated and calculated by methods 1 and 2 (see A.1.2. and A.1.3. for full calculations).

When the pH of the solution is low, then the $\text{H}_3\text{O}^+_{(aq)}$ concentration is high. By Le Chatelier's principle, the equilibrium shifts left as a result because the reverse reaction is favored, creating a higher concentration of the indicator acid and a lower concentration of its basic form. The opposite is also true: when the pH is high, then the $\text{H}_3\text{O}^+_{(aq)}$ concentration is low, and the equilibrium shifts right by Le Chatelier's principle by favoring the forward reaction, causing the concentration of the basic form to increase and the acidic form to decrease.

Thus, the color of the indicator is the color of HIn at a low pH; the color of the indicator is the color of In⁻ at a high pH. When the pH is low or high enough, one form of the indicator dominates, and the color stops changing when the pH becomes more extreme; the "effective range" of the indicator is the pH range when neither form of the indicator dominates (and thus the color changes in response to changes of pH).

The indicator solutions are pH-sensitive, so they are made into solution with a buffer, potassium dihydrogen phosphate, KH_2PO_4 (aq), before being analyzed. A buffered solution comprises of the salt of a weak acid and its weak conjugate base. This works by Le Chatelier's principle as well: adding acid to the buffer solution will favor the reaction that forms the conjugate base, and adding base to the solution will favor the reaction that forms the conjugate acid, keeping the

acidity relatively constant. The buffer also resists changes to acidity when moderately diluted: dilution will decrease the concentration of hydronium ions, which will cause the system to favor the reaction that produces more hydronium ions by Le Chatelier's principle. As long as the hydronium ions are not excessively depleted, the pH should remain relatively constant. The ability of the buffer to resist changes in pH when diluting is important because the pH was modified to a desired level (two units below the low bound of the effective pH range, the center of the effective pH range, and two units above the high bound of the effective pH range) by adding acid or base before dilution to 100mL of solution. After dilution the pH remained close to the desired pH.

On the plotted absorption spectra, all three absorbances met at the isosbestic point, the point at which absorbance is independent of pH. This point occurs because both indicator species absorb that wavelength of light equally; because the total concentration of indicator species is constant, the total absorbance is equal no matter the pH because the relative amounts of the two indicator species does not matter. This point is significant because the pK_a cannot be calculated from this point using the approximation in method 1 (see A.1.2. Equation 2): would result in the division of zero ($A_{int.} - A_{low}$) by zero ($A_{high} - A_{int.}$), an indeterminate number. The isosbestic point appears around the 490nm wavelength for the indicator (Figure 1). This does not cause a problem with these results because there were no absorbances measured very close to that wavelength, and therefore no division-by-zero indeterminate values.

Two methods were used to calculate the pK_a of the indicator. The first method used the approximation stated and derived in A.1.1. Equation 2 that uses the absorbances of all three solutions at a given wavelength to calculate the ratio of concentrations of $[In^-]$ to $[HIn]$ in the intermediate pH buffered solution at any wavelength (except for the isosbestic point).

Using this method and this equation, a few possible extraneous values for the concentration ratio may be obtained. A zero value means that the numerator of the expression is zero (and the denominator is not); this means that the absorbances of the low and intermediate pH solution are equal, but different from the absorbance of the high pH solution. An indeterminate value is possible at the isosbestic point, as mentioned above. A negative value occurs if the absorbance for the intermediate value is not truly intermediate between the low pH and high pH solution absorbances. The isosbestic point should not be considered because

The second method relies on the fact that the absorbance of a solution with two series is equal to the sum of the absorbances of the two species individually. This is expressed in A.1.3. Equation 4 as the sum of two Beer's law expressions— one for each indicator species. A linear system of two equations can be written to solve for the concentrations. The first equation is the sum of the absorbances of the two species at the low pH optimal wavelength; the second equation is the sum

of the absorbances of the two species at the high pH optimal wavelength. Because absorbance is proportional to concentration, the coefficients of the concentrations of the species are the proportionality constant $a_{species} \lambda b$. The four ab products are tabulated in the Results Table 4, along with a description of the source of the values. Once the system is solved, the ratio of the concentrations of the In^- to HIn is known, and the pK_a can be solved using A.1.1. Equation 1 in the same way as in method 1. The entire calculation for method 2 is detailed in A.1.3.

The value of b (the length of the light path through the solution in the Beer-Lambert equation) does not have to be found because it should be constant for every sample because the cuvettes were matched. The absorptivity of a solution is also constant for each species (HIn and In^-); because both a and b are constant, they can be combined into one proportionality constant for in the Beer's law plot (i.e., the slope of the absorbance vs. concentration).

There are a few notable sources of error that must be mentioned. A possible systematic error could arise from the cuvettes not being evenly matched. Our third cuvette absorbance was measured to be 0.002 while the others had absorbances of 0.000. This would result in slightly greater absorbance values for our third sample because the optical properties of this cuvette would be slightly different from the others. A random error may happen from the formation of bubbles before the samples are tested. If the sample contains small bubbles, the light going through the cuvette will be refracted and the reading on the spectrometer will be incorrect.

A gross error could arise from the uncertainty that all the cuvettes going into the spectrophotometer may have not been completely dry. If there are droplets of sample on the outside of the cuvette, then as light is incident on the cuvette, it may exhibit different refraction patterns and avoid travelling to the other end of the spectrophotometer. Also, the orientation in which the cuvette is placed into the spectrophotometer is uncertain. Although the cuvettes were always placed in the spectrophotometer so that the symbol on the cuvettes were always facing a certain direction, slight changes in this orientation could still impose a significant random error.

There could also be errors in how the results were measured. Instead of using the buffer to zero the spectrophotometer, deionized water was used. This systematic error could result in an increase in each of the values of absorbance because the spectrophotometer will measure the absorbance of the buffer as well as the indicator sample.

The errors, ranked from most to least significant, are the possibility of droplets on the outside of the cuvettes, improperly rotated cuvettes, a slightly-mismatched cuvette, small bubbles forming, and the inherent uncertainty of the equipment (very small). The fact that the standard deviation of the calculations from method 1 were so small and that the calculated pK_a values from both calculation methods would suggest that the data obtained was reliable and that errors were small.

The unknown indicator was determined to most likely be bromophenol blue. Its literature pK_a value is 4.10 (Appendix 4), which is very close to the 4.13 pK_a calculated from both methods. It has a very similar known pH range (literature values 3.0-4.6 are very close to the observed color range of 3.2-4.2) and color change (literature value of yellow to violet matches experimental observations). These values would make

Both methods incorporate approximations into the calculations. Method 1 used A.1.1 Equation 2, which uses the approximation that the concentration of HIn in the low pH solution is equal to the total concentration of indicator species and that the concentration of In^- is equal to the total concentration in the high pH solution. This approximation is useful because the HIn almost completely dominates in the low pH solution, and the In^- almost completely dominates in the high pH solution. Method 2 used A.1.3. Equation 4. There are two equations and four coefficients: the two ab coefficients of the species at their optimal wavelengths were measured, and the two ab coefficients of species not at their optimal wavelengths were estimated using absorbances (which were very near zero). Method 1 used two approximations per wavelength, but the final value was the mean of many values calculated at different wavelengths, so the total effect from number of approximations should be similar in the two methods.

One important difference between the two is that method 1 may include extraneous points. It was discussed earlier that the isosbestic point will return an indeterminate value for the pK_a . At some wavelengths where the absorbance of the intermediate pH solution is very close to the absorbance of the low or high pH solutions, it is possible that the measured intermediate value does not fall between the high and low pH values, causing a negative ratio of In^- to HIn, and also causing an indeterminate value (because of a negative logarithm; this is similar to the data at 375nm). Even at other wavelengths where the absorbance of the intermediate pH value is strictly in between the absorbance of the lower pH solution and the higher pH solution, if the difference between the high and low pH absorbances is small, anomalously large values may result as the denominator of the approximation approaches zero. However, the second method only uses two equations, each equation representing the absorbance of one of the species is at its peak (and the concentration of the other species is very low), eliminating the chance of indeterminate or anomalous values that could arise in method 1.

Even though the final pK_a results from the two methods were very similar, the second method is likely more reliable. It can be argued that the first point (outlier) and the second point (indeterminate), which were removed from method 1's data set with statistical evidence, were anomalies that could not happen using method 2's calculation for the reasons stated above, which strengthens the claim that method 2 is more reliable.

CONCLUSIONS

Using spectrophotometry and the principles behind Beer's law, the pK_a of the unknown indicator #1815 was calculated to be 4.13 ± 0.0107 by the method of using absorbances, and 4.13 by the method of using the sum of concentrations at two different wavelengths. This compares closely to the 4.10 pK_a literature value of bromophenol blue (Appendix 4), which has a similar known pH range (literature values 3.0-4.6) and color change (yellow to violet).

It was decided that the second method was less reliable than the first method. This was because the calculation was inaccurate or indeterminate when the absorbances of the three solutions were very close to one another (when the wavelength is very low, very high, or at the isosbestic point), and it was indeterminate if the intermediate value was not truly indeterminate to the other values. The procedure for method 1 may be improved by having a determining at which wavelengths the absorbances may too close, and the calculated pK_a values from these wavelengths would be omitted.

If rectangular cuvettes were used instead of cylindrical ones, there may some reduction of error, because they enforce that the cuvettes are oriented exactly the same and remain matched very well. It may also be beneficial to use the buffer solution used in the buffered indicator solutions as the blank instead of water because the absorbance of water and the buffered indicator solution may not be exactly the same.

ACKNOWLEDGEMENTS

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Jonathan Lam was responsible for authoring the Abstract, Experimental Methods, Results, Discussion, References, Appendix I, Appendix II, and Appendix III sections of this laboratory report, and served as editor for the sections written by Paul Cucchiara.

Paul Cucchiara was responsible for authoring the Conclusions, Appendix IV sections of this laboratory report, and served as editor for the sections written by Jonathan Lam.

Andrew Kim was consulted when answering the questions in the Discussion section. This includes some of the calculations in A.1.1.

The format of this laboratory report is based off of the “Laboratory Report” section of The Official Cooper Union General Chemistry Laboratory Guide, 19th edition, by Marcus Lay et al.

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APPENDIX I

DERIVATIONS AND SAMPLE (REPRESENTATIVE) CALCULATIONS

A.1.1. Derivations of Henderson-Hasselbalch and Concentration Ratio Approximation

The Henderson-Hasselbalch equation is used to calculate pKa from the pH of the solution and the ratio of the equilibrium concentration of the conjugate base to the equilibrium concentration of the acid. The derivation follows the equation.

$$\text{Equation 1 (Henderson-Hasselbalch Equation). } K_a = \frac{[H^+][In^-]}{[HIn]}$$

$$\begin{aligned} pK_a &= -\log(K_a) = -\log\left(\frac{[H^+][In^-]}{[HIn]}\right) = -\log([H^+]) + \left(-\log\left(\frac{[In^-]}{[HIn]}\right)\right) = pH - \log\left(\frac{[In^-]}{[HIn]}\right) \\ &= pH + \log\left(\frac{[HIn]}{[In^-]}\right) \end{aligned}$$

This equation is used in A.1.2. and A.1.3. to calculate the pKa from the intermediate pH buffer solution, because the pH of the solution and the ratio of the concentrations of $[In^-]$ to $[HIn]$ are found.

In section A.1.2., the ratio of $[In^-]$ to $[HIn]$ in the intermediate solution is calculated at each wavelength can be approximated from the measured absorbances of the three buffered solutions with the following simple equation:

$$\text{Equation 2. } \frac{[In^-]}{[HIn]} = \frac{A_{int.}-A_{low}}{A_{high}-A_{int.}}$$

The derivation of Equation 2 is shown below. Let the constant $c = [HIn] + [In^-]$. Thus:

$c \approx [HIn]$ for the low pH solution,

$c \approx [In^-]$ for the high pH solution,

$$A_{int}^\lambda = a_{HIn}^\lambda b[HIn] + a_{In^-}^\lambda b[In^-],$$

$$A_{lo}^\lambda \approx a_{HIn}^\lambda bc,$$

$$A_{hi}^\lambda \approx a_{In^-}^\lambda c,$$

$$\begin{aligned} \Rightarrow \frac{A_{int}^\lambda - A_{lo}^\lambda}{A_{hi}^\lambda - A_{int}^\lambda} &\approx \frac{(a_{HIn}^\lambda b[HIn] + a_{In^-}^\lambda b[In^-]) - a_{HIn}^\lambda bc}{a_{In^-}^\lambda bc - (a_{HIn}^\lambda b[HIn] + a_{In^-}^\lambda b[In^-])} = \frac{b}{b} \times \frac{a_{HIn}^\lambda ([HIn] - c) + a_{In^-}^\lambda [In^-]}{a_{In^-}^\lambda (c - [In^-]) - a_{HIn}^\lambda [HIn]} \\ &= \frac{a_{HIn}^\lambda (-[In^-]) + a_{In^-}^\lambda [In^-]}{a_{In^-}^\lambda ([HIn]) - a_{HIn}^\lambda [HIn]} = \frac{a_{In^-}^\lambda - a_{HIn}^\lambda}{a_{In^-}^\lambda - a_{HIn}^\lambda} \times \frac{[In^-]}{[HIn]} = \frac{[In^-]}{[HIn]} \end{aligned}$$

(The derivation for Equation 2 uses but does not explain Equation 4 from A.1.3., which states that the sum of the absorbances of two species is equal to the absorbance of a solution containing the both of those species.)

A.1.2. Calculations for pK_a Using Absorbances

An approximation for the ratio of $[In^-]$ to $[HIn]$ (basic and acidic forms of the indicator) in an intermediate pH at a constant wavelength and concentration is Equation 2 (section A.1.1). The pK_a of the solution can be calculated using the pH of the intermediate pH buffer solution and the ratio from Equation 2 using Equation 1 (the Henderson-Hasselbalch Equation). The composite calculation is shown below in Equation 3:

$$\text{Equation 3. } pK_a = pH_{int.} + \log\left(\frac{[HIn]^\lambda}{[In^-]^\lambda}\right) = pH_{int.} + \log\left(\frac{A_{high}^\lambda - A_{int.}^\lambda}{A_{int.}^\lambda - A_{low}^\lambda}\right)$$

Equation 3 is used in the sample calculation below to solve for the pK_a at the 440nm wavelength.

$$pK_a^{440nm} = 3.95 + \log\left(\frac{0.030-0.248}{0.248-0.376}\right) = 4.18$$

A.1.3. Calculation for pK_a Using Concentration

The absorbance of a solution with multiple absorbing species at a constant wavelength is the sum of their absorbances. This is expressed in Equation 3 using Beer's law.

$$\text{Equation 4: } A_\lambda = a_{HIn}^\lambda b[HIn] + a_{In^-}^\lambda b[In^-]$$

This expression can be used to find the concentrations of $[HIn]$ and $[In^-]$ if two simultaneous equations at constant concentration and different wavelengths are used. In this case, the optimum wavelengths are chosen as the wavelengths for a set of these equations for the intermediate pH buffer solution.

$$\begin{cases} A_\lambda = a_{HIn}^\lambda b[HIn] + a_{In^-}^\lambda b[In^-] \\ A_\lambda = a_{HIn}^\lambda b[HIn] + a_{In^-}^\lambda b[In^-] \end{cases}$$

The coefficients in this system are the slope of the Beer's law plot of the low pH solution at its optimal wavelength ($a_{HIn}^{440nm}b$), the slope of the Beer's law plot of the high pH solution at its optimal wavelength ($a_{In^-}^{590nm}b$), the absorbance of the high pH solution at the optimum wavelength for the low pH solution ($a_{In^-}^{440nm}b$), and the absorbance of the low pH solution at the optimum wavelength for the high pH solution ($a_{HIn}^{590nm}b$). The explanation of these values is found in the Discussion section.

The system of equations is solved below using Gauss-Jordan elimination, and the pK_a is found using Equation 3.

$$\left[\begin{array}{cc|c} a_{HIn}^{440nm} & a_{In^-}^{440nm} & A^{440nm} \\ a_{HIn}^{590nm} & a_{In^-}^{590nm} & A^{590nm} \end{array} \right] = \left[\begin{array}{cc|c} 0.379 & 0.030 & 0.248 \\ 0.005 & 1.402 & 0.585 \end{array} \right] \rightarrow \left[\begin{array}{cc|c} 1 & 0 & 0.622 \\ 0 & 1 & 0.415 \end{array} \right]$$

$$[In^-] = 0.415M, [HIn] = 0.622M, \frac{[HIn]}{[In^-]} = 1.50$$

$$pK_a = 3.95 + \log(1.50) = 4.13$$

APPENDIX II

COMPUTATION OF STATISTICAL MEASURES OF PRECISION

The calculations for the mean (\bar{x}), sample standard deviation (s), standard error (s_m), variance (s^2), and relative standard deviation of the pKa values calculated using method 1 are shown below. Because the data points are roughly spread uniformly over a small range and not heavily skewed, the mean will be used to represent the center and the standard deviation will be used to estimate the range (as opposed to the median and IQR). The data analyzed here is from Appendix 3 Table 8.

The data collected at the 375nm wavelength is omitted from the data because its value is undefined (the calculation takes the logarithm of a negative number).

$$n = 21$$

$$\bar{x} = \frac{1}{n} \sum_{k=1}^n (\text{calculated } pK_a)_k = 4.10$$

$$s = \sqrt{\frac{1}{n-1} \sum_{k=1}^n ((\text{calculated } pK_a)_k - (\text{mean } pK_a))^2} = 0.168$$

$$s_m = \frac{s}{\sqrt{n}} = 0.0367$$

$$s^2 = 0.0283$$

$$\text{rel. std. dev. (ppt)} = 1000 \times \frac{s}{\bar{x}} = 41.0$$

A Q test for outliers is performed below at a 90% confidence level.

$$\text{range} = 4.25 - 3.38 = 0.88$$

$$90\% \text{ confidence } Q_{crit_{21}} = 0.295$$

$$Q_{4.2510} = \frac{|4.25 - 4.18|}{0.88} = 0.079 < Q_{crit}$$

$$Q_{3.3760} = \frac{|3.38 - 4.06|}{0.88} = 0.78 > Q_{crit}$$

The Q-value for the maximum does not exceed Q_{crit} , so it is not statistically justified to remove it. However, the Q-value for the minimum value, 3.38, is far above Q_{crit} , so it is statistically justified to remove this data point. Besides the impossible data point removed earlier, this is the only questionable data point that lies far from the rest of the data; the potential causes of error leading to this are discussed in the discussion section.

Now omitting both the indeterminate data point and this statistical outlier, the statistics are re-calculated. These statistical values are used in the discussion and conclusion.

$$n = 20$$

$$\bar{x} = \frac{1}{n} \sum_{k=1}^n (\text{calculated } pK_a)_k = 4.13$$

$$s = \sqrt{\frac{1}{n-1} \sum_{k=1}^n ((\text{calculated } pK_a)_k - (\text{mean } pK_a))^2} = 0.0477$$

$$s_m = \frac{s}{\sqrt{n}} = 0.0107$$

$$s^2 = 0.0228$$

$$\text{rel. std. dev. (ppt)} = 1000 \times \frac{s}{\bar{x}} = 11.5$$

The new standard deviation is much smaller after the removal of the single large outlier. The calculation of a 90% confidence interval for the standardized is shown below.

$$90\% \text{ confidence level } t_{n-1} = t_{19} = 1.729$$

$$\text{uncertainty (u)} = t_{n-1} \times \frac{s}{\sqrt{n}} = 0.0185$$

$$90\% \text{ confidence interval} = 4.13 \pm 0.02$$

The percent error of the pK_a is calculated using 4.10 as the literature value. The percent errors of the mean of method 1 and method 2 is shown below.

$$\% \text{ Error}_1 = \frac{|4.13-4.10|}{4.10} \times 100\% = 0.8\%$$

$$\% \text{ Error}_2 = \frac{|4.13-4.10|}{4.10} \times 100\% = 0.6\%$$

(The difference in the percent errors is due to the fact that the calculated pK_a values are displayed rounded to two decimal places and appear the same but actually vary slightly).

APPENDIX III

pH COLOR CHANGES AND VISIBLE ABSORPTION SPECTRA DATA

The qualitative recorded color of a solution containing the indicator at 0.1 pH unit intervals is shown below. The solution initially consisted mostly of acetic acid with a few drops of indicator, and sodium hydroxide was added until the color change was thought to be completed.

Table 7: pH vs. Color Changes as NaOH is Added

pH	Color	pH	Color	pH	Color
2.3	yellow	3.3	dark yellow-green	4.3	violet
2.4	yellow	3.4	light green	4.4	violet
2.5	yellow	3.5	green	4.5	violet
2.6	yellow	3.6	dark yellow green	4.6	violet
2.7	yellow	3.7	very dark yellow green	4.7	violet
2.8	yellow	3.8	dark red-violet	4.8	violet
2.9	yellow	3.9	dark violet	4.9	violet
3.0	yellow	4.0	dark violet	5.0	violet
3.1	slightly-dark yellow	4.1	dark violet	5.1	violet
3.2	dark yellow-green	4.2	violet		

The absorbance versus wavelength for each of the three buffered indicator solutions is shown below in Table 8. Also shown in the Table 8 is the pK_a value calculated by Equation 3 (section A.1.2) for each wavelength.

Table 8: Absorbance for each Buffered Solution and Calculated pK_a vs. Wavelength

Wavelength (nm)	Absorbance			Calculated pK _a
	Low pH	Medium pH	High pH	
350	0.106	0.091	0.087	3.38
375	0.148	0.142	0.148	—*
400	0.255	0.187	0.090	4.10
425	0.367	0.233	0.026	4.14
430	0.369	0.240	0.029	4.16
435	0.374	0.244	0.027	4.17
440	0.376	0.248	0.030	4.18
445	0.373	0.248	0.036	4.18
450	0.371	0.246	0.044	4.16
475	0.250	0.189	0.086	4.18
500	0.125	0.146	0.181	4.17
525	0.042	0.161	0.351	4.15
550	0.010	0.264	0.650	4.13
575	0.006	0.434	1.076	4.13
580	0.004	0.490	1.207	4.12
585	0.005	0.547	1.335	4.11
590	0.005	0.585	1.409	4.10
595	0.005	0.581	1.378	4.09
600	0.005	0.521	1.213	4.08
605	0.004	0.414	0.949	4.07
610	0.004	0.303	0.688	4.06
625	0.002	0.08	0.185	4.07
650	0.001	0.006	0.016	4.25

* The pKa value is indeterminate because the calculation involved calculating the logarithm of a negative value; see calculations section for more details.

APPENDIX IV

INDICATOR LITERATURE VALUES

In Table 9, a list of literature values for the conjectured unknown indicator, bromophenol blue (see Discussion), are displayed. If multiple values are found, the value used is starred.

Table 9. Indicator Literature Values

Common name	Bromophenol Blue
IUPAC name	2,6-dibromo-4-[3-(3,5-dibromo-4-hydroxyphenyl)-1,1-dioxo-2,1\$1^{\wedge}\{6\}\$-benzoxathiol-3-yl]phenol; <i>National Center for Biotechnology Information</i> (6)
Structural formula	 <i>CRC Handbook of Chemistry and Physics</i> (5)
Molecular formula	$C_{19}H_{10}Br_4O_5S$; <i>CRC Handbook of Chemistry and Physics</i> (5)
Molecular weight	669.960g/mol; <i>CRC Handbook of Chemistry and Physics</i> (5)
pK _a	4.10*; <i>CRC Handbook of Chemistry and Physics</i> (5) 4.1; Kulichenko (3) 4.0; O'Neil (4)
Color changes	Y-B; <i>CRC Handbook of Chemistry and Physics</i> (5) Bromophenol blue (3.0–4.6) Skoog et al. (2)
Effective pH range	3.0-4.6; Skoog et al. (2), <i>CRC Handbook of Chemistry and Physics</i> (5)

Hardware Design Project #1: Braille

Data Logic and Design

Professor Risbud

Jonathan Lam

(with extra credit requirements)

Abstract

DATA INPUTS	DCBA ($\overline{B}A\overline{C}\overline{D}$)	0000 (zero)	0001 (one)	0010 (two)	0011 (three)	0100 (four)	0101 (five)	0110 (six)	0111 (seven)	1000 (eight)	1001 (nine)
BRAILLE PATTERN	W X Y Z	<input type="radio"/>	<input type="radio"/>	<input type="radio"/> <input type="radio"/>	<input type="radio"/>	<input type="radio"/> <input type="radio"/>	<input type="radio"/> <input type="radio"/>	<input type="radio"/>	<input type="radio"/> <input type="radio"/>	<input type="radio"/> <input type="radio"/>	<input type="radio"/> <input type="radio"/>

The “Hardware Design Project #1: Braille” is the second homework assignment and first major assignment for CU’s 2018 summer DLD course. It involves mapping four binary inputs (BCD 0-9) to four binary (LED) outputs, shown above. The challenge is to use as few logical gates as possible. Constraints include being limited to two breadboards, not crossing or bending wires, allowing only one of the six basic logical gates (one of each of the following: 4081 quad dual-input AND, 4071 quad dual-input OR, quad dual-input 4011 NAND, quad dual-input 4001 NOR, 4030 quad XOR, 4069 hex NOT), and a one-week time span. Projects will be graded on quality of work and number of reductions (fewer gates is better).

The extra credit challenge is to complete the task within three days of assignment, and only on one breadboard. This project meets the extra credit requirements by using 14 total gates (four AND, four NOR, four XOR, and two OR gates), staying on one breadboard, and being completed in the three-day timeframe. The main design goal in this solution was to reuse common XOR gates, which can cover many complicated checkerboard patterns. (A video of the working circuit going through all of the inputs can be found at: <https://youtu.be/WiHkPw5qH7o>.)

Attributions

The following sources aided me in the timely completion of this project:

- Anthony Belladonna and Dan Kim: for finding the large XOR pattern in W: $A \oplus C \oplus D$. This was a helpful reduction and included an already-used XOR group: $B \oplus D$. I found a very similar double-XOR pattern in X shortly afterwards.
- Anthony Belladonna: for checking my equations late at night just before building.
- The truth table generator at <http://turner.faculty.swau.edu/mathematics/materialslibrary/truth/>: for providing me multiple sanity checks that my equations worked by drawing truth tables for the inputted boolean expression (note that this does not solve/reduce boolean expressions, and therefore is only used to check work).
- Professor Risbud: for forcing us to try to lower the number of gates, because I only realized when building it how it is more of a piece of advice than a constraint (as opposed to putting less effort into developing more-reduced expressions and being left with a larger mess when building).

Difficulties

My first and greatest challenge was reducing the number of gates. After the first day receiving the assignment, I could barely get the number of gates to under 26 and fitting the spec. After the second day, I got the number down to 19, but this was not satisfactory. Only at the end of the third day could I get it down to 14, the final number. This answer involved reusing common XOR groups and discovering homologies between W and X, and between Y and Z.

When building, a difficulty I had was an abundance of very long wires that took up a lot of space. I noticed that my original ordering of the chips, with two on either side of the inputs, was not the most efficient. Just after beginning to build, I noticed a trend in the boolean expressions from the logic diagram: XORs tend to come before NORs, which tend to come before ANDs, and ORs only come at the end. I adjusted the chips accordingly, putting inputs on one end, and then the XOR, NOR, AND, and OR IC chips (in that order), followed last by the output circuits (LEDs and resistors).

The only lasting problem I had was that because I am attempting to fit all of the circuitry onto one board, there are not many channels to fit wires parallel to the long side of the breadboard. Because there are five channels on each side, and two channels are occupied by IC pins and GRD/Vcc, the recommendation was not to have over four wires parallel to one another in the three remaining channels. However, I had to maximize the use of all five channels, and the best I could do was not to exceed six wires in the five channels. This doesn't exactly fit the recommendation, but is the closest I could manage.

Non-Standard Reductions

The reductions used in this solution can be broken down into two groups: the W and X expressions, and the Y and Z expressions.

W and X expressions:

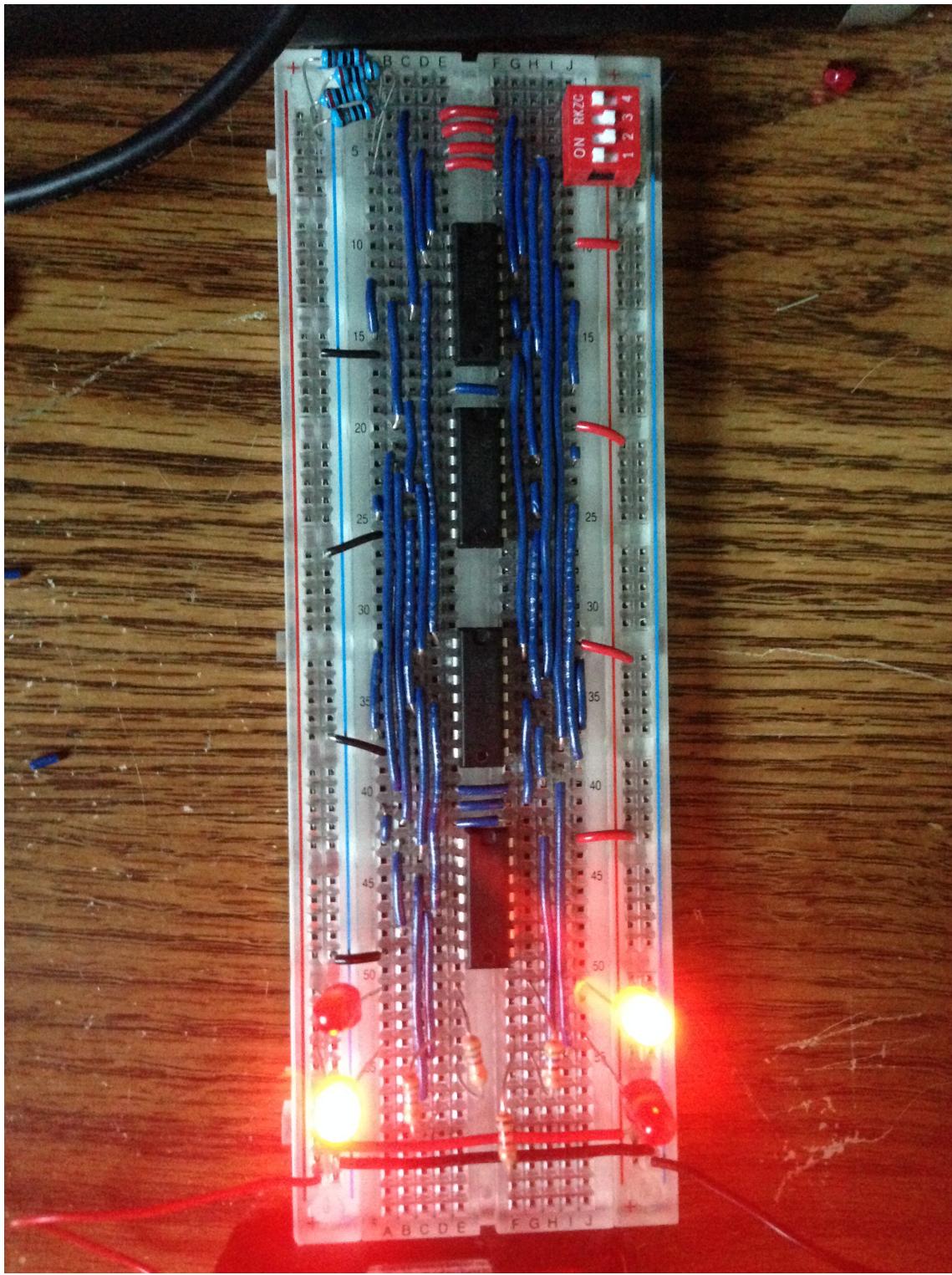
In both W and X, the K-maps were generally in the shape of either wide (W) or tall (X) checkerboard patterns. In W, I first noticed this with Anthony's help (see Attribution). For both of these, almost all of the minterms could be covered with a double-XOR pattern ($A \oplus C \oplus D$ in W; $A \oplus B \oplus D$ in X. See the K-Maps sheet for more information). These re-used the $C \oplus D$ and $B \oplus D$ XOR expressions that are also found in Y and Z.

Y and Z expressions:

Y and Z can be mirrors of one another (each is the other flipped upside down). I was especially determined to find a simple, non-redundant way to express the two. By visual inspection of the K-Maps, it is easy to find a common A.B minterm group. Less obvious are two interesting and similar groups. In Y, there are four separated minterms: $\sim A.B.\sim C.D + \sim A.B.C.\sim D + A.\sim B.\sim C.D + A.\sim B.C.\sim D$, which simplifies to $(A \oplus B).(C \oplus D)$. In Z, four similar minterms form the expression $(A \oplus B).\sim(C \oplus D)$. Notice that these two XOR groups are the same found in W and X. Because these two groups are each used in three separate instances, reusing these subgroups greatly reduces the total number of operations.

Photo of Completed Circuit (Digital Breadboard Image)

(input in image is 1001 (DCBA))



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	AB	W			
CD	00	01	11	10	
00	0	0		c	1
01	1	x	x	0	
11	x	x	x	x	
10	1	1	0	0	

maxterms

	AB	X			
CD	00	01	11	10	
00	1	0	1	0	
01	0	x	x	1	
11	x	x	x	x	
10	1	0	0	0	

maxterms

	AB	Y			
CD	00	01	11	10	
00	0	0	1	0	
01	0	x	x	1	
11	x	x	x	x	
10	0	1	1	1	

minterms

	AB	Z			
CD	00	01	11	10	
00	0	1	1	1	
01	0	x	x	0	
11	x	x	x	x	
10	0	0	1	0	

minterms

BE VERY NEAT & SHOW ALL WORK FOR W,X,Y & Z. STAY WITHIN THE SPACE PROVIDED BELOW

$$W = (A+C+D)(\bar{A}+\bar{B}+\bar{D})(A+\bar{C}+\bar{D})(\bar{A}+\bar{C}+\bar{D}) = (C+(A+D)(\bar{A}+\bar{D}))(\bar{C}+(\bar{A}+D)(\bar{A}+\bar{D})) \bar{A}\bar{B} = (C+A\oplus D)(\bar{C}+\bar{A}\oplus \bar{D}) \bar{A}\bar{B} = \overline{\bar{A}\oplus \bar{B}\oplus D} \bar{A}\bar{B}$$

$$X = (\bar{A}+\bar{B}+\bar{D})(A+\bar{B}+\bar{D})(\bar{A}+\bar{B}+\bar{D})(\bar{A}+\bar{C}) = (A+(\bar{B}+\bar{D})(\bar{B}+\bar{D}))(\bar{A}+(\bar{B}+\bar{D})(\bar{B}+\bar{D})) \bar{A}\bar{C} = (\bar{A}+\bar{B}\oplus \bar{D})(\bar{A}+\bar{B}\oplus \bar{D}) \bar{A}\bar{C} = \overline{\bar{A}\oplus \bar{B}\oplus \bar{D}} \bar{A}\bar{C} = \overline{\bar{A}\oplus \bar{B}\oplus \bar{D}} + AC$$

$$Y = AB + \bar{A}\bar{B}\bar{C}D + \bar{A}\bar{B}CD + A\bar{B}\bar{C} = AB + \bar{A}\bar{B}(\bar{C}D + C\bar{D}) + A\bar{B}(\bar{C}D + C\bar{D}) = AB + (\bar{A}\bar{B} + A\bar{B})(\bar{C}D + C\bar{D}) = AB + (A \oplus B)(C \oplus D)$$

$$Z = A\bar{B} + \bar{A}\bar{B}\bar{C}\bar{D} + \bar{A}\bar{B}C\bar{D} + A\bar{B}\bar{C}D = AB + \bar{A}\bar{B}(\bar{C}\bar{D} + C\bar{D}) + A\bar{B}(\bar{C}\bar{D} + C\bar{D}) = AB + (\bar{A}\bar{B} + A\bar{B})(\bar{C}\bar{D} + C\bar{D}) = AB + (A \oplus B)(\bar{C}\bar{D})$$

***** DO NOT WRITE BELOW HERE *****

IN ADDITION, YOU WILL BE GRADED ON YOUR COMPLIANCE WITH THE FOLLOWING LIST:

- Outputs are displayed on simple LED/resistor detectors driven up to Vcc. Do not expect the gates to "source" the current that is necessary for the output circuit to operate.
- Color code your circuit (for example, consistently use red wire for connections to Vcc (power), black wire for connections to GND (ground), and some scheme for your inputs and outputs).
- Do not "cut down" resistors or LEDs. These are the only components that are not required to be flat on the board.
- Do NOT cross wires over chips. Run wires around them, flat onto the board.
- Bends in wires must be a "soft" or "neat" 90 degrees.
- All wiring must be flat on the board.
- Keep leads as short as possible.

MAJOR
ASSIGNMENT #1:

Jonathan Lam
Prof. Richard
DLID 653
7/18/18

Final Boolean Expressions, Substitutions,
and Gate Count.

$$W = \overline{A \oplus C \oplus D} + A \cdot B$$

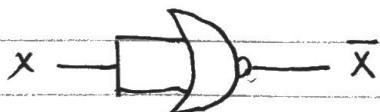
$$X = \overline{A \oplus B \oplus D} + A \cdot C$$

$$Y = A \cdot B + (A \oplus B) \cdot (C \oplus D)$$

$$Z = A \cdot B + (A \oplus B) \cdot (\overline{C \oplus D})$$

Let expressions:		AND	OR	NAND	NOR	XOR	NOT
1.	$e = A \oplus B$					1	
2.	$f = C \oplus D$					1	
3.	$g = A \cdot B$	1				1	
4.	$w = \overline{A \oplus f + g}$				1	1	1
5.	$x = e \oplus d + a \cdot c$	1			1	1	
6.	$y = g + e \cdot f$	1	1				
7.	$z = g + e \cdot f$	1	1				1
total		111	11		11	1111	11

The two NOT gates can be constructed out of NOR
gates like so:



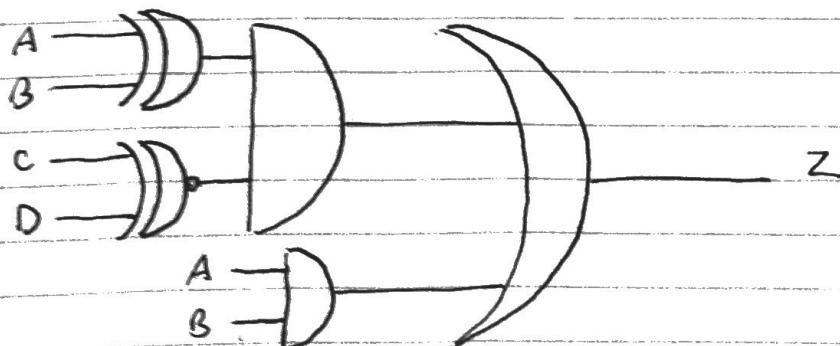
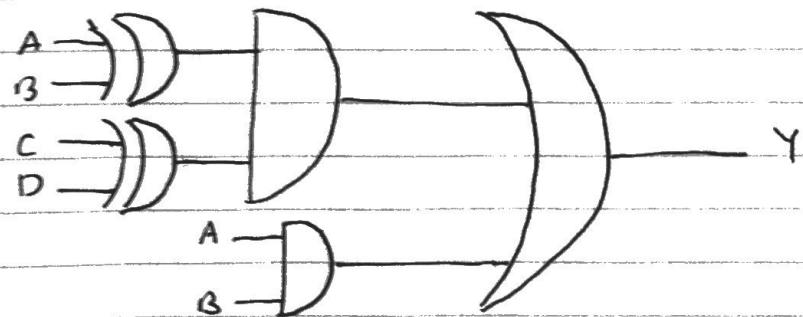
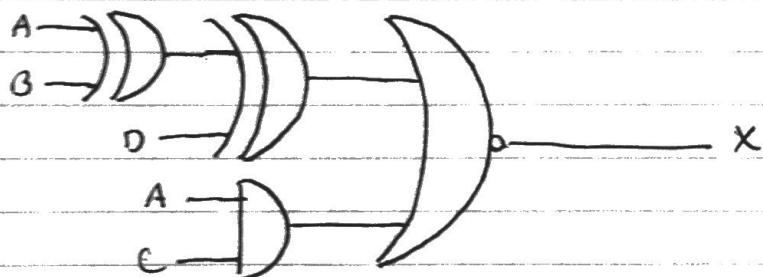
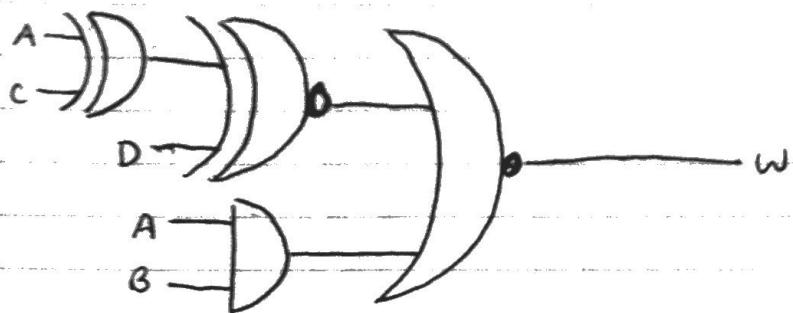
thus, the two NOT gates will be converted to two NOR gates.

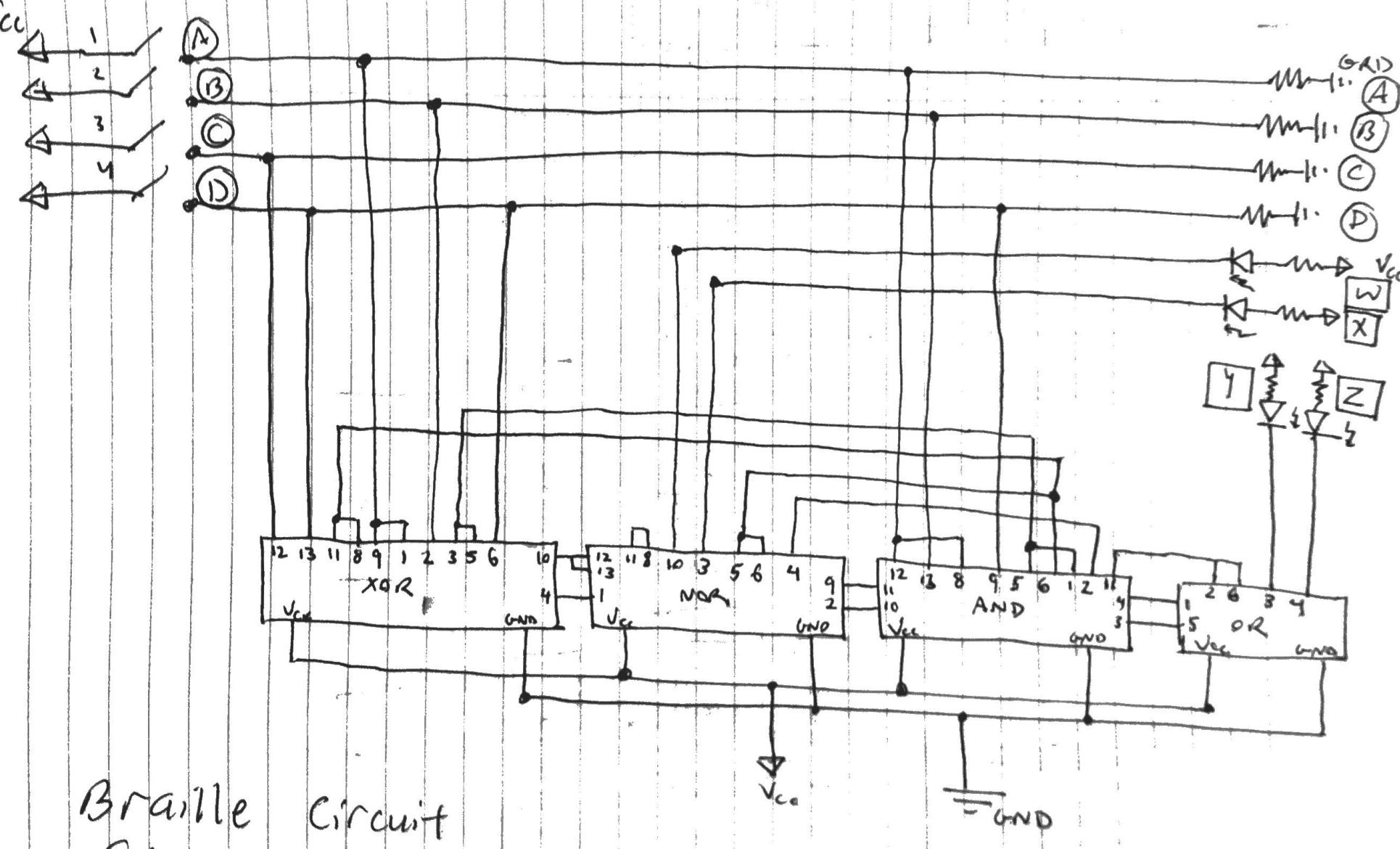
AND	OR	NAND	NOR	XOR	NOT
4	2	0	4	4	0

Thus, the circuit will be constructed from 14
gates (4 chips).

MAJOR ASSIGNMENT #1:

Logic Diagrams





Braille Circuit
Schematic

Jonathan Lam

Additional Work

Attached below is a collection of scanned notes, preparation, and (mostly frustrated and messy) solution-finding. This shows the effort and prior solution attempts to the given problem.

ECE150 Overview

Jonathan Lam

January 14, 2020

Here's some of what I remember from digging up notes from the course, roughly in order. We were told about the Waverly textbook, *Digital Electronics for Logic Design*, 6th or 7th edition, but it was never referenced in class and I never consulted it. Note that this was over the summer, so we may have had more small projects than the students who took DLD over the school year – during the school year, they focused on the three larger projects: Braille, Traffic Light, and the final project.

1 Topics

1.1 Combinational Logic

1. zero vs. one, and connotations (from here on out, (almost always) “light on zero” to get out connotation that “one” always means “on”)
2. basics of number systems (i.e., radix systems, binar, ternary, quaternary, octal, decimal, hex, etc.), binary-coded decimal (BCD), MSB/LSB, ordering with MSB first/least significant bit first (is this called endian-ness?), bit, bytes, nybbles
3. binary (i.e., logical or boolean) operators (AND, OR, NOT, NAND, NOR, XOR) (w/ truth tables, graphical symbol, symbol in a boolean expression)
4. CMOS gates, how to read a datasheet, learn which 4000-series chips to use, propagation delay, maximum ratings, etc.
5. basics of circuit analysis (i.e., Ohm’s law and Kirchoff’s laws) (enough to be able to the resistance given a voltage and desired current, etc.)
6. more tricks and properties of boolean expresssions (e.g., commutativity and associativity of both AND and OR, etc.), De Morgan’s theorem, how to represent XOR in terms of OR, simplifying boolean expressions
7. Karnaugh maps (minterms, maxterms, XOR patterns/translation to boolean expressions), graycode, “don’t cares”

8. Muxes, demuxes, decoders (and why use one over another); the logic necessary to chain/combine them, optimizing implementation to minimum number of muxes needed to map X inputs to an output, etc.
9. Pull-up/down resistors and purpose

1.2 Sequential Logic

1. what is a square wave? practical intro to how to use the 555 in all three modes (not really taught in class, we all kinda just looked up at home)
2. S/R latch design with NAND/NOR (quarter of a D-type F/F) \rightarrow clocked S/R buffer (half of a D-type F/F) \rightarrow full D-type M/S F/F
3. race conditions, state table
4. counters design: asynchronous/synchronous; sequence generators (like synchronous counters, but with arbitrary state tables/mappings)
5. J/K F/F design and purpose (e.g., examine how sequence generating logic is simpler), T-type F/Fs
6. shift registers and modes (shift left, shift right, parallel load, no change), implementation of bidirectional SRs
7. half-adder (review two's complement, fixed-width type overflows) design, full-adder design (half-adder with SRs)
8. debouncing (RC circuit, astable 555, S/R latch or F/F)
9. RAM vs. ROM, progression of ROM to EEPROM, RAM chip parameters, implementing a RAM chip (e.g., how to implement the bidirectional data lines without data loss/corruption)
10. only a very basic introduction to PLAs (definition and motivation). For our class, we never really got far in this discussion and nobody was allowed to use one on our final project. This material is covered in the Computer Architecture course – in my class, we learnt the CUPS language with the GAL22V10 chip).

2 Projects

minterms/maxterms Given a 4-to-1 mapping, write out the minterm and maxterm expressions. For us, we had to map the numbers 0-15 to: 0 if it was a prime between 2 and 13 inclusive, 1 for everything else, and 7,14 were don't cares. Basic logic gates only, 1 breadboard.

braille (major assignment 1) We were all given the same arbitrary 4-to-4 mapping (given a number from 0-9, map it to its 4-dot "braille" representation, where 10-15 are don't cares). Most of the time was spent trying to reduce it to the fewest number of gates possible – usually it can be reduced down to 11-15 gates. Documentation included K-map, boolean expression, boolean symbol representations of the final logic, as well as video (and/or live demo?). Basic logic gates only, maximum 1 chip of each logic gate type, 1-2 breadboards (XC for only one breadboard and handing in early)

counter/sequence generator Build an asynchronous 3-bit down-counter, and, given an arbitrary 8-item sequence, build it synchronously. 1-2 breadboards, D-type F/Fs and basic logic chips allowed.

adder Build a full-adder. I forget the requirements for this.

traffic light I just want to say that fulfilling all parts of this project in any of its forms was widely ruled to be impossible to finish with normal means and using only what was taught in class. However, it is good to at least get students to try and think out all of the implementations, and make some parts extra credit. (We had an all-or-nothing extra credit, so nobody got extra credit)

final project Had to choose teams and prepare proposals that had to be accepted by the prof.

3 Project requirements/expectations (in general, for larger projects)

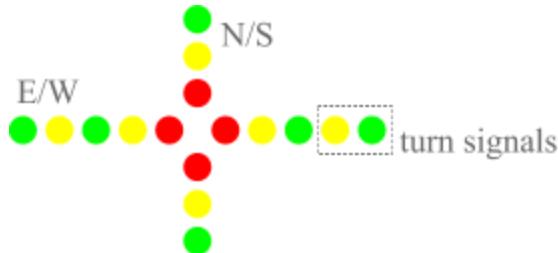
1. boolean expressions and reductions, K-maps, logic diagrams, truth tables (especially for earlier projects)
2. schematics, block/functional diagrams, videos and/or live demo
3. timing diagrams, state tables (for sequential logic circuits)
4. written report (only for braille, traffic light, and final project) w/ diagrams, explanations of nonconventional tricks, acknowledgements

Major Project 2: Traffic Lights

Jonathan Lam
Professor Risbud
DLD Summer 2018

Abstract

The aim of the project is to control a group of LEDs featuring north/south (N/S) and east/west (E/W) directions, as well as green and yellow turn lights for the E/W directions. The layout of the LEDs and the timing of each combination of lights (“stage”) is shown below (the value “X” represents a lit LED, and a blank cell represents an unlit LED). The stages are represented in BCD 0-7.



Stage (CBA)	Duration (s)	N/S			E/W				
		Red	Yellow	Green	Red	Yellow	Green	Yellow turn	Green turn
001	4	X			X				
010	21			X	X				
011	3		X		X				
100	2	X			X				
101	5	X			X				X
110	2	X			X			X	
111	18	X					X		
000	5	X				X			

The extra credit consists of two parts: a pair of two seven-segment displays, one for each direction; and an “accelerate red light” button that pedestrians can press to immediately make the green light in the other direction immediately go down to five seconds, but only if one direction (N/S or E/W) currently has a green light and the green light countdown is over five seconds. The seven segment displays should show display “FF” when their light is red or yellow; a countdown timer beginning when the green light has fifteen seconds remaining; and “EE” when the green light has more than fifteen seconds remaining. The countdown should also blink at a frequency between two and five hertz when the countdown is between seven and zero seconds. The specifications for this project dictate that the LEDs must light on a logical zero, no more than three breadboards be used (for full credit or in order to receive extra credit), and that wires must not overlap or be significantly bent.

The regular credit option was constructed for this project, but the design for the extra credit options are included below. The extra credit was not constructed because I could not find a solution to handle all of the requirements for both extra credit additions while following all the specifications.

Regular Credit Design Process and Final Design

Here is an overview of all of the major possibilities for the regular-credit part of the project: RYG-lights in two directions, and green and yellow turn signals in the E/W direction.

All of the following solutions include a 555 chip that produces a 1Hz astable clock signal. They also all use a “stage counter” that loops through the stages 000-111 (0-7). In every case, the three bits of the stage counter (S_C , S_B , and S_A) are used as address pins to a negative-logic demultiplexer (1:8 DEMUX with the COM pin tied to ground and all outputs pulled-up). Because the demultiplexer uses negative logic and most of the lights (except for the red lights) are only lit on one stage, those LEDs can be connected directly to the demultiplexer outputs. The difference between all of these designs is in the way the stage counter is triggered; i.e., what its clock signal input is.

This base design comprises four chips: a timer (555), stage counter (4024 or 4040), 1:8 demultiplexer (4051), and a two-input NAND chip (4011).

1. Counters with durations stored in RAM or shift registers.

The first idea for a design was to store all of the durations onto a RAM chip or shift registers. Depending on whether pure-binary or base-ten encoded numbers are used, each number would require five bits (binary 21 is 10101) or six bits (decade-mode 21 is 10 0001). The stored duration bits would set the duration for a presetable down-counter (e.g., a pair of 4029 four-bit presetable down counters in binary/decade mode linked together) whose clock was the 1Hz signal from the 555 timer. Once the pair of counters counts down to zero, the counters would send a high CLK signal to the stage counter, advance the shift register five or six bits (or advance the RAM one position), and then preset the countdown timer with the new value. It would also take additional chips (another timer and counter) to make the shift registers shift exactly five or six bits to get to the next stage’s duration.

The benefit of this design is that if the specifications are changed, the stored values can easily be changed because they are hardcoded in. However, the problem with using RAM is that, while space-efficient, the duration data must be inputted serially, which would either require additional logic or be inputted manually. The opposite is true for using shift registers: while it is simple to hardcode in duration values, storing data for eight stage durations will be between 40 and 48 bits in length, which would require many shift registers and take up much space.

2. Counter with MUXes linked together.

The second idea was to use an up-counter whose clock would be the 1Hz signal from the 555 timer. The counter would reset when it reached 60, for the total duration of the traffic light loop. Then, some number of MUXes would use the counter’s bits to select whether to increase the stage (1) or not (0).

This solution works by tying each input that corresponds to a second in time that should advance the state to 1, and the rest to 0. The only difference between the different solutions is the number of MUXes, and therefore the amount of pre-processing necessary. The seconds in time that should be connected to 1 are shown below, and all of the rest should be tied to 0. Finally, the base-design demultiplexer output from 000 should be connected to the RESET pin of the counter, causing the countdown to reset after a full cycle (60 seconds).

Stage (CBA)	Duration	Elapsed Time (time begins at 0)	Binary representation (FE DCBA)
001	4	3	00 0011
010	21	24	01 1000
011	3	27	01 1011
100	2	29	01 1101
101	5	34	10 0010
110	2	36	10 0100
111	18	54	11 0110
000	5	59	11 1011

Using eight MUXes, no logic would be needed, and each of the sixty input pins will be tied to GND or Vcc. Using four MUXes, “D-logic” (inverters only) would be needed for pre-processing. Using two MUXes, “DE-logic” is necessary for pre-processing, but this may take multiple logic chips (AND, OR, NAND, NOR, XOR, and/or NOT ICs). It is also possible to use one MUX and 8:1 pre-processing or zero MUXes and similar logic with only logic, but this is impractical because of the amount of logic necessary to map the six-bit Karnaugh map. Zhihao Wang helped worked through solutions with different numbers of MUXes.

While this MUX logic is simple and space-efficient using either two or four MUXes, it makes the extras difficult to integrate into the project because there is no downcounter that can easily be used to determine how much time is left in the stage, and therefore was not selected as the final design.

3. Map current stage bits to next stage’s duration.

Like the first idea, this design involves pre-setting a count-down timer with the five- or six-bit duration of the next stage. However, unlike the first idea, it involves using logic with the current stage’s bits to preset the duration of the next stage, instead of having hardcoded values. This generally uses fewer chips than the other two solutions, and can easily fit onto two breadboards. This idea was first suggested by Dan Kim.

This table shows a mapping using the six-bit base-ten representation (FE represent the tens-place digit; DCBA represent the ones-place digit).

Stage (CBA)	Duration (s)						
	Decimal	F	E	D	C	B	A
001	4	0	0	0	1	0	0
010	21	1	0	0	0	0	1

011	3	0	0	0	0	1	1
100	2	0	0	0	0	1	0
101	5	0	0	0	1	0	1
110	2	0	0	0	0	1	0
111	18	0	1	1	0	0	0
000	5	0	0	0	1	0	1

3a. Using basic logic gates to map bits to next stage's duration.

This is the more straightforward solution. The data inputs to the preset JAM inputs on the counters (T_F through T_A) can be written as functions of S_C , S_B , and S_A . This can be done the same was as creating any other three-input map: by creating Karnaugh maps for each output and creating reduced mathematical functions to implement. Because a demultiplexer will be used with only the correct stage corrected, it can be used to simplify functions that are only 1 for one stage (F, E, and D). D_{XXX} refers to an output of the demultiplexer. Here is one example set of expressions only requiring seven logic gates.

$$\begin{aligned}
 T_F &: \overline{D_{010}} \\
 T_E &: \overline{D_{111}} \\
 T_D &: \overline{D_{111}} \\
 T_C &: S_A + S_B + (S_A \oplus S_B \oplus S_C) \cdot S_C \\
 T_B &: (S_B \oplus S_C) \cdot (S_A + S_B) \\
 T_A &: S_A \oplus S_B \oplus S_C
 \end{aligned}$$

3b. Using the DEMUX to map bits to next stage's duration.

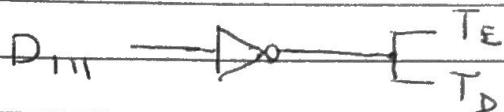
This solution uses the demultiplexer already included in the base solution to simplify logic without using additional logic gates, and is used in the final design. It only requires NOT and NAND gates for the logic. Using a decoder/demultiplexer to simplify the logic was also suggested by Dan Kim.

$$\begin{aligned}
 T_F &: \overline{D_{010}} \\
 T_E &: \overline{D_{111}} \\
 T_D &: \overline{D_{111}} \\
 T_C &: \overline{D_{000} \cdot D_{100} \cdot D_{111}} \\
 T_B &: \overline{D_{010} \cdot D_{011} \cdot D_{101}} \\
 T_A &: \overline{D_{001} \cdot D_{010} \cdot D_{100} \cdot D_{111}}
 \end{aligned}$$

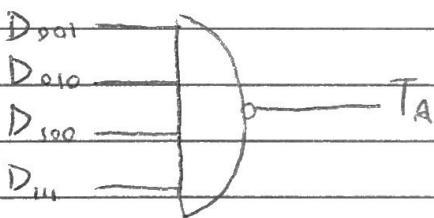
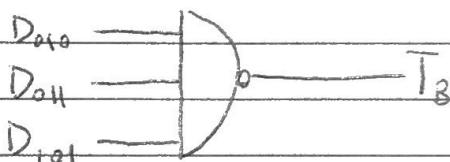
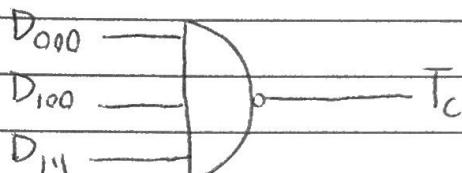
TRAFFIC LIGHT LOGIC DIAGRAMS

JONATHAN LAM

countdown timer JAM inputs ($T_F - T_A$)



(D_{xxx} are demultiplexer outputs with negative logic)



outputs (LEDs)

$D_{000} \rightarrow Y_{E/W}$

$D_{010} \rightarrow G-N/S$

$D_{011} \rightarrow Y-N/S$

$D_{101} \rightarrow U/T$

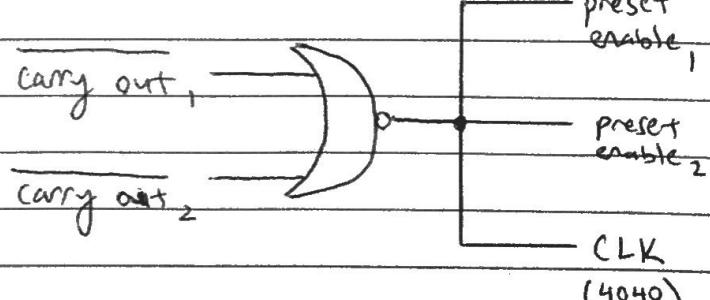
$D_{110} \rightarrow Y/T$

$D_{111} \rightarrow G-E/W$

$D_{000} \rightarrow D \rightarrow R_{E/W}$

$D_{010} \rightarrow D \rightarrow R_{N/S}$

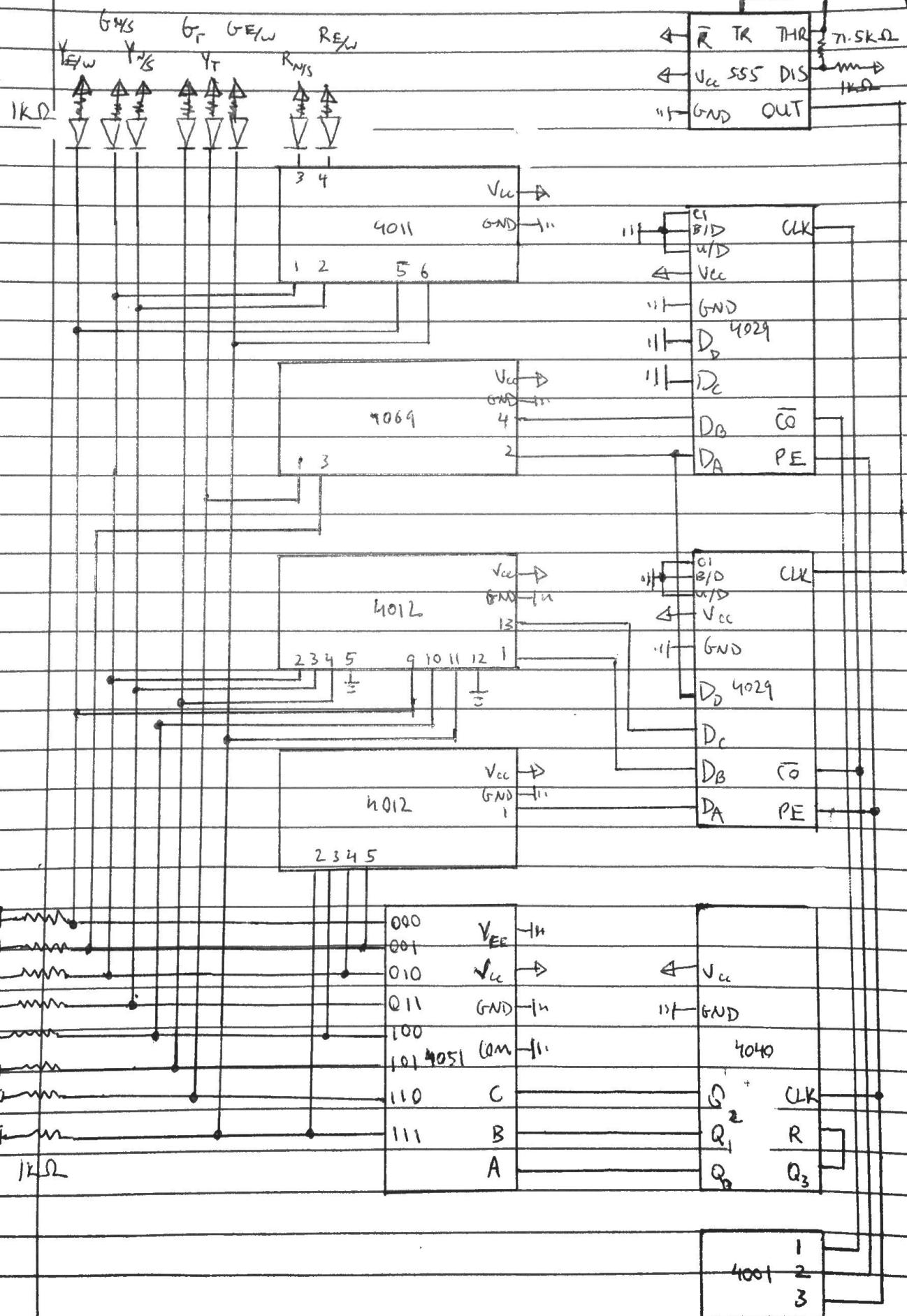
advance starte clock



CLK
(4040)

TRAFFIC LIGHT SCHEMATIC

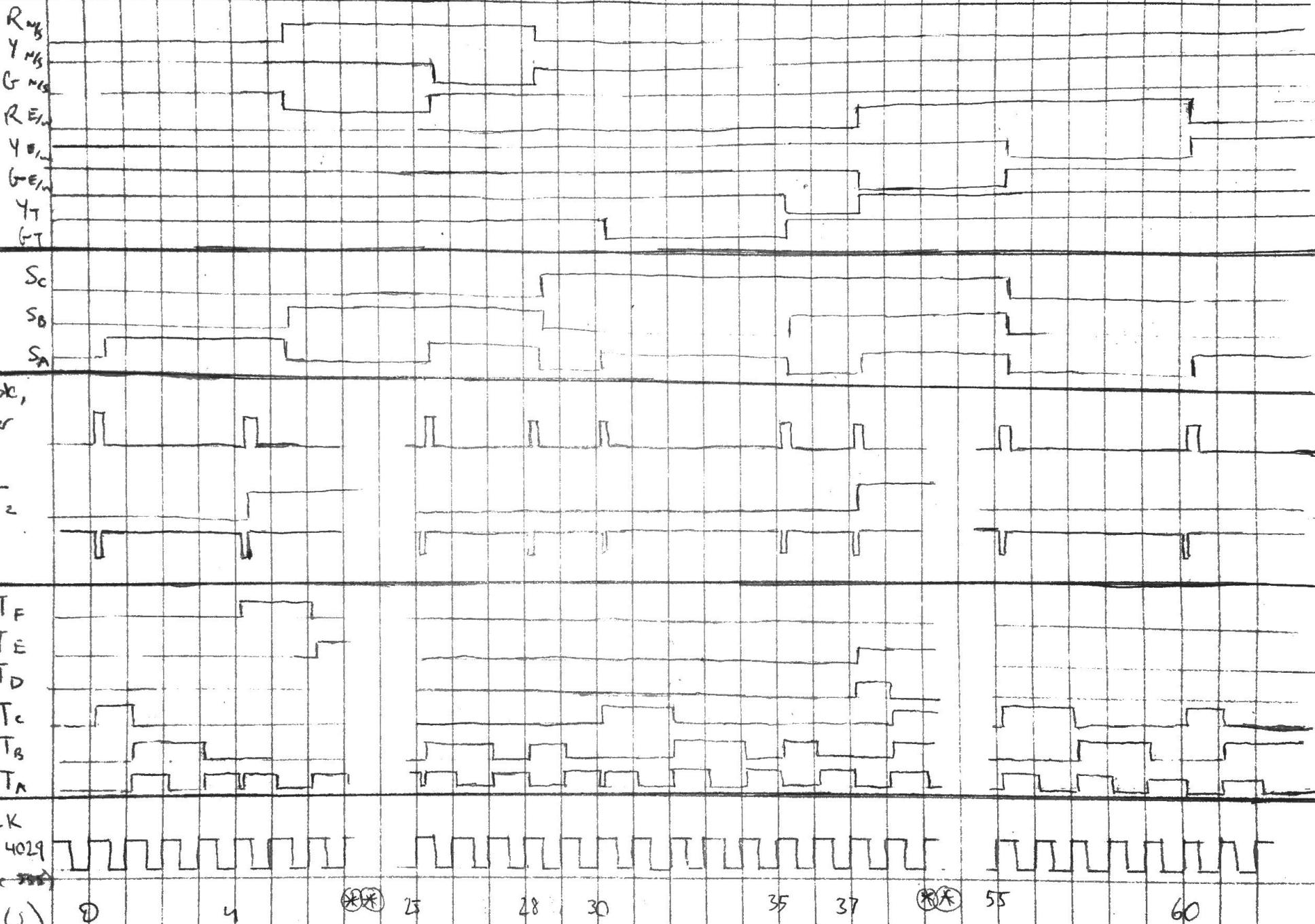
JONATHAN LAM



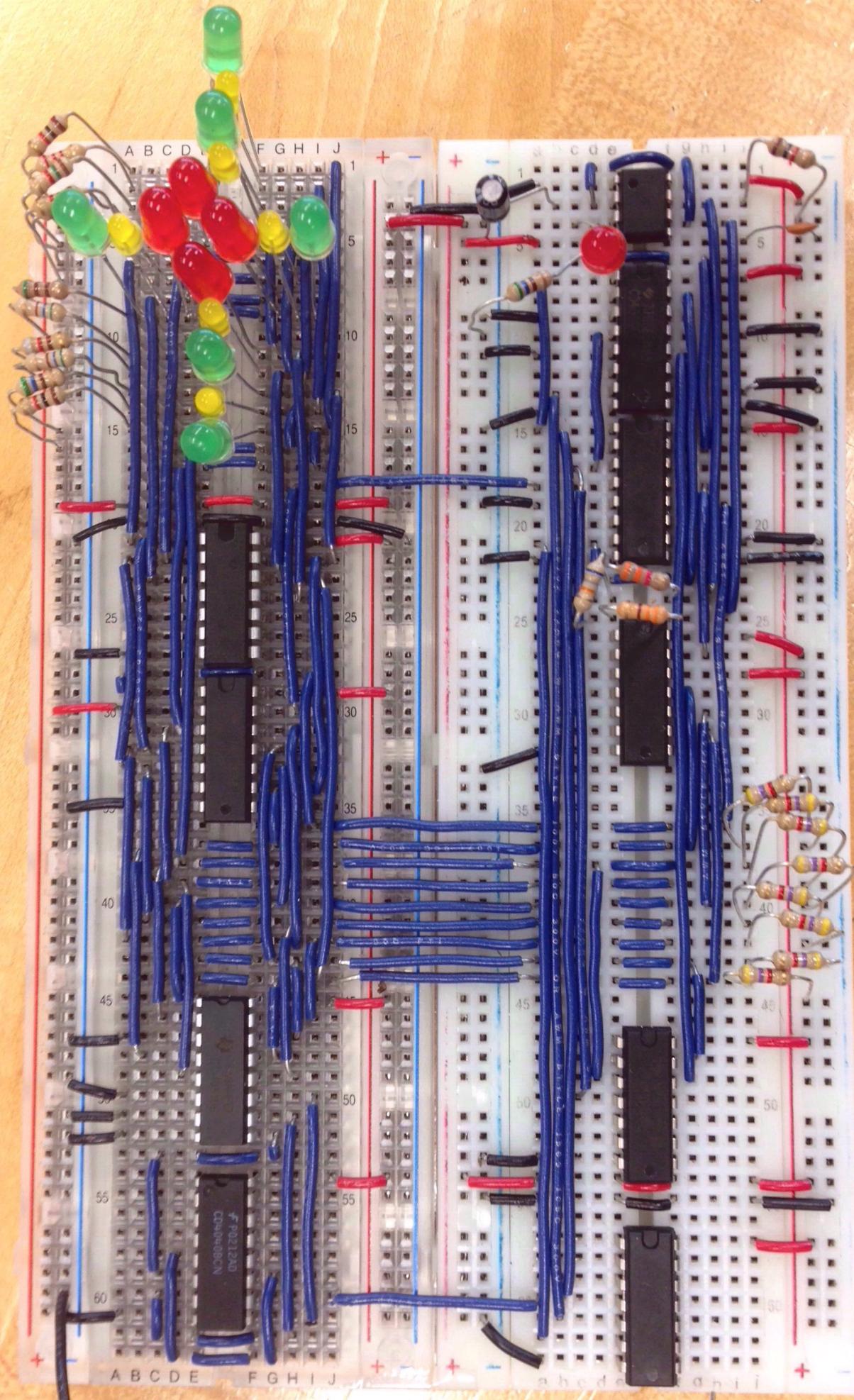
TIMING DIAGRAM FOR TRAFFIC LIGHT

JONATHAN LAM

LEDs
(negative logic)



(*) The green-light intervals are abridged to fit entire cycle onto this timing diagram.)
(*) note that Stage counter (4040) is falling-edge triggered, while all other clocked devices are rising-edge triggered.)



Extra Credit Design

Rough drafts of logic diagrams of the extra credit circuits are attached after the descriptions.

Part One: Accelerate Pedestrian Button Circuit

This circuit is centered around a J/K flip flop whose output (Q) indicates whether or not the accelerate button can be pressed. Most of the time, Q is 0, which means that pressing the button will not do anything.

Q is set to 1 by sending a high pulse to J when one of the green-light stages (D_{010} or D_{101}) are entered. Q is set to 0 by sending a high pulse to K when the button is pressed or when the countdown bits EDCBA is 00101 (five seconds remaining).

If the button is pressed when Q is high, then the JAM inputs FEDCBA are preset to the value 00101 (five seconds remaining) using a 2:1 MUX (i.e., 4053), and a high pulse is set to the PRESET ENABLE pins on the downcounters (4029).

This circuit ensures that the remaining time for the current stage is set to five seconds only if the right conditions are met: if one direction has a green light that has over five seconds remaining.

Part Two: Pedestrian Timer Circuit

This circuit uses a J/K flip flop that indicates whether the seven-segment displays are displaying the remaining time or not, similar to the accelerate pedestrian button circuit.

Q is set to 1 by sending a high pulse to J when one of the green-light stages (D_{010} or D_{101}) is active and the countdown bits EDCBA are 10101 (this can re-use some of the gates from the accelerate pedestrian button circuit, since the lower four bits are equal). Q is set to 0 by sending a high pulse to K when the downcounter reaches zero (both counter carry out pins are low).

A similar process is done with another J/K flip flop, but when EDCBA are 00111 (seven seconds remaining) for the timer to begin blinking at seven seconds. This output is tied to the RESET pin of a second 555 timer, which is set to astable mode between two and five hertz, whose output is connected to the BLANKING pin of the BCD seven-segment display driver (4543).

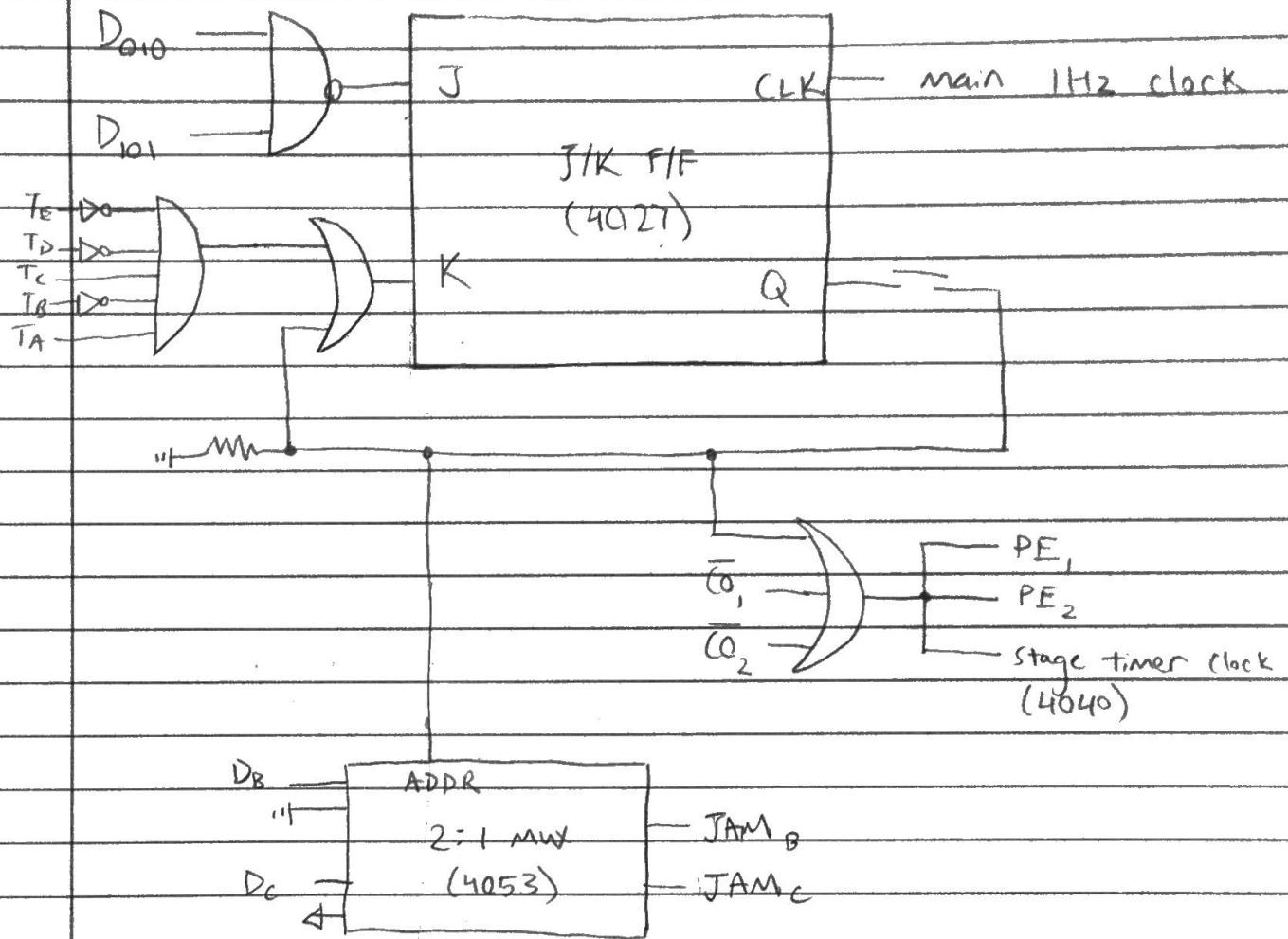
To make the seven-segment display show “EE”, the phase is inverted and the inputs to the BCD seven-segment display driver are set to 0001. (This is the number 1, but all of the LEDs are inverted; therefore, only the 1 is *not* lit, leaving behind an “E”. This trick was brought up by Nathaniel.) Similarly, the “F” can be displayed by inverting the phase, inputting 0001, and turning off the bottom display LED (segment “d”), which can be switched on and off using a 4:1 pair MUX (4052).

Lastly, to keep the input at 0001 to show “E” or “F”, the LATCH DISABLE pin is set low when the countdown is at one second remaining and remains low until the countdown begins again. This maintains the input to the BCD seven-segment display driver at 0001.

The inputs to the BCD seven-segment display driver are displayed in the following table. These assume that a common-cathode seven-segment LED is in use. If a common-anode seven-segment LED is used, the PHASEs and d segments should be reversed.

Light Color	Time remaining ≤ 15 seconds	Phase (PH)	Displays input (DCBA DCBA)	Displays showing	Bottom segment (d)
red/yellow	n/a	1	0001 0001	F F	1
green	no	1	0001 0001	E E	from display driver d output
green	yes	0	$00T_F T_E$ $T_D T_C T_B T_A$	time remaining	from display driver d output

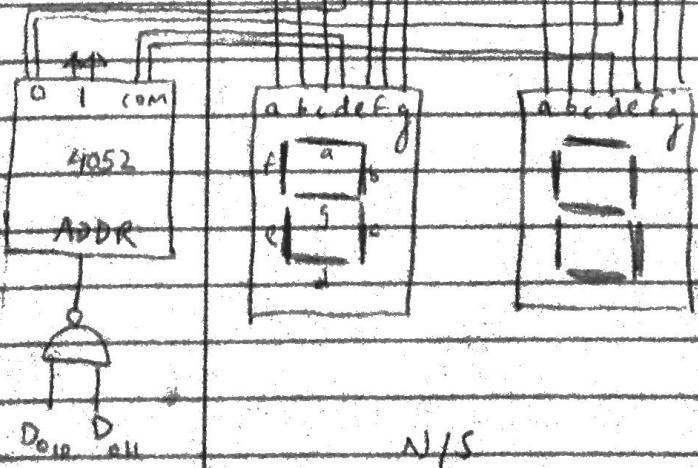
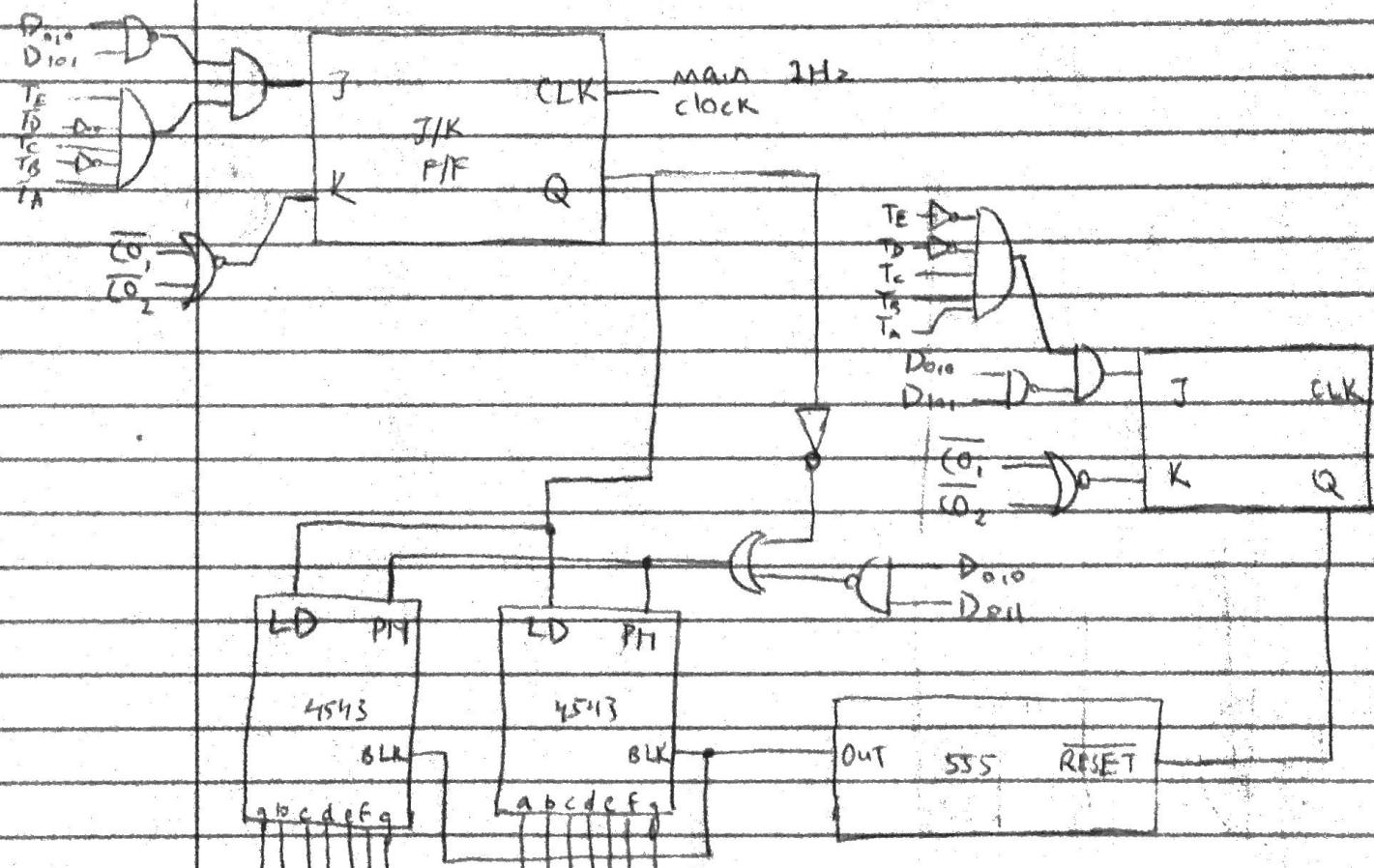
TRAFFIC LIGHT EXTRA:
ACCELERATE PEDESTRIAN BUTTON CIRCUIT
 JONATHAN LAM



TRAFFIC LIGHT EXTRA.

PEDESTRIAN TIMER CIRCUIT

JONATHAN LAM



Repeat N/S setup
for E/ls

Replace D₀₁₀ and D₀₁₁
with i D₀₁₀ and D_{in}

Obstacles and Problem-solving Moments

The first major difficulty was finding a way to make the LEDs light up for the correct amount of time. The idea of using a stage counter quickly arose, but it took the first day to come up with some good idea for ways to advance the stage counter at the right time. I brainstormed with Nathaniel K., Zhihao W., and Dan K. to find multiple possible solutions (outlined in “Regular Credit Design Process and Final Design”).

The most difficult design block was working out the details of the two extra credit designs. Most of the time working this project was spent hypothesizing with the aforementioned peers to come up with slimmer, more space-efficient designs for the accelerate green light circuit and the pedestrian timer circuit. Unfortunately, none of us could figure out how to incorporate all of the extra credit portions onto three boards because every solution took far too many chips.

The final problem was meeting the specification in the timing: a tolerance of one second from the total cycle length of 60 seconds. While the values of the resistors was calculated to produce a 1Hz frequency using the 555 timer, there was always some inconsistency caused by the 555 IC, the resistors, and the capacitors. By experimenting a little bit with an oscilloscope and slightly-different valued resistors, I was able to choose a resistor combination that met the specification *most of* the time (staying within the specification at least $\frac{3}{4}$ of measured cycles), but I was unable to find a solution that always worked.

(Estimated total project time: 50 hours. Actual total project time: probably around 70 hours, including time actively thinking about it but not physically designing or building.)

Attributions

- Zhihao Wang: for working through the MUX-based solutions with 8, 4, 2, 1, and 0 (with similar logic) MUXes with me.
- Dan Kim: for coming up with the idea of mapping current states bits to the duration of the next stage, and for proposing to use a decoder/DEMUX to simplify the logic for the mapping, both of which are included in my final design.
- Nathaniel Kingsbury: for reminding me that the 4029 counters can be used in decade mode to make the transfer to two (base ten) seven-segment displays easy; while seven segment displays were not implemented, the duration mappings and the 4029 counters in the final implementation were left in decade mode. Also for coming up with the idea of inverting the phase to (more) easily produce an “E” and “F” on the seven-segment displays using a BCD encoder chip (4543).

8×8 Tron

Summer 2018 ECE 150 (Data Logic Design)

Professor Risbud

Final Project Report

Nathaniel Kingsbury

Jonathan Lam

0. Abstract

Our aim will be to build the classic arcade game Tron (from 1982). In this multiplayer game, players move through an area and leave a trail behind themselves that acts as a wall. When a player hits any trail (be it their own or some other player's), they lose. Players are required to move constantly, and all move approximately once per second. If a player moves to one edge of the screen, they "wrap-around" to the other side of the screen. In our implementation, the screen will be an 8X8 grid of bi-color (red/blue) LEDs. Each of the two players will be assigned a color for their trail, and will be given a set of four buttons to change their direction of movement. Every second, both players will move forwards in their current direction of movement. Players will start out in predetermined locations for fairness. When one player hits a trail, the game will shut off (the clock will stop and motion will end), and a "victory LED" will turn on in the color of the winning player. If the two players enter the same spot on the same turn, or both hit a wall at the same time, the game will end but no victory LED will light, which will signal a draw. A "new game" button will be provided to reset the game and allow players to start over.

1: reference: <http://www.cs.brandeis.edu/~pablo/tron/t1.html> ("The opposite edges of the screen communicate with each other.")

1. Inventory

IC Chips

<u>Count</u>	<u>IC #</u>	<u>Description</u>
2	555	Timer
2	4013	Dual D-Type Flip-Flop
17	4015	Dual 4-Stage Static Shift Register With Serial Input/Parallel Output
5	4029	Presettable Up/Down Counter
1	4040	2-stage binary ripple counter
6	4051	Single 8-Channel Analog Multiplexer/Demultiplexer
1	4052	Dual 4:1 Analog Multiplexer/Demultiplexer
3	4053	Triple 2:1 Analog Multiplexer/Demultiplexer
2	4585	4-Bit Magnitude Comparator
3	4071	Quad 2-input OR gate
1	4081	Quad 2-in AND
1	4011	Quad 2-Input NAND Gate
1	4025	Triple 3-in NOR

Resistors and Capacitors

<u>Count</u>	<u>Value</u>	<u>Description</u>
1	1000 μ F	Decoupling capacitor
3	0.1 μ F	Signal-decoupling capacitor (prevents noise on a single signal, rather than on power and ground)
4	0.22 μ F	Edge-trigger capacitor
1	5.1k Ω	Edge-trigger resistor
1	6.8k Ω	Edge-trigger resistor
1	20k Ω	Edge-trigger resistor (in parallel with 33k Ω resistor)
1	33k Ω	Edge-trigger resistor (in parallel with 20k Ω resistor)
1	10k Ω	Edge-trigger resistor
2	3.3 μ F	555 Timing Capacitor
2	.015 μ F	555 Control Voltage Capacitor
1	470k Ω	555 timing resistor
1	910 Ω	555 timing resistor
10	1k Ω	Pull-down resistors (8) and 555 timing resistors (2)
16	20k Ω	Pull-up resistor
65	470 Ω	Current-limiting resistor
65	430 Ω	Current-limiting resistor

Other Components

<u>Count</u>	<u>Description</u>
9	Pushbutton
9	Breadboard
65	Bicolor (blue/red) 5mm LED
4	Ribbon Cable Header (14-wide)

2. Design and Methodology

2a. Explanation of design

In brief, our design works as follows: an approximately 1 Hz clock with a duty cycle of nearly 100% synchronizes all events. The falling edge of this clock triggers the counters in the players' controllers to increment, and then the rising edge triggers the current coordinates to be written to memory, and to be checked against the memory to determine when the game ends (i.e. to determine if either player hit either trail). The brief delay between the falling and rising edges of the clock is large enough to make sure that the counters have fully updated before any writing or checking occurs, but is brief enough that it is not human-noticeable (so nobody will complain that they pressed a button to change directions and the game didn't respond).

The memory block consists of 8 8-bit shift registers and 3 muxes for each player (so a total of 16 shift registers and 6 muxes). Based on the y-coordinate of one player, the muxes select which shift register is active in both player's memory modules at once, by connecting that shift register's data in, Q8 (data out), and clock connected with the rest of the circuit (the inactive shift registers get no clock signals, so they simply store data for future use, and control the display). Hence, at any given time, corresponding shift registers in each player's memory modules are selected. Writing to memory and checking against memory is accomplished serially -- the rising edge of the master clock triggers another super-fast clock to give 16 pulses really rapidly. For the first 8 cycles, the first player's y-coordinate is used to select shift registers, and for the second 8 cycles, the second player's y-coordinate is used to select shift registers. Data is shifted cyclically on each falling edge of the super-fast clock (i.e. whatever is in Q8 of a shift register appears on that register's data in) except for the shift register for the player whose coordinates are being checked at the point corresponding with that player's current x-coordinate, at which point a 1 is fed into the data in regardless of the current contents of Q8. Because 8 clock pulses occur for each player, in the end nothing has changed within the shift registers for either player, except for the 1 bit that has been "written" into each memory bank. During this process, immediately before writing to one player's shift register, both players' shift register data outputs are checked for a 1.

At that moment, seeing a 1 on Q8 of a player's shift register signifies that that player has been in that location. In that case, a 1 is stored to a win/loss flags register, where it triggers the master clock to shut down. If the two players move to occupy the same spot simultaneously, a comparator similarly ends the game.

During an endgame, a win/loss LED lights up with the color of the winning player. In the event of a tie, there is no winner, so the game ends but the win/loss LED does not light. Pressing the "reset" or "new game" button causes the counters in the controllers to preset, and all registers to reset, causing the game to restart. See below for a verbal step-by-step in-depth explanation of the design, including a description of what's going on on the signal level with reference to how this plays into the larger game state. Additionally, on page 16, a timing diagram providing a visual representation of this information is given.

[0. Initial state]

When initially powered, the LEDs will appear lit in a random pattern, due to the indetermination of the original states of the bits in the shift registers (in the flip flops). Pressing the reset button will begin the game.

[1. Reset button pressed; rising edge of reset signal]

While the reset signal is high, all of the shift registers storing the LED states are reset, clearing the board. The preset enables on the counters in the controllers go high, which writes the starting positions to the controllers. Additionally, the win/loss shift register is cleared, which enables the slower (1 Hz) master clock.

[2. Reset button released; falling edge of reset signal]

On the falling edge of the reset signal, the timing counter is reset, which enables the fast clock to give 16 pulses to write the starting positions to the shift register banks.

[3. Wait for user input]

During this portion of the cycle, nothing dynamic occurs inside the game, save for the charging of the timing capacitor on the master 555 timer. The purpose of this period of time is to slow things down enough to allow for user input -- at any time, if the user presses a directional button, it updates a pair of D-type flip-flops in their controller, (potentially) changing which of their counters (x or y) is active, and whether it is in up mode or down mode. This can occur anywhere in the cycle, as it is independent of the rest of the circuit; however, in order to make things usable, this long period of time is needed so that things don't happen altogether too fast for informed user input.

[4. Falling edge of low-frequency clock pulse]

The falling edge of the low-frequency clock is used to indicate the beginning of each player's motion. This triggers the counters on the controllers to advance.

[5. Rising edge of low-frequency clock pulse]

An edge trigger on the rising edge of the low-frequency clock pulse sets the preset enable pin of the countdown 4029 counter high, allowing the x-position of player one to be inputted to the counter. The edge trigger is calibrated to last just long enough to overlap the first rising edge of the high-frequency clock pulse.

[6. Rising edge of first high-frequency clock pulse -- "Read"]

On the first rising edge of the high-frequency clock, the 4029 preset with the x-coordinate does not count down due to preset enable being held high. However, in any case, the checking logic does check to make certain that there is nothing already in the position currently being read. In the case where the x-coordinate that had been preset into the 4029 is a 0, this gets written into the win/loss shift register.

[7. Falling edge of first high-frequency clock pulse -- "Write/Shift"]

This falling edge is directed to the correct shift register's clock, so that only the correct rows in both memory modules are shifted. The data input to the shift register comes from a 2:1 multiplexer that outputs a guaranteed logical 1 if the portion (group of 8 clock cycles) of the update cycle corresponds with the "write" time for the player corresponding with that memory bank (indicated by Q4 of a counter) and if the time within the cycle is correct to do a writing (from the carry out of the down counter fed the current player's x-coordinate). When these conditions are not both true, the multiplexer outputs the output of Q8 of the selected shift register otherwise. This writes a 1 into the memory module at the correct coordinate position, and maintains all of the other bit values.

[8. Rising edge of second fast clock signal until falling edge of sixteenth fast clock pulse]

The same rising-edge checking and falling-edge writing of data and shifting (from the previous two steps) occur during these cycles. The one change is that the 4029 is allowed to count down, such that it goes low on the nth rising edge of the high-frequency clock (counting from 0). This way, on the nth rising edge, the output of the checking logic is actually written to the endgame shift register.

[9. Rising edge of 4040 Q4 clock signal]

This happens concurrently with the falling edge of the eighth fast clock signal, as the 4040 counter is falling-edge triggered and Q4 goes from low to high on the eighth pulse. The Q4 output is connected to the address pins of the two 4053 2:1 multiplexers to switch

the shifting and reading from player one to player two (changing “phase” from zero to one; see PH input in 3b). While this is concurrent with Q4, the longer propagation delay of a change in address to output update for the 4053 multiplexers than the propagation delay of the shifting allows us to use the same edge to trigger both events and correctly shift before changing phase. The preset enable of the 4029 countdown counter is set high using an edge trigger on the rising edge of the 4040 Q4 clock signal, and calibrated to last just past the rising edge of the next high-frequency clock pulse.

[10. Rising edge of the 4040 Q5 clock signal]

This happens concurrently with the falling edge of the sixteenth fast clock signal. This is connected to the reset pin (pin 4) of the high-frequency clock timer, which stops the shifting and writing, and stops the counter as well keeping the system in this state until the master clock or reset button reset the 4040 and re-enable the fast clock. Assuming no endgame conditions, this returns things to state 3.

[11. Endgame Conditions]

If at the end of the counting of the controllers, the x and y coordinates of each are the same, or if at the end of the read/write cycle there is a 1 in the endgame shift register, the game ends. (This is accomplished by NORing the two least significant outputs of the shift register together with the output of a pair of comparators to create a unified “game over” signal). There are a few stages to this -- a multiplexer connected to the “game over” signal immediately holds the clock signal going to the counters low, to prevent any spurious edges going to the counters from causing bugs. Additionally, the “game over” signal goes to the reset pin of the master clock, shutting down the game in a more general way until the reset button is pressed. At this point, a few other signals come into play -- the individual red and blue pins of the endgame LED go to the stages in the shift register that signify one player’s loss, such that the LED lights red when blue loses, and lights blue when red loses. Additionally, the common ground pin goes to an additional signal that goes high during a tie, such that during a tie the game stops, but the LED simply doesn’t light, regardless of the signals going to the red and blue independent LEDs.

[11. Falling Edge of master clock]

Return to step 3. This indicates that another second has passed, and the next move is completed.

During the design process, we quickly found that it would be easiest to divide the problem into a modular solution, so that the physical building process could be divided, each team member would have a more specialized focus on a smaller project and have to worry about fewer technicalities of modules they are not building (allowing quicker build times), modules could be

tested in isolation, and so that future revisions to the internals of any section can be done so long as the outputs remain the same (i.e., modules are black-box abstractions).

2b. Modules

<u>Name</u>	<u>Count</u>	<u>Description</u>
Controller	2	includes interface for users and determines coordinates
Input management	1	selects correct controller inputs for writing and special tie condition
Memory	2	stores previous locations of players
Write/Endgame detection	1	processes new inputs and checks for endgame conditions
Timing	1	includes timer ICs and manipulation of clock signals
Reset	1	signal to restart game

2c. Notes about final design

The wires are color-coded as follows (CLK, RST, and LED categories take priority):

Green	CLK: oscillating timer signals, regular or inverted, from either 555 timer
White	RST: directly connected to the reset button
Yellow	Controller modules
Blue	LED: blue LED on display; or Input management module
Orange	Memory module
Brown	Write/Endgame detection module
Red	LED: red LED on display; or VCC
Black	GND; or Tie signal output (goes to ground pin of the bicolor win/loss LED)

The final design comprises nine breadboards and an LED display (solder protoboard), including two controller breadboards connected to the other seven by ribbon cables. Each controller has the four directional control buttons for its respective player, and the reset button is located on the display. The ribbon cable allows a player some mobility with his or her controller.

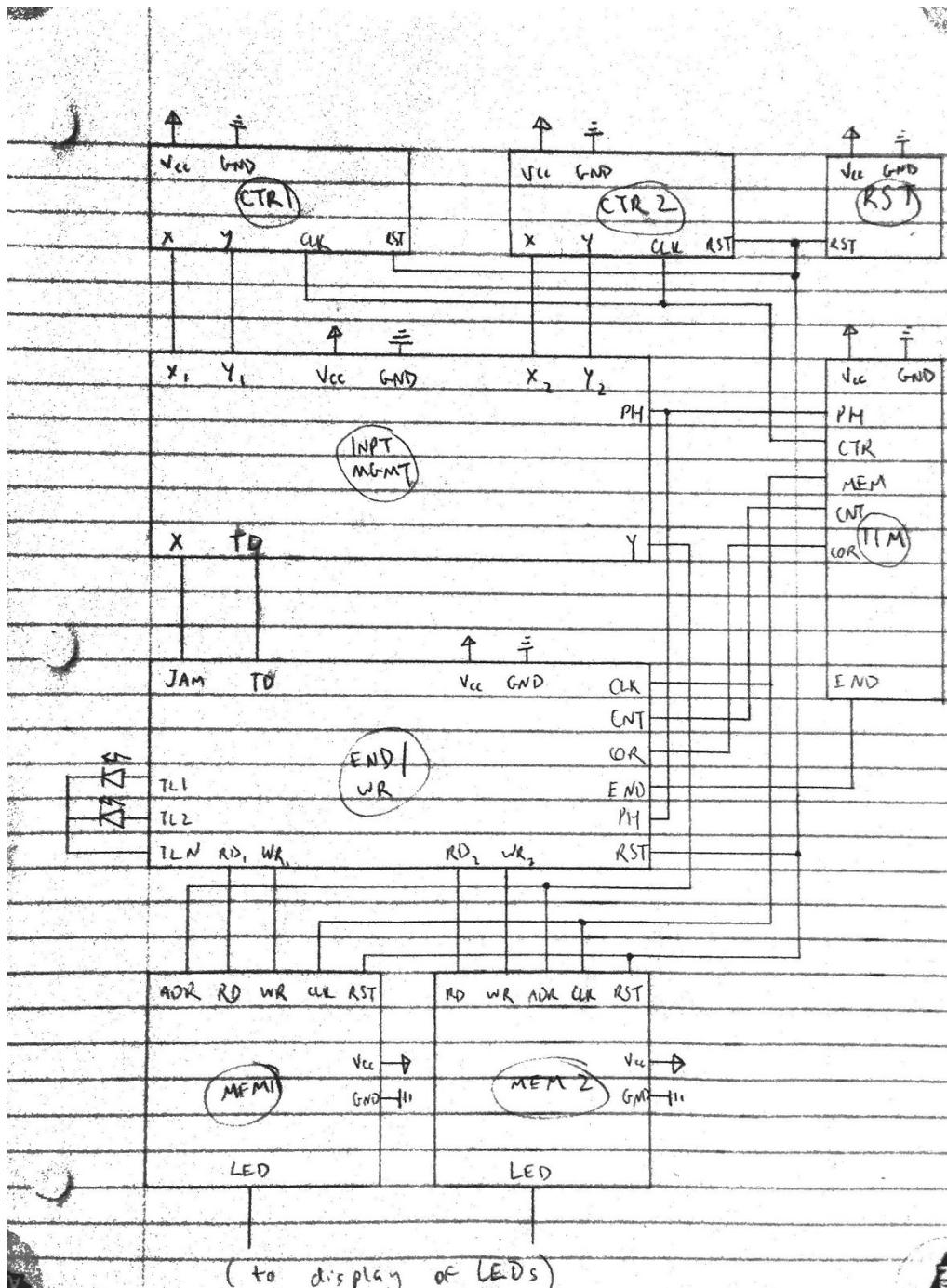
3. Schematic

Because of the size and the modular design of the Tron machine, the schematic is split into its modules. For each module described below, a table of module input and output signals, as well as the source or destination modules of those signals, is provided. Every module is completely standalone and can be unit-tested by supplying appropriate inputs and checking the module outputs.

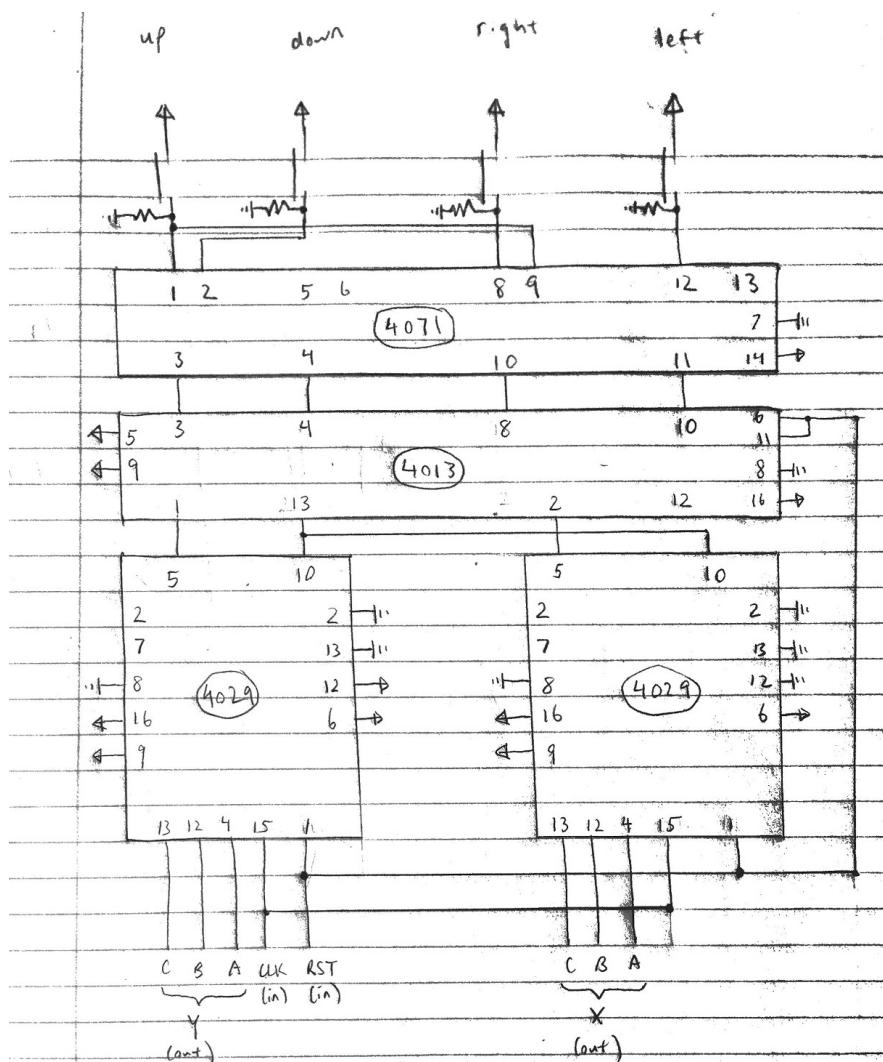
A single controller module and memory module schematic are provided below to reduce redundancy. Each of these modules are duplicated, with slight changes in the copy of the controller module (see the provided notes).

3a. System

The diagram below displays the connections between every module.



3b. Controller module



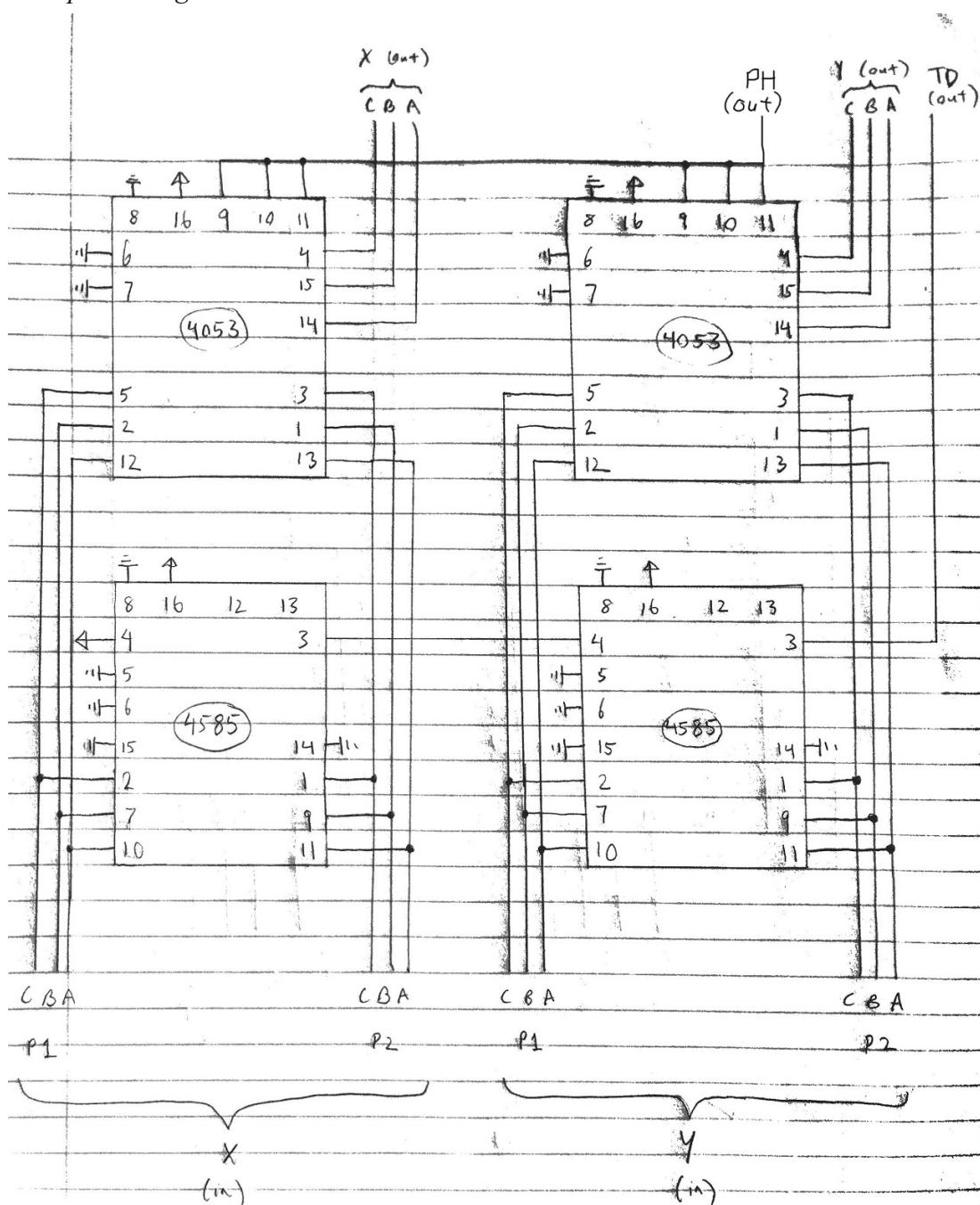
<u>I/O Channel</u>	<u>I/O</u>	<u>Source or destination</u>
RST	in	reset module RST output
CLK	in	timing module CTR output
X (CBA)	out	input management X inputs
Y (CBA)	out	input management Y inputs

Notes:

The schematic shown above is the controller for player one. The controller for player two is identical, except for the following changes (which create a different starting position and direction):

- Pin 9 (DATA 2) on the 4013 is connected to GND.
- Pins 13, 12, 6 (JAM inputs 3, 2, 1) on the right 4029 are connected to GND, VCC, GND, respectively.

3c. Input management module



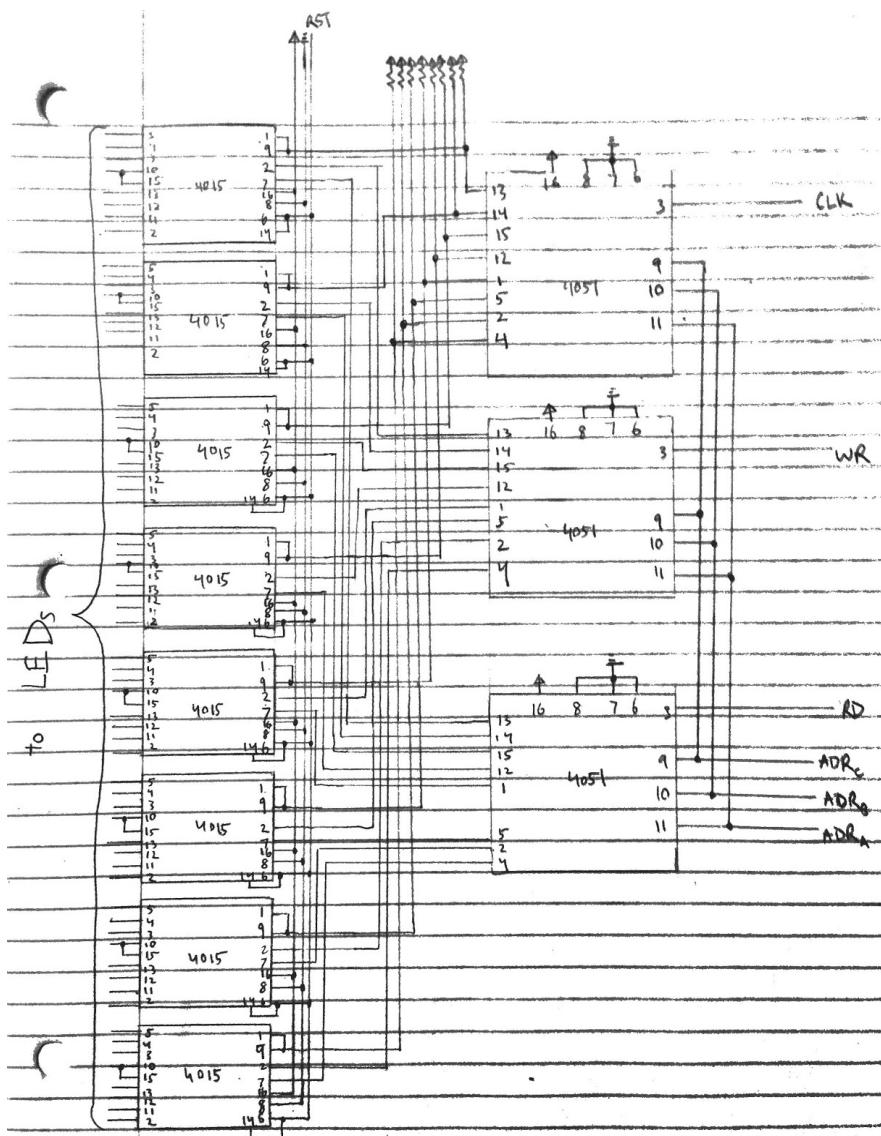
I/O Channel

X (P1 CBA, P2 CBA)
 Y (P1 CBA, P2 CBA)
 PH (phase)
 X (CBA)
 Y (CBA)
 TD (tie detection)

I/O Source or destination

in	controller module X outputs
in	controller module Y outputs
in	timing module PH output
out	write/endgame module JAM inputs
out	memory module ADR inputs
out	write/endgame module TD input

3d. Memory module

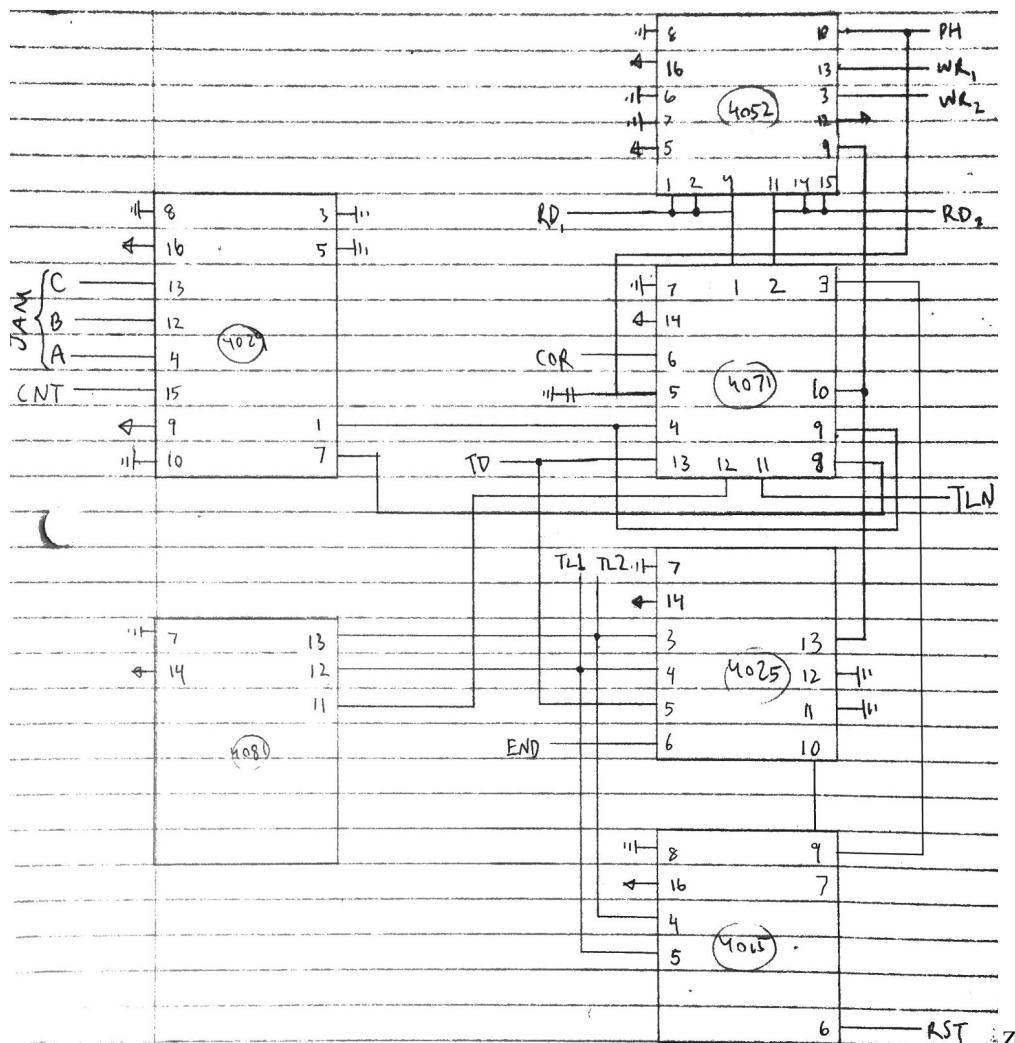


I/O Channel	I/O	Source or destination
ADR	in	input management module ADR outputs
RST	in	reset module RST output
WR (write)	in	write/endgame detection module WR output
CLK	in	timing module MEM output
RD (read)	out	write/endgame detection module RD input
LED	out	display LEDs

Notes:

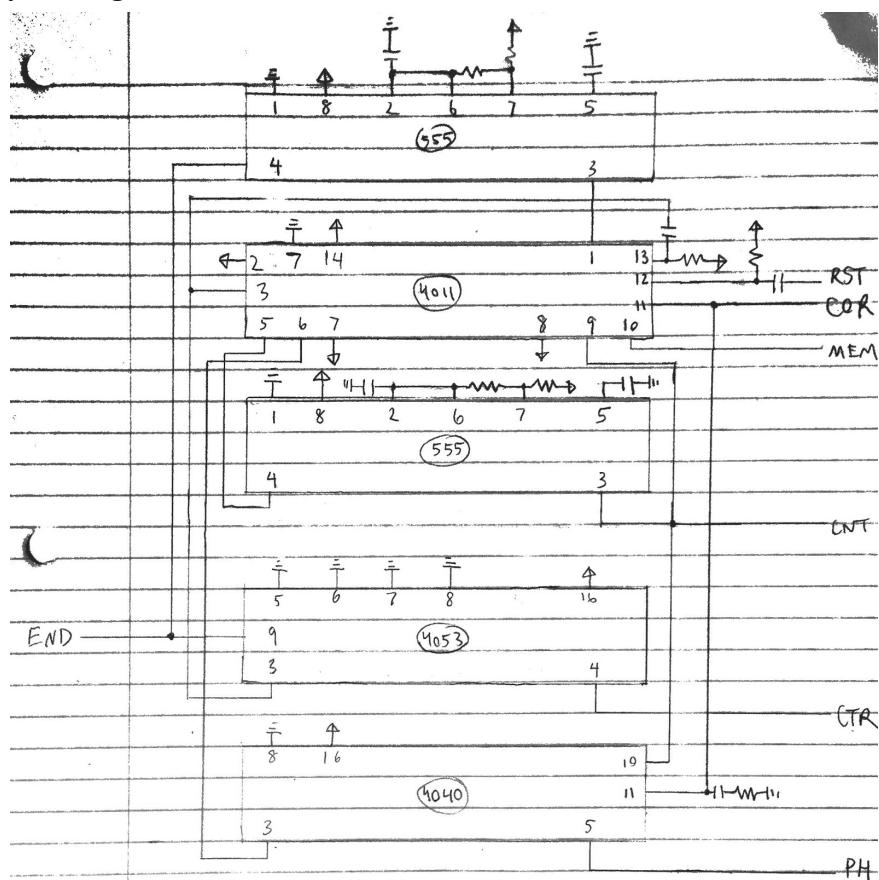
- This is duplicated for the second player. The CLK, ADR, and RST inputs are the same.
- The LED output goes to an 8x8 array of bicolor LEDs. Every output from one memory module is the same color. In our design, this was implemented on a solder protoboard.

3e. Write/Endgame detection module



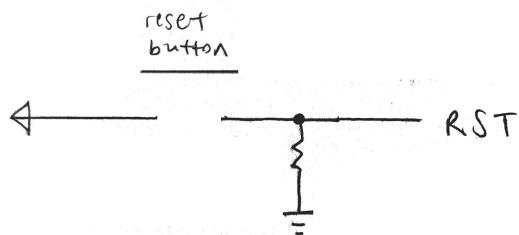
I/O Channel	I/O	Source or destination
CLK	in	timing module MEM output
CNT	in	timing module CNT output
COR	in	timing module COR (clock or reset) output
PH (phase)	in	timing module PH output
RST	in	reset module RST output
JAM (CBA)	in	input management JAM outputs
TD (tie detect)	in	input management TD output
RD (read)	in	memory module RD output
WR (read)	out	memory module WR input
END	out	timing module END input
TL1	out	winner LED player 1 indicator
TL2	out	winner LED player 2 indicator
TLN	out	winner LED cathode

3f. Timing module



<u>I/O Channel</u>	<u>I/O</u>	<u>Source or destination</u>
END	in	write/endgame detection module END output
MEM	out	memory module, write/endgame detection modules CLK input
CTR	out	controller module CLK input
COR	out	write/endgame detection COR (clock or reset) input
CNT	out	write/endgame detection CNT input
PH (phase)	out	write/endgame detection, input management PH input

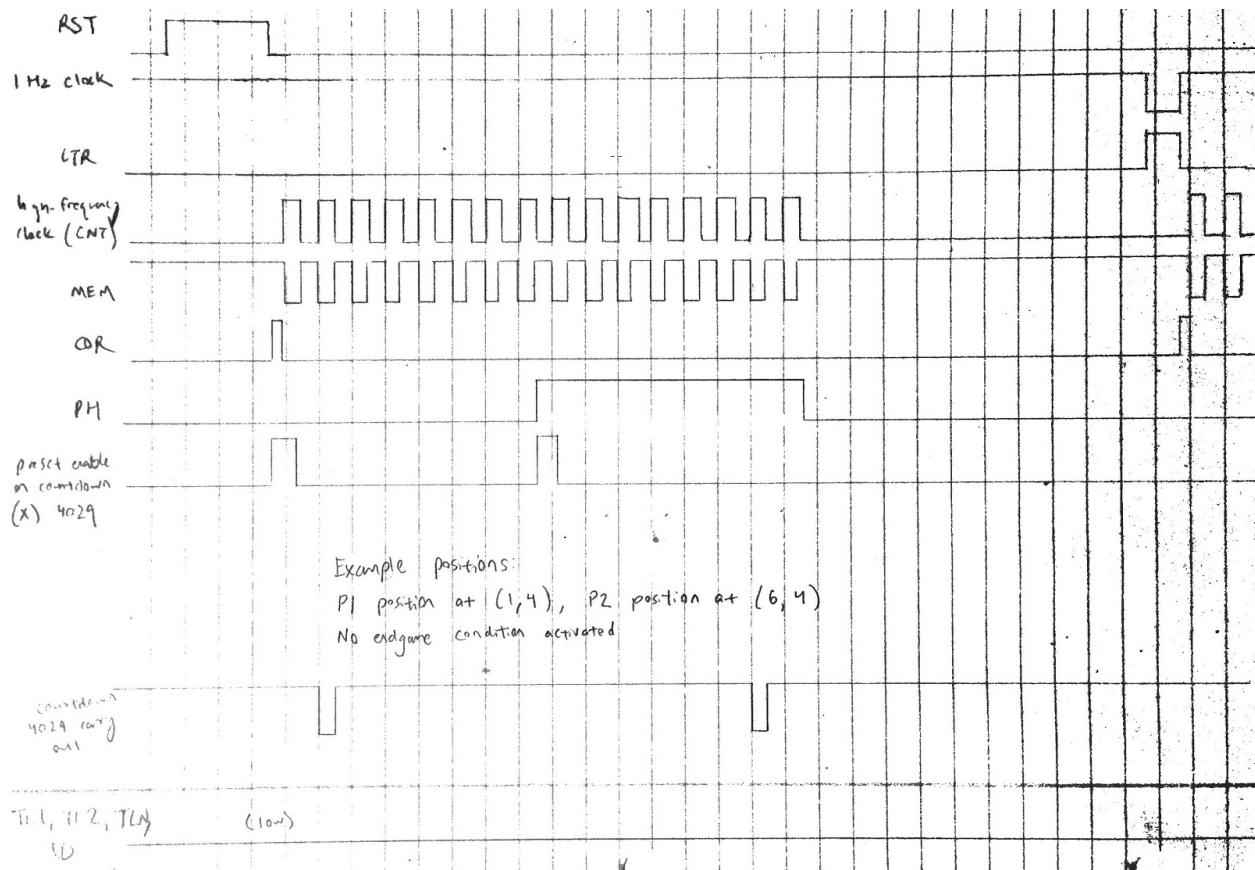
3g. Reset module



<u>I/O Channel</u>	<u>I/O</u>	<u>Source or destination</u>
RST	out	controller, memory, write/endgame detection modules RST inputs

4. Timing Diagram

Selected signals essential to the general timing of the circuit are shown in the timing diagram below.

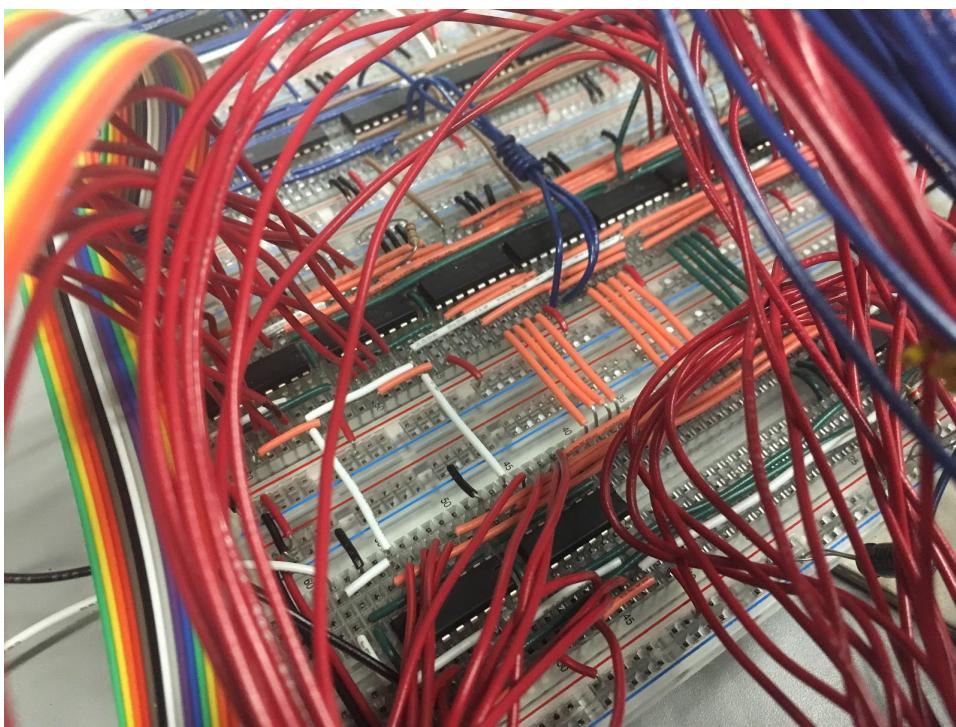
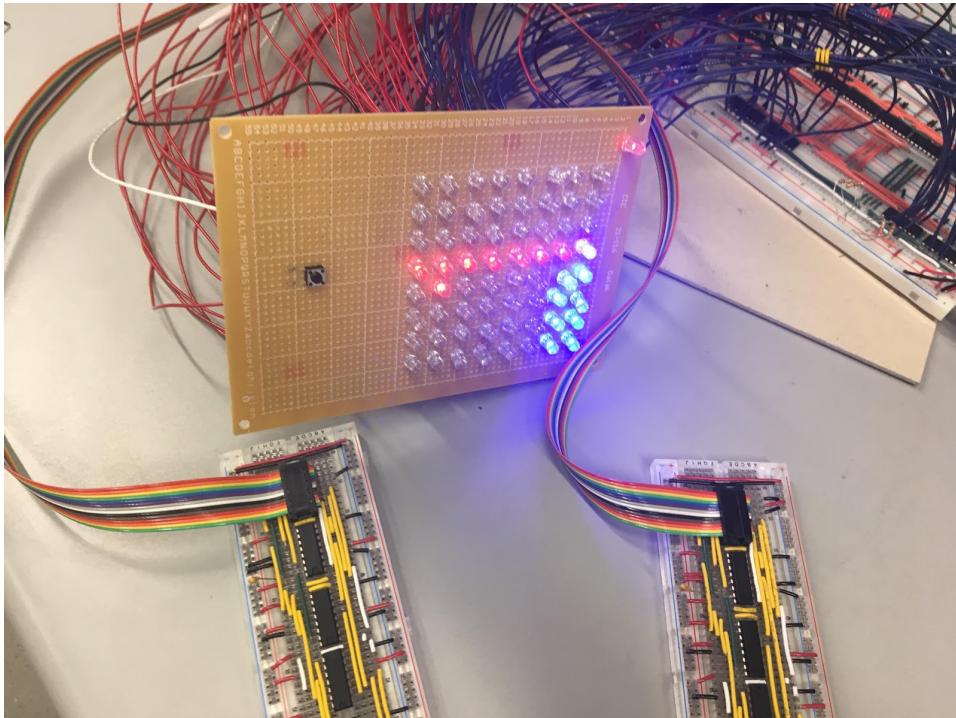


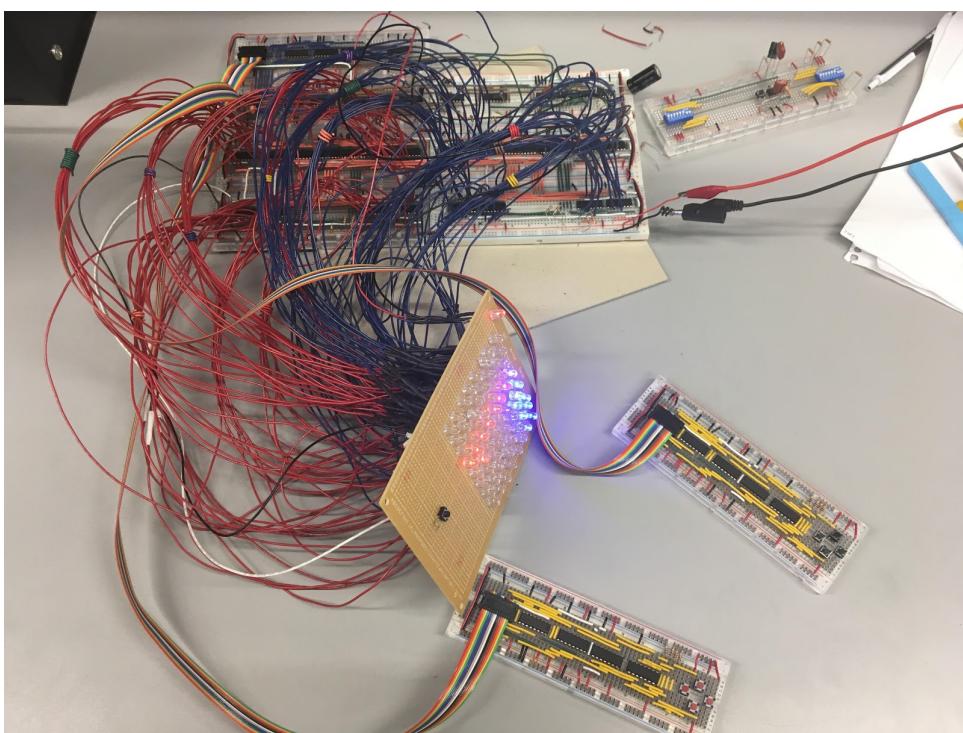
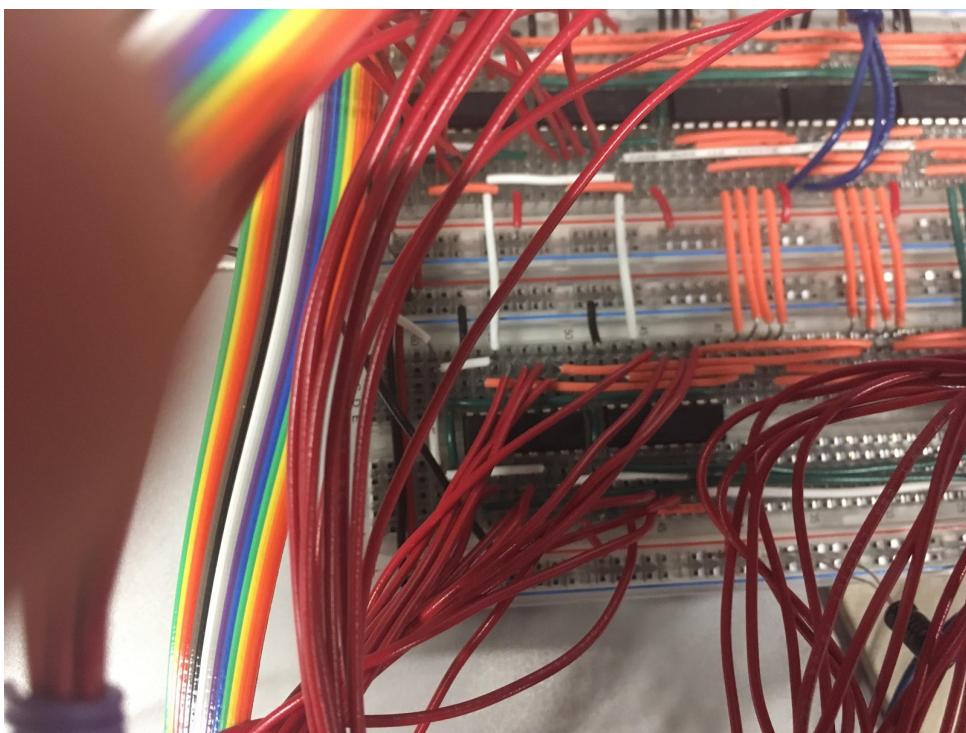
Notes:

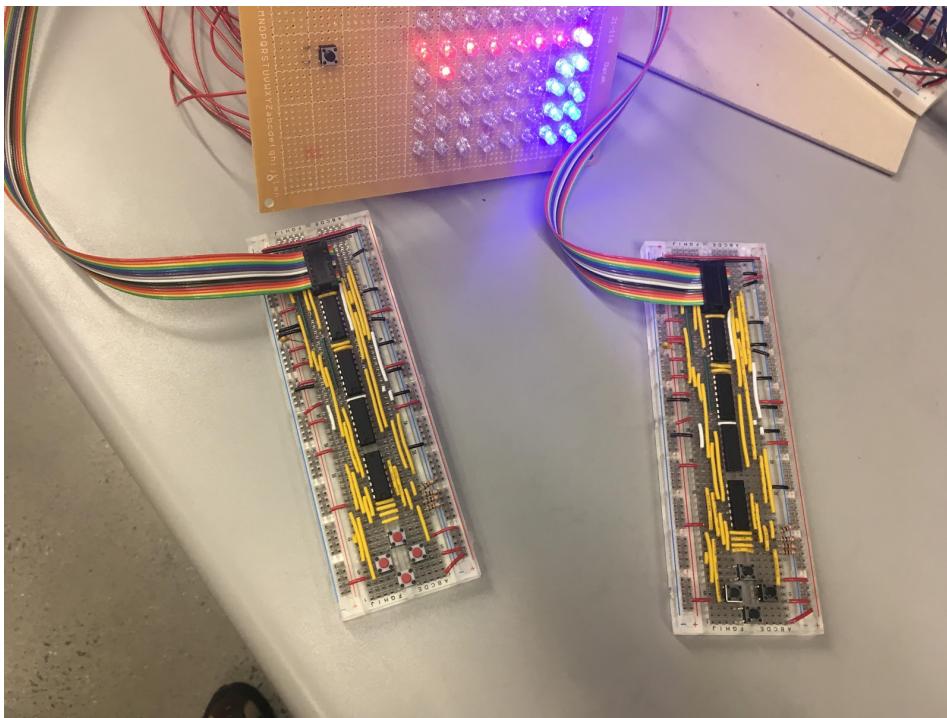
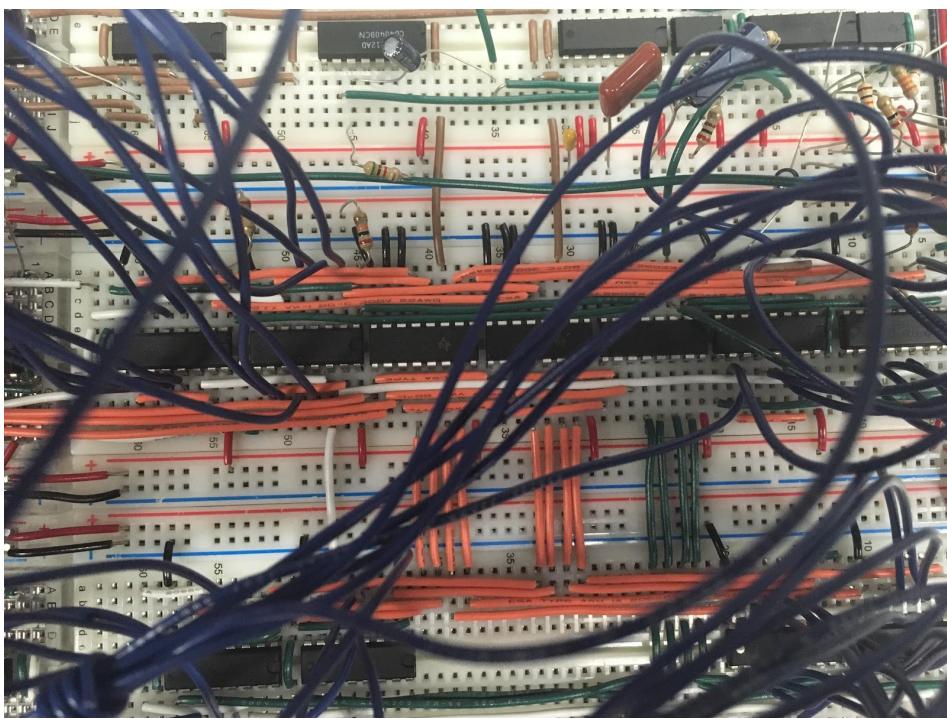
- Timing is not drawn to scale. Propagation delay between events may be exaggerated, and transition (LOW-HIGH or HIGH-LOW) delays are not emphasized.
- The RST signal at the beginning of the timing diagram only happens at the beginning of the game. After that, normal game operation is continued by the 1Hz clock signal, which gets disabled at endgame.
- The meaning of the abbreviations RST, CTR, CNT, MEM, COR, and PH can be found in the module schematics or the system schematic. The “preset enable on countdown 4029” and “countdown 4029 carry out” refer to the 4029 counter used to count down to the correct x position of a player (in the write/endgame detection module).
- On an endgame detection, TL1, TL2, or TD goes high, and the main clock is disabled. The reset button must be pressed (a high pulse on the RST signal) to restart the game.

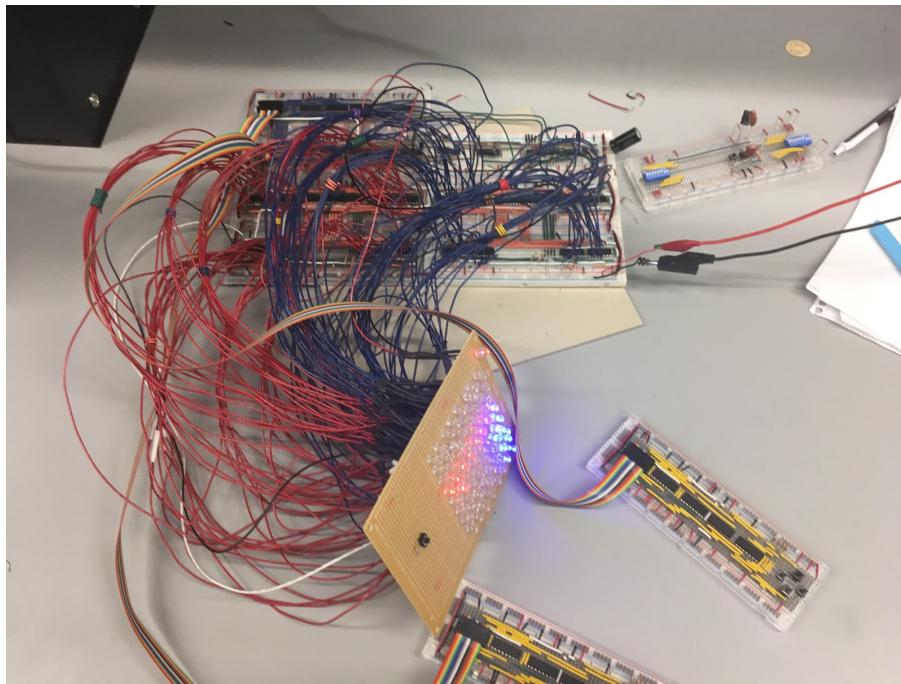
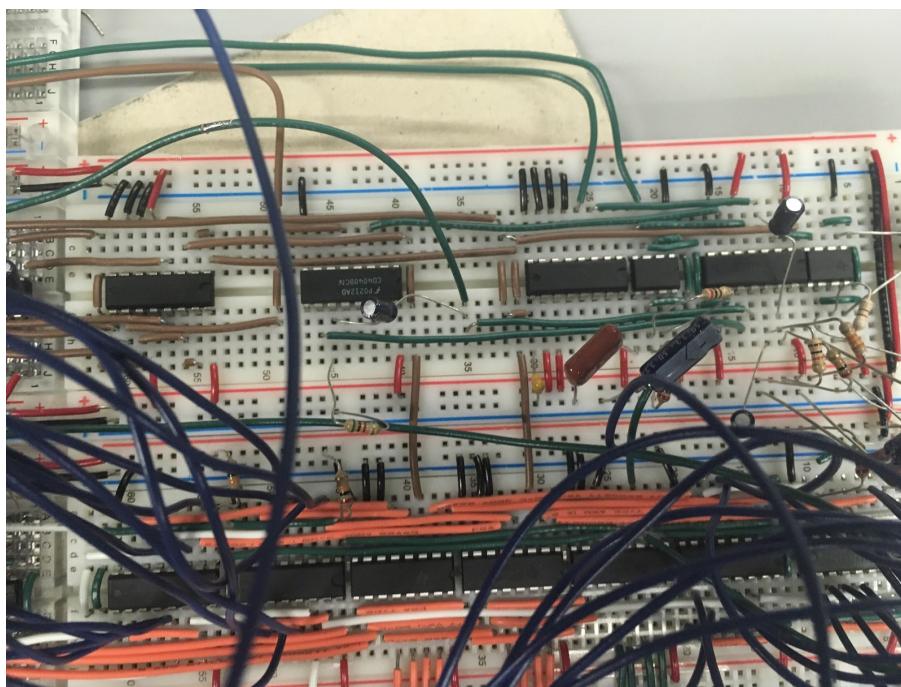
5. Media

Images









Link to video

<https://drive.google.com/file/d/1CWRF6Q1VLNOdmRWxrGb-mySU7Je7T2X5/view?usp=sharing>

6. Debugging Process and Possible Future Extensions

Significant bugs

Listed below are a selection of bugs encountered during the construction of the project, and which took a considerable amount of debugging time or a modification to the original design.

- The pull-down resistors on the clock signals within the memory module were too small, leading to the clock signal going in between consistent HIGH and consistent LOW instead of going truly HIGH. This led to inconsistencies while shifting, which were eventually fixed by increasing the size of the pull-downs from $1\text{ k}\Omega$ to $20\text{ k}\Omega$.
- The drop in voltage across power and ground caused by many LEDs being lit on the display simultaneously when powered by a battery pack caused several carefully-calibrated RC edge-detector circuits to fail. Switching to a power supply solved the problem.
- The initial position (position of players when the game is reset) of the players was not being written to the display, and therefore the LEDs at the starting position did not light (and players didn't lose when crashing into that spot), but pressing one of the direction keys on the controller still influenced the de-facto starting position (the first LED to light and first position to be written to). A NAND logic gate was added to also trigger writing the players' positions on the falling edge of the reset button.
- The 4029 counter determining when the offset in the selected shift register is correct was counting one too many times, creating an incorrect offset when inputting data into the shift registers. This required the observation that the edge triggers for the preset enable pin of that counter had to be increased. Careful calibration by increasing resistor size allowed for the preset enable to be HIGH for the correct amount of time.
- Inconsistencies with counters skipping controllers was fixed by adding decoupling controllers between VCC and GND. Later on, future inconsistencies caused by noise in the CLK signal to the controllers prompted the addition of small ($0.1\text{ }\mu\text{F}$) capacitors between the CLK signal and GND to reduce noise.
- The initial endgame detection allowed the CLK signal to the controllers to return high, creating another rising edge (and thus causing the players' position to jump once on endgame). A multiplexer, with one input tied to GND and the other to the CLK signal, with its addresses connected to the endgame condition, was added to eliminate the last rising edge.
- A glitch state caused noise in the address pin to the multiplexer described in the previous bug, prompting a capacitor to be put between that address and GND to reduce the noise.

- The zeroth-row LEDs were connected with shorter wires and with electrical tape. This caused problems and required much time un- and re-soldering LED connections that broke. (This is not a bug, but a time-consuming fix to the machine.)

Possible Extensions:

In future iterations of this project, better care should be taken to eliminate the flicker in the LEDs. Because all eight LEDs are shifted (because the shift registers used had serial input), the quick flashing may be distracting or unpleasant to view. This can be improved by using parallel-load shift registers or using resistor-capacitor circuits.

Another possible improvement is that the machine can prevent users from turning back on themselves, killing themselves immediately. This is usually disallowed by the machine in Tron games, but we felt that it did not affect gameplay significantly (as the player can simply learn to avoid trying to double-back) and didn't include in our implementation. Additional "add-on" extensions for a future implementation could also include a switch to enable or disable wraparound, making the game "best two out of three," and causing the master clock to speed up as the game progresses (either every n ticks of the clock or with successive matches).

7. Acknowledgements

1. Professor Risbud, for approving and evaluating the project.
2. Dr. Brian Kingsbury, for (informally, as part of normal conversation) bouncing ideas back and forth with Nathaniel as to the likely sources of bugs.

Data Structures and Algorithms I
Fall 2018
Homework #2

1. Describe where the listed data are stored in memory.

For activation records, the names used correspond to the following numbered sections (to match the wording of the assignment):

Name	Section
parameters	1
machine status info	2
local and temporary variables	3
a) static memory	global variable
b) activation record — 1	function parameter
c) activation record — 1	function parameter
d) activation record — 3	local variable of function
e) activation record — 1	function parameter
f) heap	dynamically allocated
g) heap	dynamically allocated
h) activation record — 3	local variable of function
i) heap	large string (dynamically allocated)
j) heap	element (dynamically allocated) of vector
k) heap	element (dynamically allocated) of vector
l) activation record — 3	local variable of function
m) heap	element (dynamically allocated) of list
n) heap	dynamically allocated
o) activation record — 2	holds register data
p) static memory	global variable
q) activation record — 3	local variable of function

2. Answer questions about implementations of lists, stacks, and queues.

- a) One stack would be the primary stack, and the second a temporary stack used only for pushing. The enqueue operation would be accomplished by pushing to the primary stack (retains constant time of push operation to stack). The dequeue operation would simulate popping out the bottom-most value in the stack; this would be accomplished by popping each value from the stack and pushing all of those values (except for the last one) into the temporary stack (at this point, the temporary stack is almost a reverse version of what the primary stack was before the pop operation, and the primary stack only contains the last element). The last element can then be dequeued with a pop operation, and all of the items from the temporary stack can be returned to the main stack by popping from the temporary stack and pushing to the primary stack again. This is linear because the number of constant-time operations is proportional to the size of the list (in this case, number of operations = (2 push + 2 pop operations) * (n-1) + 1 pop, or roughly $4*n$).
- b) This approach would also have a primary and temporary stack. In 2a), the primary stack had the most recent item on top of the stack and the oldest on bottom; this design is reversed for this exercise. To dequeue, a pop operation is performed on the primary stack (because the most recent item is on top). To enqueue, the primary stack would have to be emptied into the temporary stack by repeatedly popping from the primary stack and pushing into the temporary stack for each element of the stack, pushing the new value onto the (now empty) stack, and then returning all of the values from the temporary stack by the same series popping and pushing. This method uses roughly $4*n$ operations like the pop operation in 2a), and therefore has worst-case linear time.
- c) One stack would be the primary stack (stack 1), and the other stack (stack 2) would only be used for holding all of the values that are lower than or equal to all of the values that come before it in the stack.

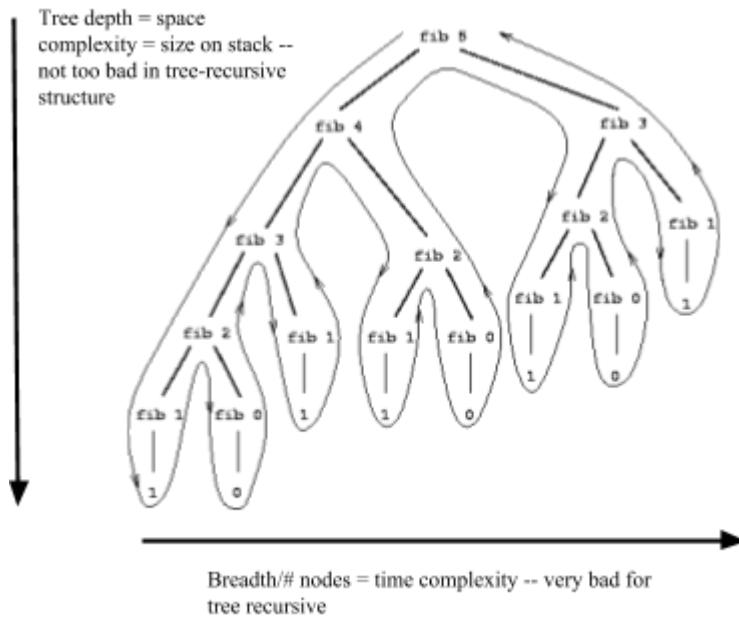
Push operation: Push to stack 1. If stack 2 is empty, push value to stack 2 as well (it is by default the minimum value). If not, pop from stack 2, save its value, and push it back to stack 2. If the value to be pushed is lower than or equal to the value at the top of stack 2 (if it is the minimum value of the stack or equal to the current minimum value), push to stack 2; otherwise, don't.

Get minimum value operation: Pop from stack 2. The top value is the minimum of the values in stack 1.

Pop operation: Pop from stack 1, and return this value. Pop from stack 2. If the two popped elements are not same (i.e., if the popped element is not the minimum of the stack), push the value popped from stack 2 back onto stack 2.

d) There is no clearly better choice. These two solutions are analogous to 2a) and 2b): each would have one constant-time operation to enqueue/dequeue from the beginning of the linked-list, and a constant-time operation to perform the opposite operation at the end of the linked-list. The only difference is the what is considered the “beginning” and “end” of the linked-list, which should not change its ability.

e) While the time complexity of a tree-recursive function such as fibonacci (“branching” out twice for every function call) might be exponential (the number of function calls, or nodes of the tree, is exponential), the stack space is only the maximum depth of the tree; in the case of Fib(50), this would be a depth of 50 recursive calls until a base case is obtained, not an unreasonable number that would run a computer out of stack space. It is the depth of the tree because every time a function returns, it gets removed from the call stack; the recursive fibonacci implementation is slow because it branches out into many nodes and has to travel up and down the call stack many times. An (annotated) illustrative diagram courtesy of SICP is shown below:



Data Structures and Algorithms I

Fall 2018

Homework #3

1. Sorting

- a) Insertion sort adds an element onto an already-sorted array—if it is the largest element of the sorted array, then no swaps are made; otherwise it is swapped into its correct position in the sorted array. If an array is near sorted, few swaps will need to be made, and most of the swaps that will need to be made will be placed near the end of the already-sorted array. (For an already-sorted array, this will be linear, because N comparisons and 0 swaps will be made.)
- b) Bubble sort only swaps adjacent elements that are in the wrong order, and then checks if any swaps were made in the last pass. If most of the elements are in the right order, few swaps and few passes will need to occur; if it is already sorted, this is linear because no swaps are made.
- c) Selection sort does many comparisons ($O(N^2)$) but few swaps ($O(N)$), whereas insertion sort usually does fewer comparisons ($O(N^2)$) but more swaps ($O(N^2)$). Movement in memory is generally much slower than comparing objects, especially for larger data, so the reduction in memory swaps with selection sort outweighs the fact that it is generally slower than insertion sort.
- d) For sorted or nearly-sorted arrays, this creates $O(N^2)$ behavior, the worst-case behavior for quicksort. This is because the partition operation performs N operations but almost no swaps, which is followed by a recursive quicksort with size $N-1$, which is similarly unoptimized.
- e) Mergesort is typically not linear (its running time is $O(N\log N)$), but it is possible to implement it to look for natural “runs” of numbers to ignore while sorting. This would take linear time (one pass) for already sorted arrays. (Timsort includes a merge sort with natural runs for better performance on nearly-sorted arrays).
- f) It is possible using a radix sort—the integers would then be sorted digit by digit into bins, and none of the integers would be compared against each other.
- g) An indirect sort is useful for reducing the number of swaps of the actual data, which is useful when swapping elements in memory is slow, i.e., when the data is large or there is no constant time access to elements (which is the case in a linked list).
- h) A typical implementation of radix sort is stable, because the order that elements were placed into bins is the same order that they are taken out. (Identical elements must be placed in the same bin, and the order they are taken out is the same as the order they were relative to each other in the original sequence.)

- i) Linear does not mean always faster than linearithmic ($N \log N$)— in this case, the high overhead of the median-of-median-of-five pivot selection makes it generally slower than the median-of-three pivot selection for most sequences.
 - j) It is not efficient— essentially it would be recursively performing a quicksort on the smaller halves until a singleton sequence is obtained (the smallest number). A one-pass search for the smallest element (comparing every element against the minimum value so far in the sequence) would be much faster.
-

2. Trees

- a) Preorder traversal, inorder traversal, and postorder traversal are generally implemented recursively. (Preorder recursively traverses children after processing current node, postorder recursively traverses children before processing current node, and inorder traverses left subtree, current node, and then right subtree).
- b) A pre-order traversal is used to evaluate an expression tree: the two subtrees of an operator have to be recursively evaluated to numbers first before the operator itself can get evaluated (evaluate children before parent).
- c) The storing of pointers to left children and right sibling is useful when the number of children of a node is unknown, in order to reduce space but still fully describe the tree's structure. However, to store pointers to the two children of a binary search tree is preferred because it still describes the whole tree, doesn't increase space (still only two pointers to nodes, because nodes can only have two children) and it will be advantageously performant to access the right child of a node directly (as opposed to accessing it as the right sibling of the left child).
- d) Yes. This would be a sequence that oscillates at each depth with a lessening amplitude. For example, the sequence 1, 100, 2, 99, 3, 98, ..., 49, 50 would be such a sequence that would create a tree of depth 99.
- e) If a grandchild exists in an AVL tree, its height must be equal to the height of the tree minus two (grandchild) plus or minus one (AVL tree condition). Thus, its minimum height is $h-3$.
- f) Insertion operations in an AVL tree may be slightly slower because of the rotations and keeping track of height of a node. If there are few elements to enter to a search tree, and if the elements are randomly ordered (i.e., not likely to yield worst-case linear behavior), then it might be more efficient to use a simple binary search tree.
- g) An inorder traversal can be used to iterate through an AVL tree in order based on its keys.
- h) Only one rotation is necessary to restore balance (this is true for any insertion into an AVL tree).

- i) Because each node of a balanced binary search tree can only have two children, it might take many node accesses to reach the desired leaf node. For very large amounts of data in a tree, the data is usually stored on a hard drive, and every access is a (slow) memory access. In a B+ tree, having more children nodes per node allows for memory accesses to be much more efficient (usually optimized to memory block sizes).
- j) The minimum depth would be three, because there would have to be at least enough leaf nodes to store all of the data values (100^3 leaves on the third depth, assuming that the tree is perfectly filled with 100 children per non-leaf node, is one million).

Explanation of blood glucose level determination script (Amy pay attention)

By Jonathan Lam

Draft 1 (will probably take many iterations and explanations)

Colors are associated with three primary (additive) color values: red, green, and blue (RGB). Each color is thought of as a positional vector or point in 3-space (the “color space”).

From provided data, two colors are selected as endpoints (highest and lowest possible blood glucose values) of a line segment. These will be called P0 and P1. These are the color values of the color of the solution at the lowest and highest glucose concentrations. There is another point selected with the average color of the indicator (this comes from the image processing, which is not included here).

Let the point on the segment P0P1 closest to point P be called Q. Q is found by adding the vector component of PP0 orthogonal to P0P1, and adding it to P. (Alternatively, it can be found by adding the projection of PP0 to P0.) The ratio of the norms of P0Q and P0P1 are passed to a function calibrated to the color changes between P0 and P1.

BGLD.js is one written solely in terms of components and basic arithmetic. BGLD2.js is written more abstractly for ease of understanding. Neither are tested nor final.

Future improvements:

This approach is linear, and makes many assumptions about the linearity of color spaces and color changes. (Hopefully it's right or close to right?) The calibrated function can make a non-linear association if the color change is linear.

If the color change of the indicator is not linear (has multiple color changes that do not result in a linear simultaneous change of r, g, and b), this algorithm can be implemented with multiple line segments with endpoints at every calibration point. The orthogonal distance from each line segment is calculated, and the segment that is closest will be used in the final calculation.

Also play around with color schemes. RGB is the most common, but others include HSL and HSV. These might be useful for color subtraction later on.

Diabetes Testing Design Proposal

A. Objective

Diabetes is a chronic illness involving the inability of the body to properly produce or respond to insulin, creating irregularities in blood sugar levels which can have dangerous health effects. The goal of this project is to create a means to test blood sugar that is reasonable for the people with diabetes of Kampala, Uganda to use regularly. The low average income of a person in Kampala is not enough to support common methods of testing blood glucose, such as using glucometers and test strips multiple times daily, so the final product must be cheaper to manufacture than current methods. To help reduce costs and improve sustainability, the product must be able to be produced locally. Because blood sugar levels can fluctuate widely in the span of a few hours, it must be convenient and affordable for people to test their blood sugar using this method multiple times a day. The device must be accurate enough to detect high and low levels of glucose, but accuracy to modern standards of glucose testing are not the primary objective of this project—it is more important to create reasonably-accurate, affordable devices than high-accuracy, budget-breaking existing solutions. Safety of the user is, as always, a top concern, and care to limit the risk of infection or excessive blood loss is important.

The goal of this project are not to improve existing educational media or treatment methods, but only to create a device to test blood glucose using the criteria above.

B. Background

Diabetes (diabetes mellitus) is a disease which affects the body's ability to create or use insulin, a hormone created in the pancreas that regulates blood sugar. Type I diabetes is an autoimmune disease, in which the insulin-producing cells in the pancreas are attacked by the immune system, so the body is unable to produce insulin. Type II diabetes occurs when cells become resistant to insulin. The body may still produce insulin, and usually overproduces insulin in an attempt to keep blood sugar levels normal (Higuera). There is no known cure for diabetes, so close monitoring and constant treatment are necessary to keep a diabetic patient healthy. Patients with Type I diabetes may need as many as ten blood sugar level tests a day; patients with Type II diabetes not on oral medication may also need a few tests a day

Diabetes is an increasing global health concern. The World Health Organization (WHO) states that the number of people with diabetes globally has risen from 108 million in 1980 to 422 million by 2014, a 300% increase (“Diabetes Key Facts”). They also note that the prevalence of the disease is increasing quicker in middle- and low-income nations.

This project focuses on the capital city of Uganda, Kampala. The WHO reports that the prevalence of diabetes is 2.8% (“Uganda Country Profile”), causing 1% of the deaths in Uganda in 2016. A study published in *Tropical Medicine & International Health* in January 2016 analyzed the rates of impaired fasting glycaemia (IFG) and diabetes in Uganda, and reported the prevalence of diabetes to be 2.7% in urban regions and 1.0% in rural areas. According to a 2014

census by the Uganda Bureau of Statistics (UBOS), Kampala is the largest city in Uganda, with a population of 1,507,080, roughly four times as populous as the next largest city (“UBOS National Population and Housing Census”). Because of the increased prevalence of diabetes in cities and the increasing prevalence of diabetes in third-world countries, Kampala is a point of interest.

Uganda is a low-income nation: according to the UBOS Key Economic Indicators Q2 2017-2018 edition, the GDP per capita at current prices is 2,475,413 shillings, which is USD \$681 at a selling rate of 3,633 shillings per USD (“UBOS Key Economic Indicators”). Other estimates of the national average are even lower: the United States Agency of International Development (USAID) and the Frederick S. Pardee Center for International Futures published a report in November 2017 stating that the GDP per capita is \$580 (Rafa et al.). According to this report report, Kampala has the second-highest district GDP per capita of \$2,655, exceeded only by Wakiso (\$3,250). The study also reports that “Kampala is roughly 5% of Uganda’s population, but it generates 22.5% of [Uganda’s] GDP.” Therefore, the focus is not on the poorer rural areas of Uganda, but actually one of the wealthier ones, but cheaper means of blood glucose testing can be beneficial to a poorer region of Uganda as well. The difference is that Kampala has the resources of a large city, and manufacturing will most likely be concentrated in cities of comparable size.

Using this estimate of GDP per capita in Kampala creates the estimate of a monthly income of \$221, and a daily income of roughly \$7. (For the \$580 estimate for GDP per capita in Uganda, the values are \$48 and \$1.59, respectively.)

The most common method of blood sugar testing currently is by using glucometers with test strips. A person pricks a finger with a needle to obtain a small volume of blood, which is placed on the test strip, which is then analyzed by the glucometer. The test strips have on them the glucose oxidase enzyme, which reacts with glucose and oxygen to form glucono delta-lactone (which hydrolyzes to form gluconic acid) and hydrogen peroxide. The glucometer has two electrodes which send a current through the test strip, and the amount of gluconic acid on the strip determines how much current flows. The glucometer is calibrated to determine the glucose level from the amount of current detected.

Most current glucose strips cost between \$0.40 and \$2.00, although diabetes business expert David Kliff claims that mass-producing strips cost large diabetes strip manufacturers only \$0.15, with a large profit (Gebel). The cost of a glucometer typically ranges between \$20 and \$80, but some with more advanced features may cost hundreds of dollars; the cost of lancets to pierce the skin, which may need to be replaced periodically, often cost between \$0.05 and \$0.22 (“Cost of a Glucose Meter”).

These costs are very high for the average person in Kampala. First of all, a glucometer may cost several days of a person’s income. If a person with Type I diabetes has to have ten tests a day, it may cost a few dollars per day, which makes up a large part of a person’s daily income.

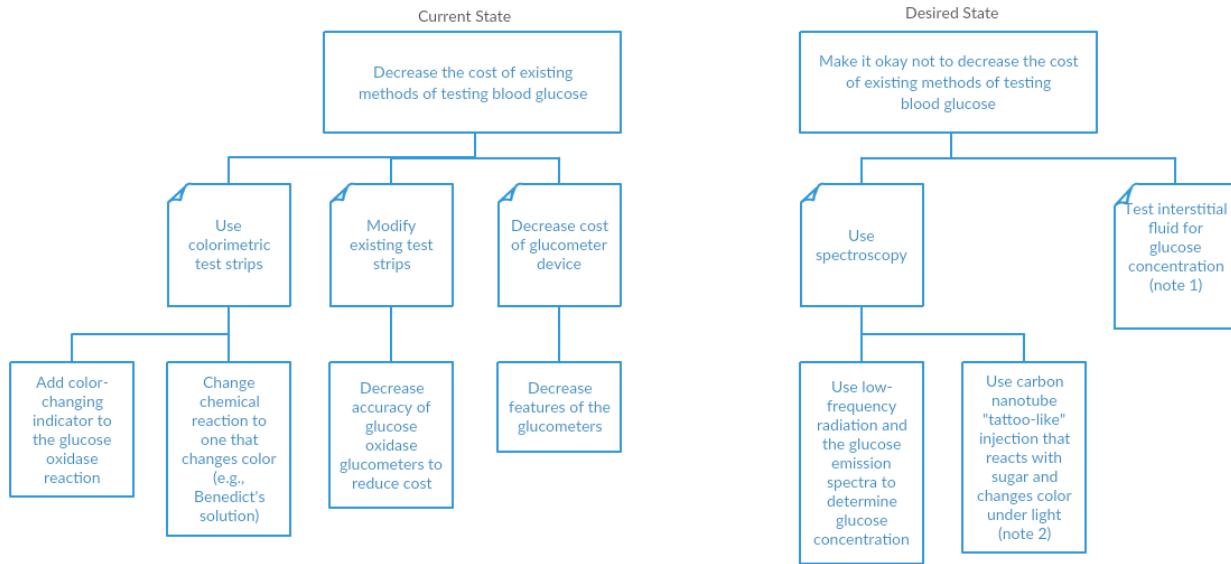
Another common test is continuous glucose monitoring (CGM), which has a sensor under the skin and takes measurements of blood sugar every few minutes. But the cost of these devices is

very high: the machine itself may cost \$2,500 (Wan et al.), very impractical for low-income people. There is also the HbA1c screening test to measure long-term average blood glucose concentration, but this is not designed for regular screening.

C. Methodology

(Because the final solution has not been agreed upon, this section, the expected results, and the cost sections will all be generalized for all possible solutions.)

Duncker Diagram



Notes:

1. Source: <https://www.sciencedaily.com/releases/2018/04/180409170952.htm>

2. Source: <https://engineering.mit.edu/engage/ask-an-engineer/how-do-glucometers-work/>

There are two main approaches to the problem: to decrease the cost of existing methods of testing blood glucose, or to work on alternative methods of testing blood glucose.

The glucose-oxidase reaction used commonly in glucometer test strips can be used along with a color-changing chemical reaction to test glucose concentration. This doesn't require a glucometer (and electricity), nor does it need the expensive metal electrodes in the test strips. This was experimented with previously by G Cubed Solutions (Ofek et al.).

Another possibility is to use experimental methods of determining blood glucose level. MIT students experimented with the possibility with injecting (similar to tattoos) carbon nanotubes that reacted with glucose, and changed color when infrared light was shone onto them so that glucose level could be shown colorimetrically (Jensen). While injections are expensive and invasive, modifications of this method can be explored. A different method using spectroscopy could involve shining infrared (or lower frequencies) of light at a major blood vessel and testing for glucose's emission spectrum. This is similar to the idea of infrared vein finders ("Vein Visualization Technology"). Because spectrometry machines may be expensive, because it is

non-invasive and quick, it may be desirable to have one community-use spectrometer machine in a diabetes center.

Gantt Chart (provisional)

Task	Week														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Introduction and initial research	X	X	X	X											
Design proposals			X	X	X										
Research and design					X	X	X								
Implementation							X	X	X	X	X	X	X	X	
Testing and analysis													X	X	X

D. Expected Results

The expected result must be a cheap product that uses common chemicals or technology that can be manufactured locally in Kampala. The device will be simple to use and cheap.

If the device is a modification of the existing glucose oxidase reaction commonly used in glucometers, it must be cheap (at most \$0.01 or less per strip) to be affordable. This may include colorimetric strips that conduct a chemical reaction and approximates the blood glucose concentration by observing the color of the resulting strip. If the device involves spectroscopy, it will be a non-invasive technique. It may be either a small, personal device or an advanced machine that can be used at a clinic and perform quick tests.

In either case, the final product will be easy to use and either cheap for personal use (an improvement of the glucose testing strip), or very convenient to be used by the community (spectroscopy).

E. Cost

The cost will depend on the choice of final project, but the final design should be cheaper to manufacture than current models, including labor and materials. If glucose oxidase is used with an indicator, glucose oxidase can be bought at \$45 to \$110 per kilogram ("Glucose Oxidase Price"), which would cost \$0.000045 to \$0.00011 per milligram, and only a few milligrams of glucose oxidase and acid-base indicator (to detect levels of gluconic acid) will be necessary to create a simple and cheap colorimetric test strip.

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Assignment 7: Ethics (Voland Chapter 8)

The NSPE Code of Ethics (<https://www.nspe.org/resources/ethics/code-ethics>) was used as an outside resource in question 1.

1. Identify the specific section(s) of the NSPE Code of Ethics that relate to the following actions and summarize the main gist of the code in less than 4 sentences each.
 - a. Whistle-blowing when confronted by unethical behavior within your firm: NSPE II.1.a. This section clearly states that if any unsafe behavior (“circumstances that endanger life or property”) are observed, then the proper authority should be notified. This holds priority over any of the other codes.
 - b. Disclosing a potential conflict of interest: NSPE II.4. This section states that engineers should truthfully disclose any potential conflicts of interest. This includes not deciding in both corporate and public sector decisions, not receiving compensation from multiple parties, and not accepting government contracts, as these can all cause disloyalties from the main employer (i.e., a conflict of interest.)
 - c. Accepting a gift from a client or contractor: NSPE II.3.c., II.4.b., II.5.b. Section II.3.c. states that all interested parties (including those that paid for the communication) must be acknowledged in any official statement. Section II.4.b. states that engineers should only be paid by one party unless earlier agreed upon. Section II.5.b. states that engineers should not receive give or receive any contributions that could be seen as causing impartiality. Together, these statements mean that engineers should be virtuous, not accepting gifts or payments from outside parties that may make them impartial, and to acknowledge all contributing parties.
 - d. Preparing a misleading proposal: NSPE II.3.a., III.3.a. The example given by the text is of Ford engineers manipulating a test to get better results. This is the equivalent of lying to the public: if important information is missing or downright incorrect (as was the case of the Ford engineers), clients may cause harm to themselves by taking faulty information to be true.
 - e. Failing to reveal a potential hazard in a design: NSPE II.1.a. Voland states that “One may fail to protect the safety, health, welfare, and property of the public by *not notifying employers or clients of such dangers* (II.1.a)” (Voland 281). Accidents related to known dangers, such as the bad integrity of the O-rings on the Challenger or the health risk of asbestos, may have been easily avoided if all parties involved are aware of these dangers. Hiding information about potential dangers to increase profit or because it is assumed the dangers are obvious are not acceptable; it is the duty of an engineer to make sure the dangers are known to others.
 - f. Working on a project for which you are not qualified by education or experience: NSPE II.2.a. A lack of expertise in a field may cause injury to the engineer, who may not know how to properly operate equipment or know proper safety techniques. It may also cause injury or dissatisfaction to the client, if the quality of the product is that of a product created by a qualified engineer.

- g. Approving a report of work that was not directly supervised by you or your direct control: NSPE II.3.b.
- h. Criticizing another engineer's work: NSPE III.6, III.7. Section III.6 states that engineers should not try to gain employment by unfair methods such as unfairly criticizing other engineers' work. Section III.7 states that engineers should not attempt to malign other engineers without justification being sent to authorities.
2. Compare and contrast the Ford motor company case involving engine emission tests with the BART case (Case history 8.4). In what ways are these two cases similar? In what ways do they differ?

These two cases are very different because one involves unethical engineers that hid their behavior from the company, and the other involves an unethical company that hid their behavior from the public; the major similarity is that they both involved some sort of serious unethical behavior that resulted in lawsuits against the company. There were also whistleblowers in both cases.

In the Ford motor company case, employees fudged data by tuning the engine during a test. In doing so, they intentionally lied to the public about the performance of their engine. The whistleblower was a different engineer who found the results to be wrong. Luckily, when he told the president of the company, his feedback was immediately acknowledged and changes were put into place. This prevented further complications with the wrong data.

On the other hand, in the BART case, the whistleblowers had the opposite luck. The company executives fired them for insubordination. However, by disregarding the potential safety issues, the company faced much worse problems than the Ford company (which had quickly responded to the whistleblower's feedback), as they had several train accidents because of these problems.

3. Review the Citicorp Center crisis in Section 8.1 (also known as "The Fifty-Nine Story Crisis). Briefly discuss the massive structural oversight, the process that led to the building's eventual structural integrity, identify the ethical and personal dilemmas involved and how these were handled by structural engineer LeMessurier.

The engineering oversight in the design of the Citicorp Center was due to its interesting design (which was due to the building constraints of having a church underneath) and changes in the original design in order to reduce costs (by making faulty assumptions). The building was built on high stilts with four main columns. Steel braces used in the columns were originally designed to be welded together; however, the engineers building the beams for the columns believed that they were building beams for diagonal trusses, which in turn caused them to use fewer bolts than necessary (the original design involved welding the beams together, but this was more expensive). The weakness caused by the insufficient bolts meant that high-wind storms (a "sixteen-year storm") could topple the building.

The beginning of the stabilization was when LeMessurier thought about the design of the building and recalculated some of the forces on the building when

wind hit the building. He then realized that there were not enough bolts to resist the much-increased tension in the bolts. Then, LeMessurier quickly contacted Citicorp and told them of the problem, and steel plates were welded onto the building to reinforce the bolts.

The ethical and personal dilemma is that LeMessurier has a moral obligation to make the building safe but also a reputation to uphold. Luckily, because LeMessurier realized the great danger of his building quickly and performed calculations to determine the necessary fixes, a disaster was avoided. He risked his career to acknowledge the faults in his design and fix them—in the end, this actually benefited his reputation.

4. Review the case entitled Titanium Oxide – Keep it a Secret! Do you agree with the court’s decision to issue an injunction against the engineer? Explain your reasoning and other counterarguments that might be made by the court?

Similar to the other case, in which an injunction was filed against Donald Wohlgemuth to prohibit him from releasing trade secrets, the engineer is not allowed to work on titanium oxide projects for fear of disclosing Du Pont's trade secrets. This is most likely reasonable: the likely motive of the engineer is higher pay or some other benefit; if this is the sole reason, however, this breaks the NSPE II.4 codes. A selfish reason such as higher personal benefits should not be the reason to leak trade secrets to another company.

That being said, if there was a greater motive, such as unethical behavior or poor worker treatment at Du Pont, then the engineer should be able to argue this position in court and be allowed to work at another company. If this is the case, then his motive to change companies is not an unloyal move because the employer was unfair. This is less likely, however, because he responded to a job advertisement looking for his particular job expertise.



EID101E

Diabetes Testing and Education in Kampala

Professor Anita Raja



What is Diabetes?

- Affects body's natural ability to manage insulin
- High blood glucose
- Type 2 diabetes focus



Problem Statement

In Kampala, Uganda, there is no affordable and effective way to measure blood glucose levels for diabetics and very little widespread education about diabetes.

Design Considerations





Target:
Kampala,
Uganda

Background



4.2% ~60,000

Diabetic Prevalence

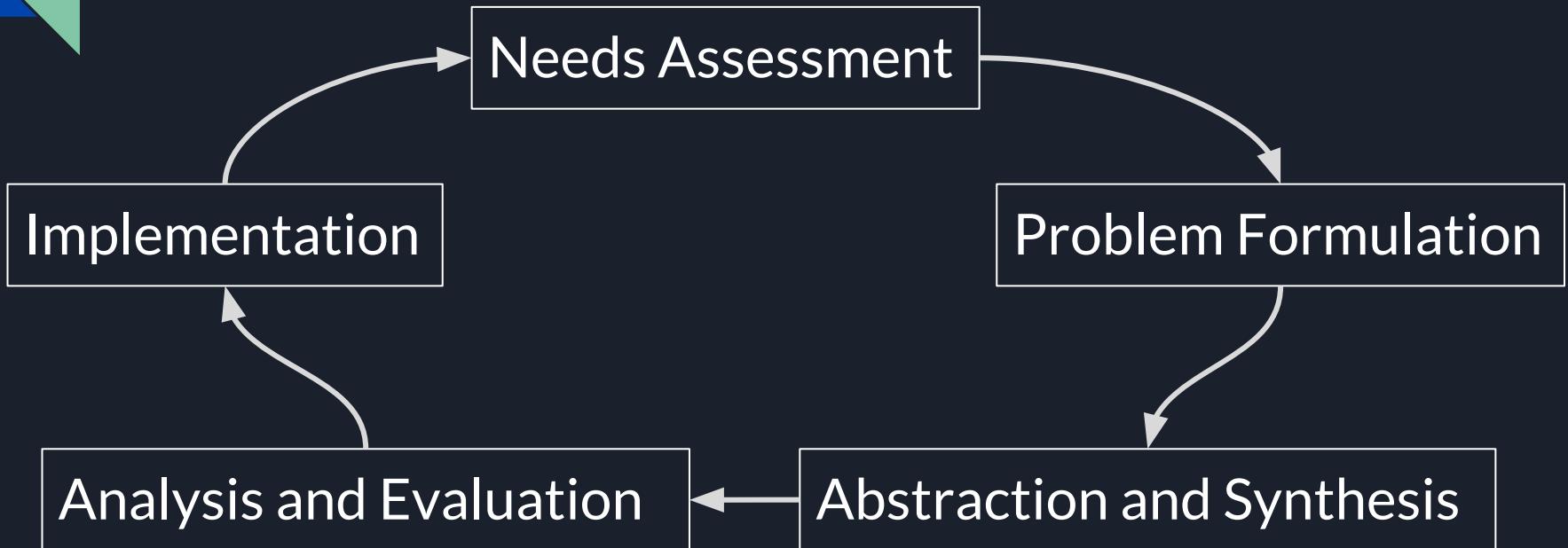


\$287.62

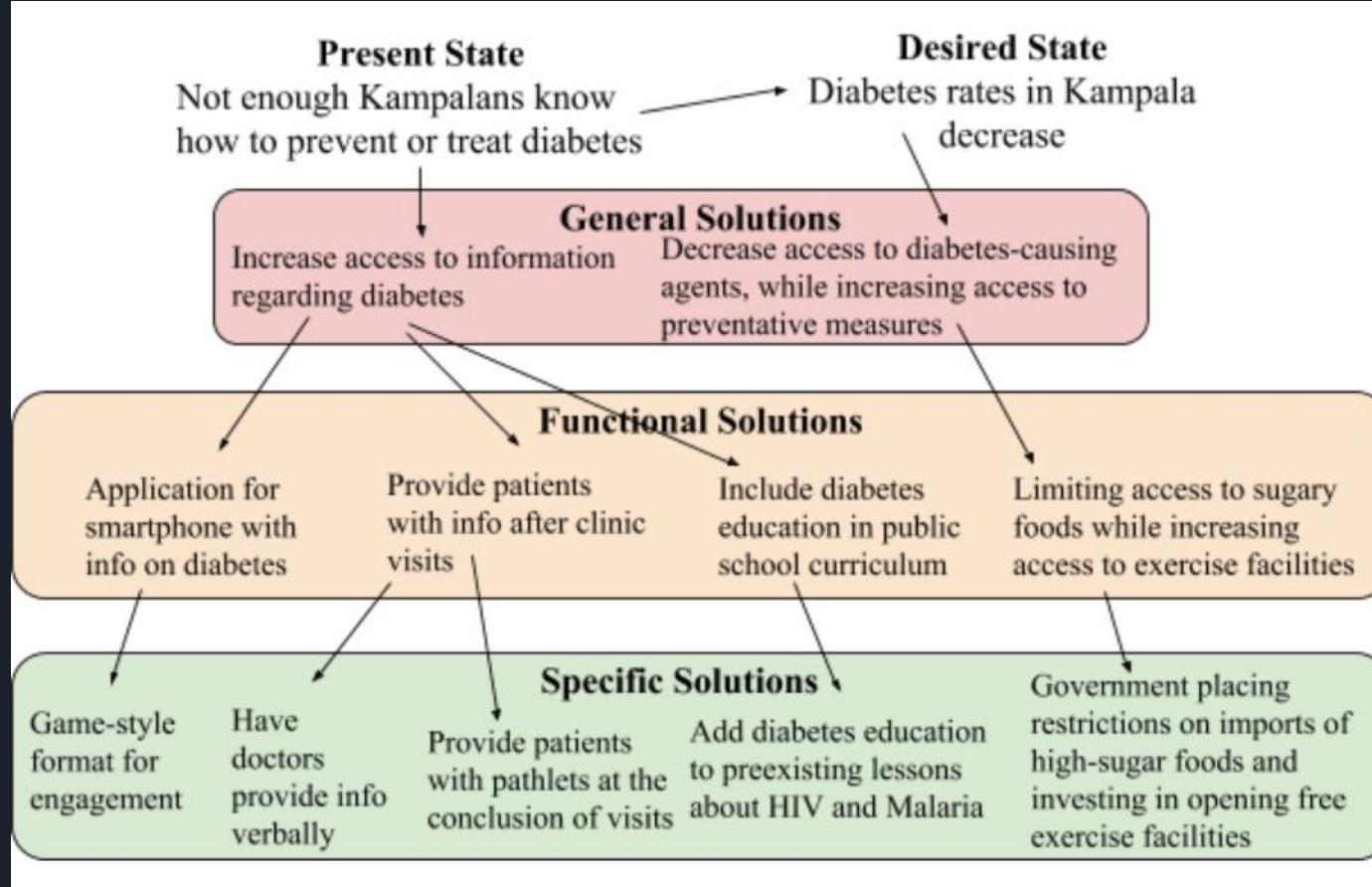
Average Monthly Household Income

Engineering Design Process

Abstraction / Synthesis



Duncker Diagram



Continued Development: Task 1

Gantt Chart of Task 1, Group 2

	Oct 1 - Oct 7	Oct 8 - Oct 14	Oct 15 - Oct 21	Oct 22 - Oct 28	Oct 29 - Nov 4	Nov 5 - Nov 11	Nov 12 - Nov 18	Nov 19 - Nov 25	Nov 26 - Dec 2	Dec 3 - Dec 9	Dec 10 - Dec 16
Preliminary Research and development of design process											
Initial designs of device/solution											
Solidworks/KiCAD drawings											
Rough Prototyping											
Continued Development, refinement, testing											
Final product Development											
Website / Presentation Development											
Video Development											
Documentation											
Attempts to Contact Experts	Professor Katz	Bonex Mwakikunga (breathalyzer)	Einstein Experts	Mr. Dino Melendez							

Task 1: Blood Glucose Testing

Group 1



Jon L.

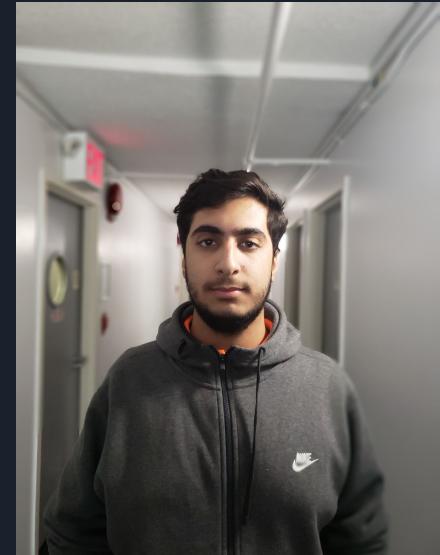


Emily Y.

Group 2



Joshua Y.



Radi F.

Task 2: Diabetes Education

Group 1



Harper C-B.



Pia R.

Group 2



Brandon H.



Derek L.

Task 1

Low-cost, sustainable glucose
management device for people in Kampala

\$0.40+ per
test strip*



* <http://www.diabetesforecast.org/2012/jul/the-cost-of-test-strips.html>

Task 1, Group 1

Colorimetric paper strips with solution

Glucose oxidase + indicator

Easily detect changes in color



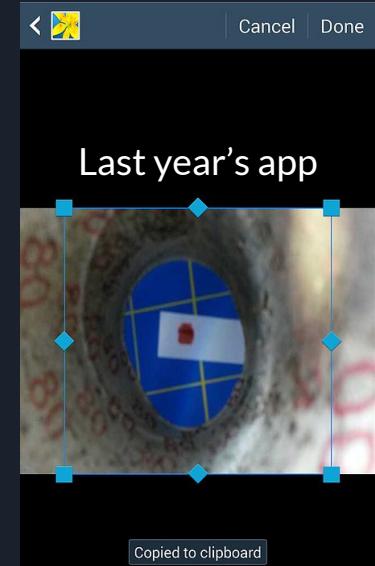
120 mg/dL

Methodology

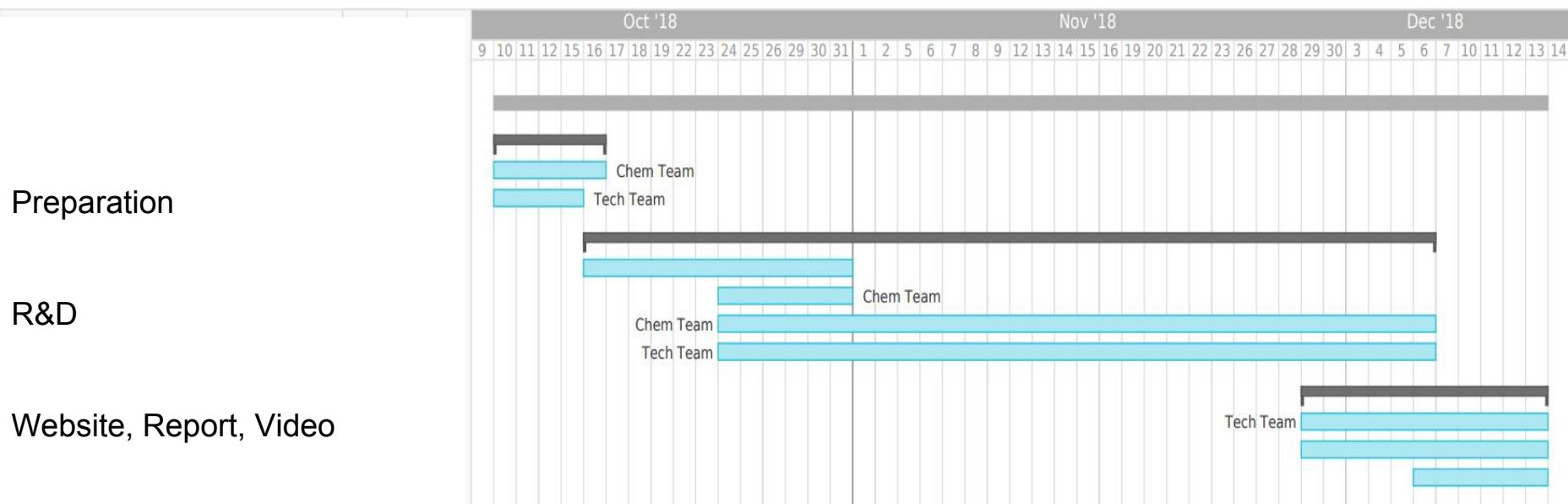
Testing different reagents for glucose

Testing different indicators

Testing color analysis algorithms



Progression & Cost Analysis



Preparation

R&D

Website, Report, Video

Item	Cost for Consumer
Chemicals/Materials	< \$0.01 / strip
Software and Information Distribution	\$0

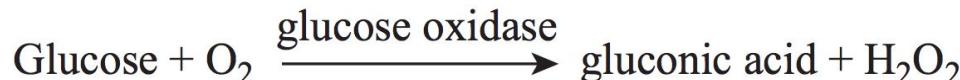
Task 1, Group 2

- Non invasive urine and breathalyzer testing.
- Communal approach to diabetes management.

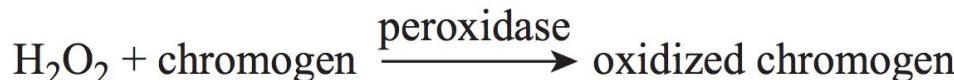
Urine testing

Cost analysis: ~ \$0.01

Reaction A:



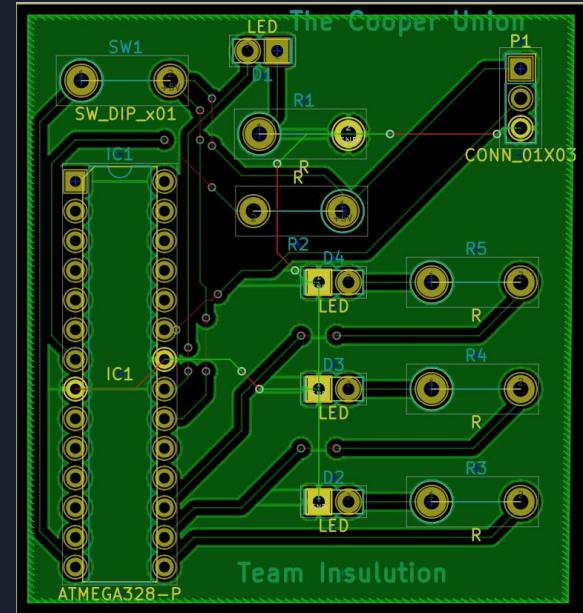
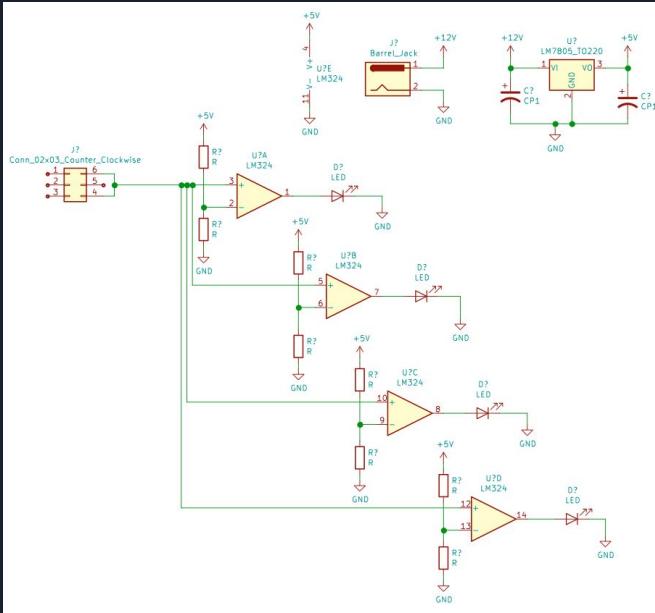
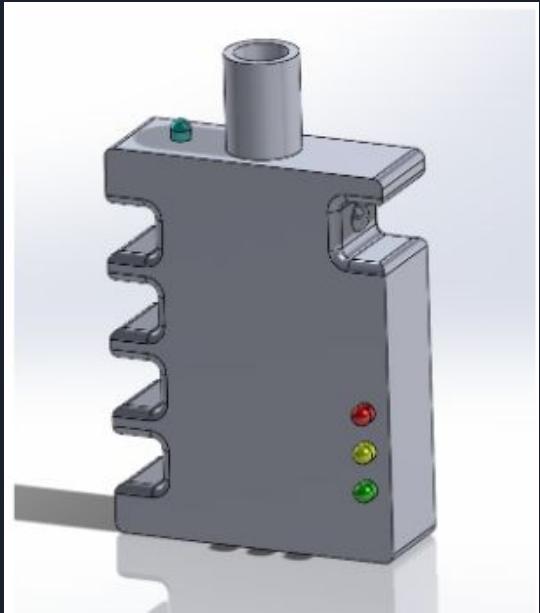
Reaction B:



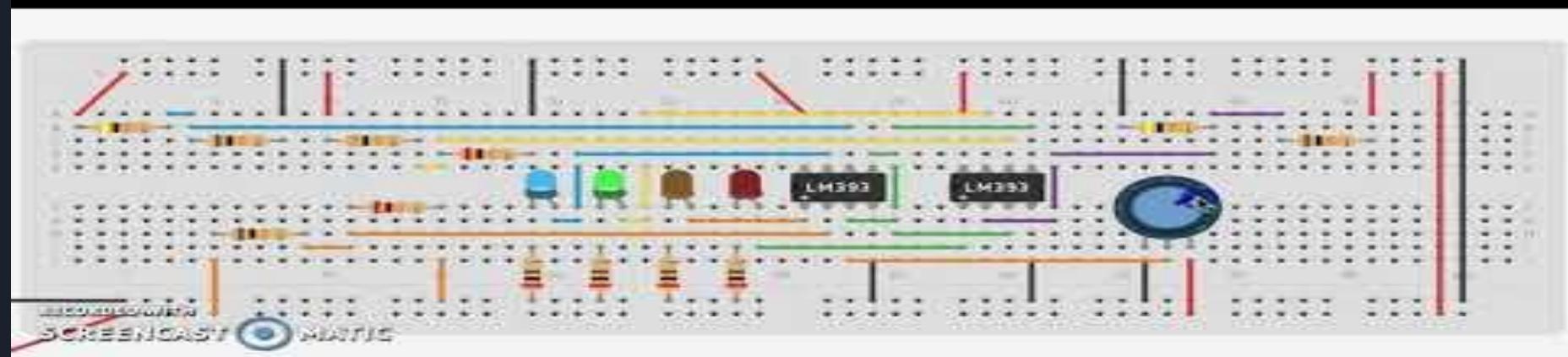
GLUCOSE 30 seconds	NEG	g/dL(%) mg/dL	1/10 100 Trace	1/4 250 1+	1/2 500 2+	1 1000 3+	≥2 ≥2000 4+
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Acetone Breathalyzer

- Measure Acetone content in breath.



Acetone Breathalyzer



Parts List:

Solar panel: ~\$5, ~\$3 for electronics, ~\$10 housing

Task 2

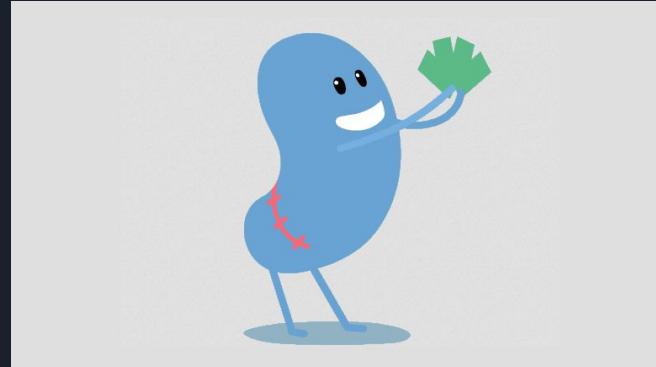
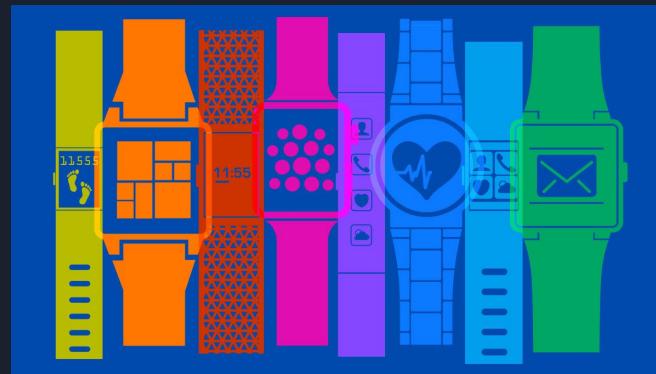
Self-care technologies and preventative education



Task 2, Group 1

Solutions:

- Wearable tech
- Educational app

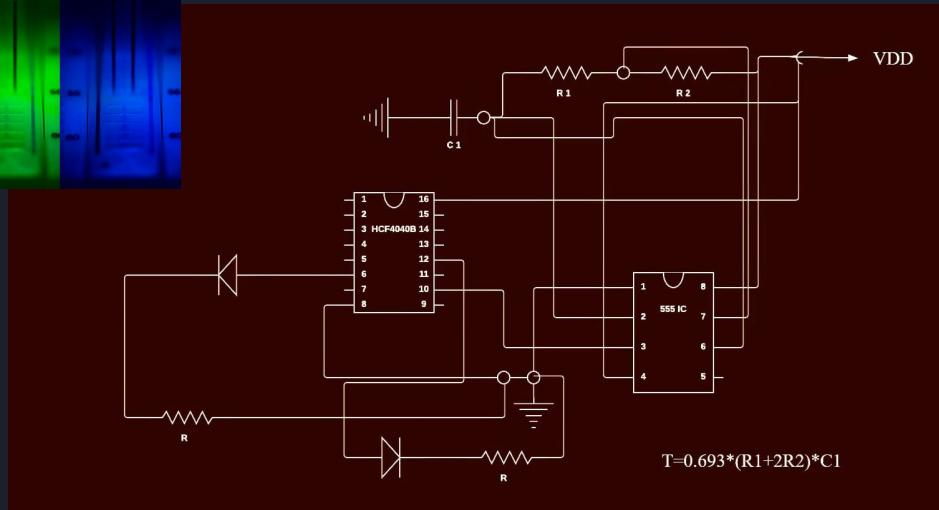


Wearable Tech

The Tech

555 timer,
potentiometer, and
counter

Solar powered



Wearable Tech

The Wristband

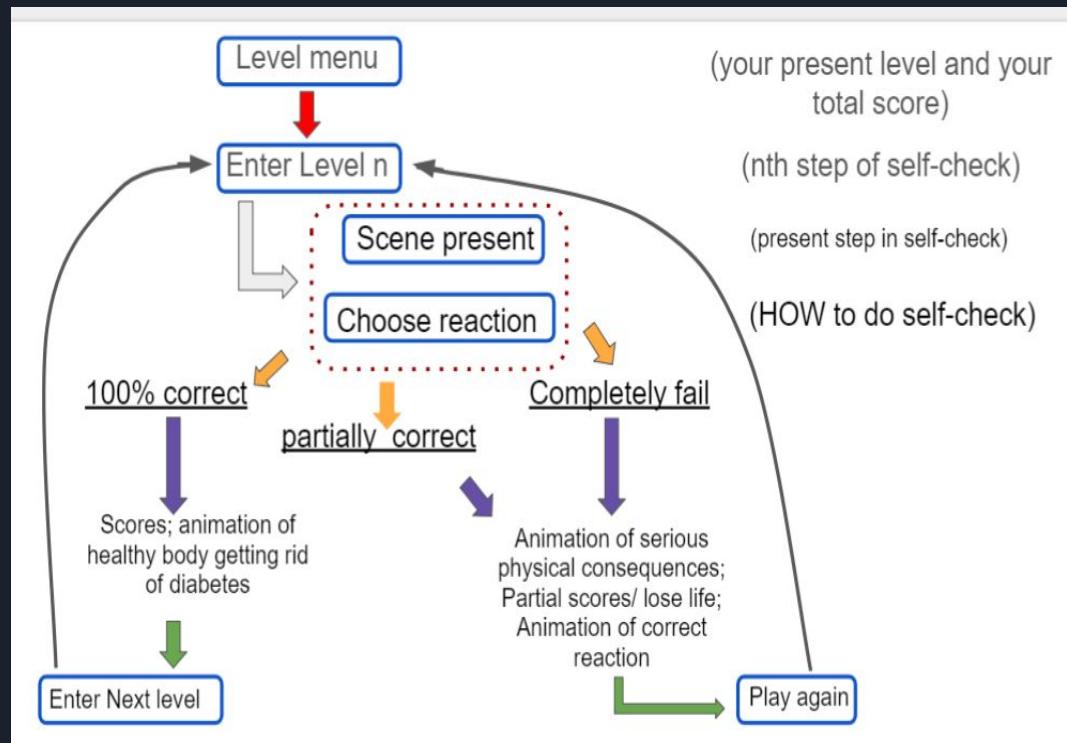
Locally, reproducible
bioplastic

Cost analysis: ~\$10



App

- General
- Treatment standards
- Exercise
- Diet



Task 2, Group 2

Water Purification and Diabetes Education



25% or 350,000+

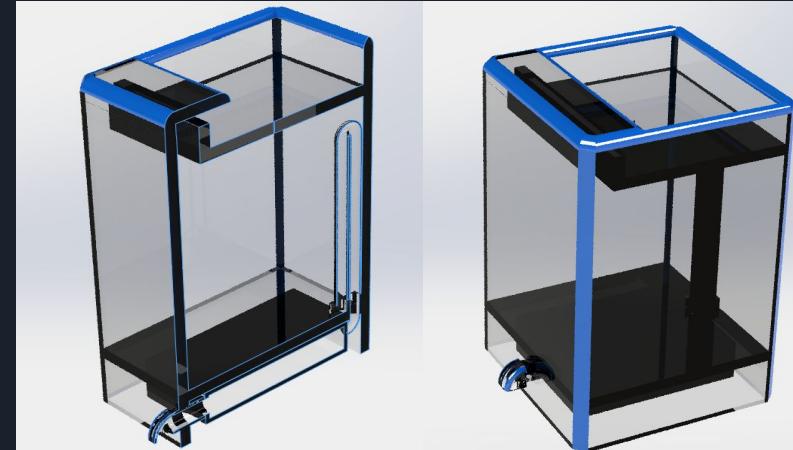
No access to clean water

Purification Methodology

Testing the amount of charcoal
and chlorine needed

Create a siphoning method

Cost: ~\$15-20



App Methodology

Creating a compatible sensor on filter

Program app





Acknowledgements

Professor Raja

2016 and 2017 EID 101E Group

Diabetes Research Team at Albert Einstein
College of Medicine and Johnson&Johnson

Mr. Liva of Bergen County Academies



Thank You!

Emily Y., Jonathan L., Joshua Y., Radi F.,
Derek L., Brandon H., Harper C-B., and Pia R.

Optimized Colorimetric Test Strips & Mobile App Accompaniment for Blood Glucose Regulation

Catherine Chen, Vincent Wang, Peter Baccarrella,
Jonathan Lam, Amy Leong, and Emily Yasharpour

The Cooper Union
for the Advancement of Science and Art

EID-101 Section E
Professor Anita Raja
December 20th, 2018

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EXECUTIVE SUMMARY

Diabetes mellitus (diabetes) is the group of diseases characterized by excessive blood glucose levels due to the body's inability to produce or use insulin. Regular blood sugar tests are required for the well-being of diabetics, but in many developing nations there are no means to inexpensively and effectively measure blood glucose levels—the most prevalent method is to use an electrochemical glucometer with one-time-use test strips. Glucometers typically range from roughly \$25 to \$60 and individual test strips cost between \$0.40 to \$2.00. This financial constraint is dire in countries such as Uganda, where the average income in Kampala, its largest city and second wealthiest district by GDP per capita, is roughly \$300 per month (UBOS, 2017).

Our project uses indicator solutions to visually determine blood glucose levels by a color change, extending the research from the 2017 EID-101 Section E G-Cubed group. Glucose oxidase, the primary reagent for glucose, and TMB, the primary indicator, create the color-changing chemical reaction. The solution will be distributed in bottles to be dispensed dropwise onto copy paper. A fibermesh membrane will be placed on top of the paper to filter out red blood cells. A mobile application that uses camera input to reasonably estimate the glucose level based on the color of the strips was also created. A study by the Uganda Bureau of Statistics found that 86% of 18 to 30 year-olds own a smartphone and most Kampala households have access to a smartphone so a mobile app is reasonable (UBOS, 2017).

The product would be distributed in a kit with a bottle of glucose oxidase-TMB solution and the fibermesh membrane, as well as instructional manuals and a link to the app. A cost analysis showed that each strip averaged out to less than one cent per unit, meeting the low-cost design criteria.

DESIGN PROBLEMS AND OBJECTIVES

The 20th century marks the rise of the diabetes pandemic. The 21st century marks the rise of the diabetes epidemic. With 1.6 million deaths and drastic yearly increases in diabetic prevalence, diabetes is on track to becoming the leading cause of death of South Africa by 2040. The situation is especially serious in Sub-Saharan Africa, where rapid urbanization and changes to a western lifestyle and diet only further increases the diabetic population. This project will target Kampala, Uganda, one of the fastest growing cities in the world (Vermeiren, 2012). Here, the diabetic population is estimated to projected to increase 4.2% annually (UBOS, 2017).

To ensure the diabetic's well-being, blood glucose levels have to be regulated daily. Over the span of a single day, external factors such as food consumption cause blood glucose levels to fluctuate. In order to properly use insulin, an accurate and recent reading of the diabetic's blood glucose level is necessary. However, the combination of financial costs of glucose regulation and lack of cultural acceptance for diabetics in Kampala make regulation extremely difficult.

Therefore, this project focused on optimizing a low-cost and sustainable glucose management device for the diabetics in Kampala, Uganda based on the results of the 2017 EID-E group. The other design criteria were ease of use, safety, and cultural sensitivity. Since the 2017 EID-E group had achieved a low-cost colorimetric test strip by reducing its function to simply measuring blood glucose levels, our colorimetric strip aimed to lower the cost through different chemical reactions and improve the accuracy of the colorimetric test strip using a red blood cell filtration mesh.

Our main design goal focused around being low-cost. In the United States, diabetics use glucometers and test strips in conjunction to measure their blood glucose level. The cheapest price for a glucometer and test strips are \$15 and \$0.33 per strip (prices found on Amazon), respectively. Since the average household in Kapala make approximately \$287.62 monthly (UBOS, 2012-2013), the test strip was designed to be significantly less than commercial

products through a combination of some sustainable parts and cheap disposable parts. Our design also replaced the necessity of a glucometer with a free mobile applications to further reduce costs. Since Kampala is the capital of Uganda and is in a period of rapid urbanization, this plan is viable because technological literacy is common in the younger generations and phones are ubiquitous in every Kampalan household.

DETAILED DESIGN DOCUMENTATION

I. Solutions Brainstorm and Decision

The problem statement was very broad: to create a low-cost diabetes monitoring device that can reasonably accurately determine blood glucose levels in a safe, secure way. A Duncker diagram and a decision matrix were used to aid brainstorming ideas.

Figure 1a. Duncker Diagram Present State

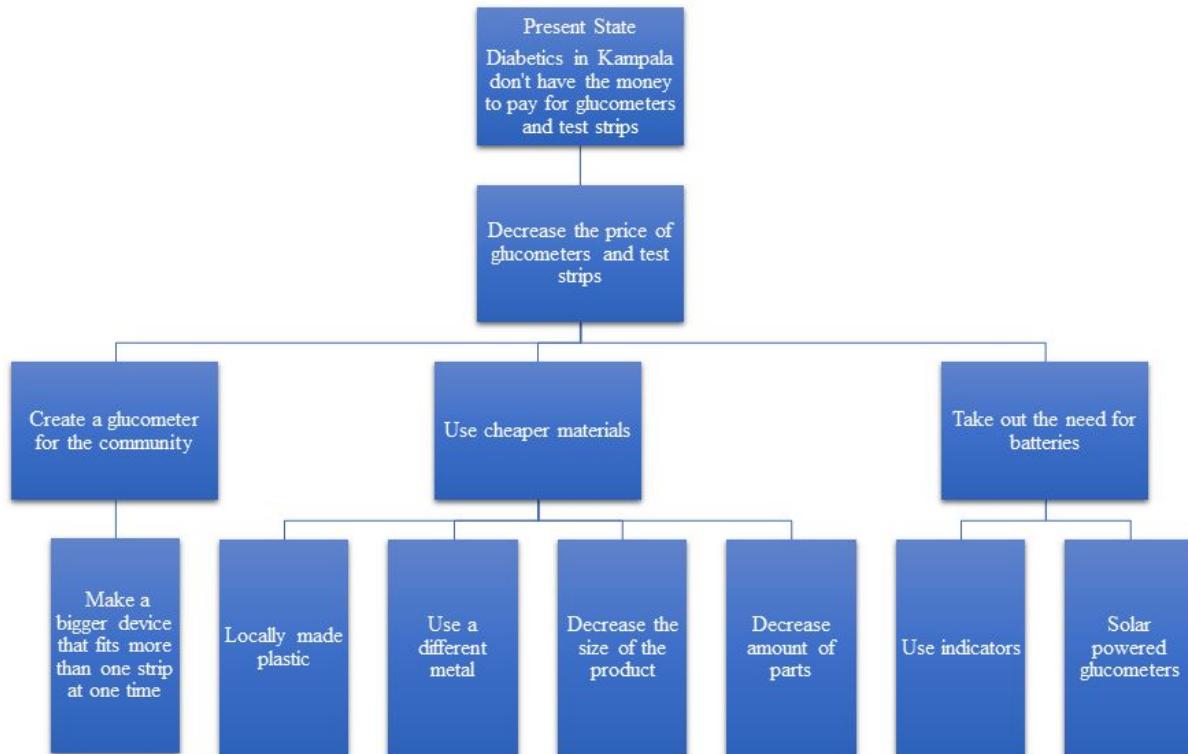
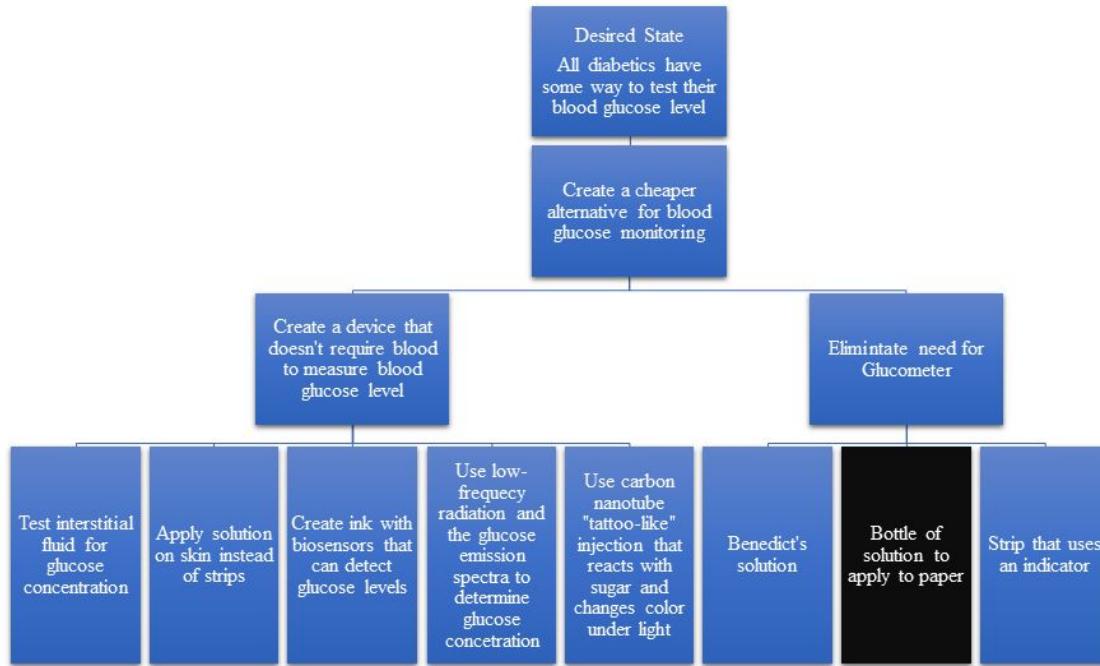


Figure 1b. Duncker Diagram Desired State

A decision matrix was made for some of the top solutions to help determine the best choice. This is shown in Figure 2.

Figure 2. Decision Matrix

Weighting	Cost	Portability	Performance	Ease of Use	Sustainability	Locally reproducible	Total
	100	50	100	85	60	70	
Test strip	9 900	9 450	9 900	7 595	6 360	5 475	3680
Community glucometer	5 500	0 0	9 900	8 680	6 360	4 280	2720
Carbon nanotube tattoo	1 100	9 450	9 900	8 680	8 480	0 0	2610

For the Duncker diagram, there were a few notable solutions on both major branches. If the present state was maintained, then glucometers would still be the main way to test blood glucose, and the project's goal would be to lower the cost of conventional blood glucose monitors to be affordable for Kampalans. The cost of test strips could be decreased if the strips were smaller, which would decrease material costs. It was also suggested to decrease the cost by changing the electrode material away from precious metals like gold into carbon or other materials (test strips originally used carbon, but metal ones proved to be more accurate; however, the accuracy of carbon test strips may be reasonable enough for our project). Lastly, another brainstormed idea was that the test strips could be more effectively sized by tearing it from a roll, so a piece of the test roll as large as it needs to be could be obtained.

However, there was more focus on moving away from traditional electrochemical glucometers and test strips. For these solutions, the technical knowledge of the team is not enough to be able to produce test strips nor glucometers, which are usually manufactured in factories.

For the decision matrix, various design alternatives were considered so that the strengths and weaknesses could be taken into account. It allows us to review each alternative thoughtfully by prioritizing our goals. The goals for this project consisted of cost, portability, performance, ease of use, sustainability, and locally reproducible. Since we mainly wanted to focus on the low cost and the performance aspect, we decided that those factors would weigh the most. We wanted to create something that the people of Kampala can buy at a reasonable price, while it being as accurate as possible. This sets the test strip at an advantage already since it is the most inexpensive method. However, the test strips were ranked as one of the lowest in terms of ease of use and sustainability. Since those factors were not ranked as high, it was a compromise that was worth taking. With the decision matrix, we were able to narrow down some alternatives and were able to see that the color test strips was the best method as the total is the highest with the score of 3680

Additionally, existing research on glucose monitoring devices not involving glucometers mostly were non-invasive solutions, or did not require drawing blood samples. For example, a study was conducted at the University of Bath about the potential for an adhesive patch that measured the glucose concentrations of interstitial fluid (“Bloodless Revolution in Diabetes Management,” 2018). A study by MIT studied the potential for a carbon nanotube tattoo comprised of materials that appear different colors, depending on blood glucose concentration, under near-infrared light (Jensen 2011). Solutions such as these were very interesting, but the equipment, materials, and skills necessary would be far beyond the scope of the team’s expertise. It was also believed that these types of solutions would be too costly to fit the design criteria, and would mostly be used in first-world countries where drawing blood may be a problem.

The last source was that of a team in the EID-101 Section E class of 2017 (Chan et al, 2017). They created a “colorimetric test strip,” which used an indicator to test the products of a glucose oxidation reaction. This allows the user to visually determine blood glucose level based on color, without any equipment. While this still requires blood drawing like a glucometer, it is purely chemical (not requiring an electrical power source), and the analysis is optical (not absolutely requiring any special equipment for a sighted person). The group developed an app to work alongside it to ease the blood glucose level (BGL) determination. Interestingly, they had tried to use an indicator, TMB, known to change color with glucose, which failed; they turned to the commonplace starch-iodine colorimetric reaction, which appeared to perform well.

This final design was chosen because it was promising, the level of technicality was within the reach of the team, and still had many aspects to improve upon. Because their idea was novel, the 2017 research team encountered and listed many problems in their report, such as:

1. The TMB changed color prematurely, probably due to improper use.
2. Adding an colorimetric indicator to a solution containing blood was contaminated with the red color of the red blood cells (RBCs).
3. As a drop of the indicator dried, it formed rings and gradients of different colors.

4. The mobile app was not complete, perhaps mostly due to time constraints. The color analysis was a simple averaging of colors, which was not ideal due to problem 3. There was little data used to calibrate the app, and no report was given to the accuracy of its BGL determination.
5. Lighting was inconsistent. An attempt was made to make lighting consistent by using the app in a box, but there is little data about how well this worked.

The 2017 research team informed us of these issues, and there was regular communication between their team and ours. Our design focused on tackling each one of these problems. A more specific breakdown of our team's goals can thus be written analogously to these problems:

1. Correctly use the TMB indicator, and figure out the conditions of best use.
2. Filter out red blood cells before use with indicator.
3. Find a way to analyze the image differently to account for the changes in rings. For visual BGL determination, choose a metric that is easy for people to understand that takes this into account.
4. Take more time to complete a mobile app. Run a greater number of trials in a wide variation of conditions, and estimate its accuracy.
5. Take lighting into account when measuring the blood glucose level, especially in the app's algorithm.

To tackle this wide variety of problems, the group was divided into multiple subteams. The subteam and role of each person is displayed in Table 1.

Table 1. Team Member Roles

Name	Team	Roles
Peter Baccarella	Chemistry	Laboratory worker
Catherine Chen		Laboratory worker, production of mesh
Vincent Wang		Laboratory worker
Emily Yasharpour		Laboratory worker, production of video
Jonathan Lam	Technology	Webmaster, software developer
Amy Leong		Algorithm development, notetaker

A Gantt chart of the project schedule is displayed in Figure 3. The timeline for the Gantt chart begins roughly when the solution idea was finalized.

Figure 3. Gantt Chart

development										
Final Deliverables										
Website development										
Technical report										
Video editing										

Unfortunately, a large part of the research and development phase began very late, so that much of the data collection occurred in the last two to three weeks. This delayed some of the progress on the mobile app development and addition of content to the website.

II. Chemical Design

The idea of a colorimetric test strip was tested by G-Cubed solutions (Chan et al, 2017) the previous year. The test strip currently consists of a mixture of chemical indicators, a filter mesh and a small strip of plain white printer paper. The printer paper was chosen because it is the cheapest, uniform paper that was found. The chemical mix is made up of TMB or 3,3',5,5'-Tetramethylbenzidine, Horseradish peroxidase, and glucose oxidase dissolved in a mixture of ethanol and deionized water. When it comes into contact with glucose, the glucose oxidase will break it down and produce gluconic acid and hydrogen peroxide. Horseradish peroxidase then oxidizes the TMB using hydrogen peroxide and produces a blue color change. The filter mesh is used to filter out the Red blood cells from the sample of blood. This is done to remove the red color in the blood as to not affect the color of the test. The filter mesh is made up of electrospun polymers with a weave small enough to limit the passage of cells including RBC through it.

The mixture of chemicals and the amount to put on the test strip was found based on the effective units of each reagent. The Glucose oxidase mixture was 30 units per ml, the Horseradish Peroxidase was 60 units per ml and it was decided to make the TMB mass equal to the peroxidase due to a lack of unit measurement.

The test strip is made by placing the sample blood through the filter mesh, onto the piece of paper then adding the chemical mixture. This was found to be the best order due to the red color that developed from putting the chemical mixture first.

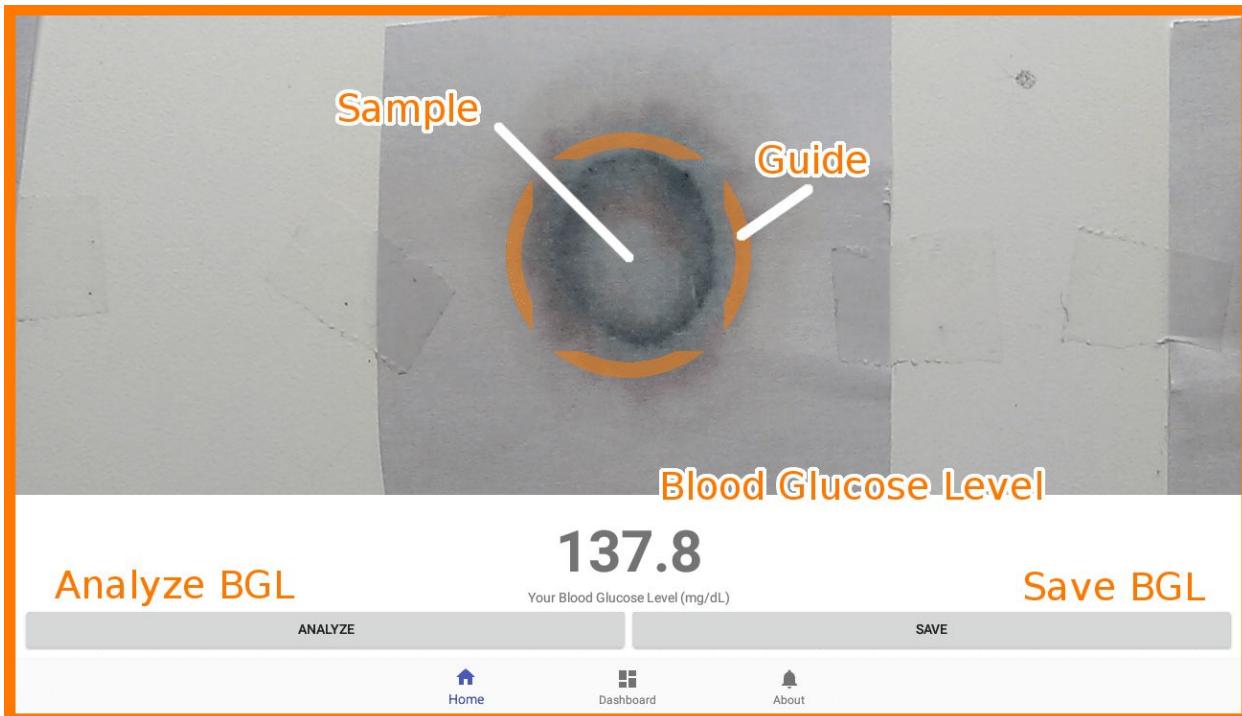
III. App Design and Color Analysis

The idea of using a mobile device (with a camera input) as a method to more accurately determine blood glucose level from the test strips optically was initially tested by G-Cubed Solutions (Chan et al, 2017). While it may seem unreasonable to restrict app access to those users who have smartphones, the Uganda Bureau of Statistics (UBOS) found that 86% of Kampalans from ages 18 to 30 own a smartphone, and that most Kampala households have access to a smartphone (UBOS, 2017). There is no cost to obtaining a (free) mobile application from a mobile application vendor (e.g., iOS's App Store or Android's Play Store), with only the one-time need for Internet access for its download. The prevalence of capable computing devices in Kampala, as well as the absence of cost of distribution, make the idea of mobile-application identification capable for reaching a large part of the target population.

The mobile app has three tabs. The first would be for scanning an image to get blood glucose level; this comprises of a live camera stream (see Figure 4), with markers to guide the user where to place the colored spot on the paper; this was the most important part of the app, and the most significant time was placed in this area. The second and third tabs would be a tabulated list of

blood glucose levels from past scans along with timestamps of the measurements, and the final tab is a simple how-to page. The blood glucose level determination in the app works in two stages: color detection and color analysis.

Figure 4. Screenshot of Tab to Scan Image and Determine BGL



The color detection by the G-Cubed group asked users to select the region of the image with the color from the indicator solution, and the color in that region was averaged. The color was then approximating using a HSL lineariation (hue, saturation, lightness) color values on a model generated by two test data points at a low and high BGL. The initial algorithm for The Regulators involved thresholding out “background” pixels and averaging the rest of the pixels; however, this was not effective for images with uneven background colors or indicator colors with multiple rings, as the samples had. A more efficient method involving clustering similarly colored pixels was used. Contrary to the G-Cubed solution, RGB values were used; HSL was only used in the very early experimentation stages.

Stage 1: The current color detection is a set of heuristics determined somewhat by trial and error. The major steps were threshold all of the pixels into clusters (i.e., breaking down the 2^{24} color space down to 2^{12} clusters), and filtering out clusters based on number of pixels (too few would indicate an insignificant splotch, such as a speck of dust, and too large might indicate a background color), center (the center of the clustered pixels should be near the center of the camera input), error using the “jump method” (Ercolanelli, 2016), and color (the dark blue ring was determined to be the best indicator of color, and thus the algorithm biased dark and primarily-blue clusters). The few clusters that remained would be averaged (weighted averaged based on number of pixels per cluster), and the R, G, and B values of this averaged cluster would be determined to be the most useful ring for the blood glucose level determination.

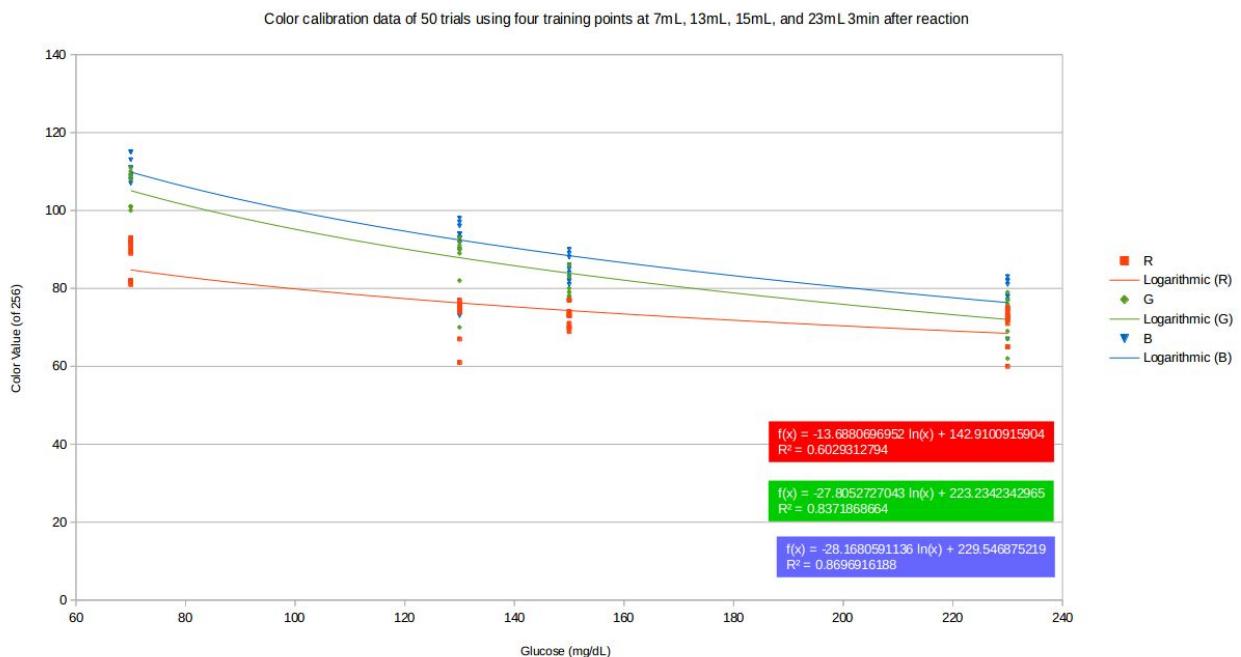
Unfortunately, the color thresholding is slow (it cycles through every pixel, and the time necessary to analyze one scan is roughly 10 to 20 seconds); there were no attempts to improve performance because this is only a minor inconvenience, and this will be an area for further study with potential for downsampling or smarter sampling of relevant areas.

Stage 2: The averaged cluster color would be inputted into the inverse trend line equations generated by the model to guess at the blood glucose level. The three estimates (one for R, G, and B) would be averaged (weighted based on coefficient of determination) to get a final BGL determination. This offers results better than the ones from last year’s app because it does not require any user input and can capture more complex patterns (i.e., the rings of color).

The calibration "trials" involved running the heuristic filtering on four samples in constant lighting, and plotting the final cluster against BGL concentration. A trend line was created for each color (see Figure 3). (A polynomial trend line worked best, but its end behavior did not make sense; the close-behind logarithmic models seemed more reasonable). Unsurprisingly, the trend line for the blue component was strongest, indicating that the difference between the blue could most reliably be used to determine BGL. For these curves, there was slightly yellow fluorescent lighting as the only light source, and the samples were printouts of images of

laboratory samples for 70mg/dL, 130mg/dL, 150mg/dL, and 230mg/dL BGL samples three minutes after application. These were considered to be a wide range of acceptable BGL levels. The lighting conditions were poor and not varied because of a lack of time for testing, and therefore is an area for improvement in the algorithm.

Figure 5. App Color Calibration Curves (RGB Color Values vs. BGL)



The concentrations of the samples for calibration were known. When the heuristics are performed on these samples, there is some variation. If used correctly and lighting is consistent, the variation in readings of the same sample varied by up to roughly $\pm 30\text{mg/dL}$. While this may seem like a wide range of error, diabetics' blood sugar levels can range far greater ("Blood Sugar Levels Chart," 2015), so it should still be a useful metric. With further experimentation, however, it is expected that the the algorithm should improve and variation should decrease, and user error and lighting will be better accounted for.

For Kampalans who lack access to smartphones, an alternative is to use a color guide to indicate blood glucose level from color or appearance. This is a simpler solution; however, as the color is

not even throughout the splotch of color created by the indicator, using this may introduce some user error. This would be similar to the color guide of a universal pH indicator strip, similar to that shown in Figure 6.

Figure 6. Universal pH Indicator Strip with Color Reference



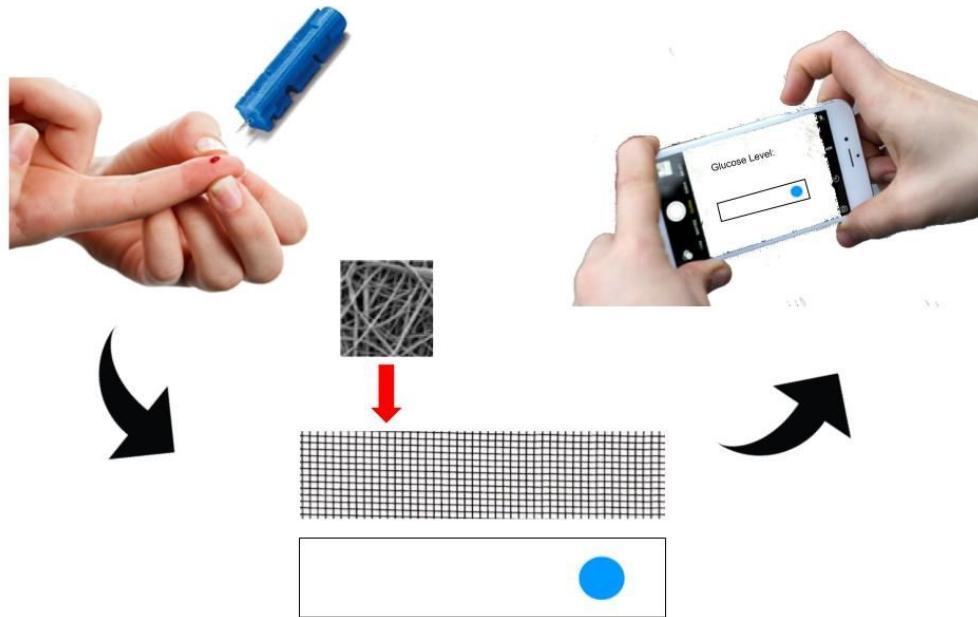
(image courtesy of <https://www.grainger.com/product/3UDD2>)

Such a color reference has not yet been developed, because more research into what colors (e.g., red, blue green), what aspects of the colors (e.g., hue, saturation, lightness), and what areas or patterns of the image that are most representative of blood glucose level is necessary. Future research into using machine learning with all of the samples conducted will likely create a more accurate color analysis reference. Machine learning should also help account for slight variation in lighting and placement, as well as to potentially speed up image analysis by only analyzing relevant portions of the image.

IV. Overall Product

The final distributable product would be a bottle with a dropper cap of reagent/indicator solution, filter, white paper (optional), instructions to download the mobile application, a color reference guide, a short summary of diabetes and The Regulators project, as well as pictorial how-to manuals for usage of the strip (with filter), mobile application, and color reference guide.

Figure 7. Product Usage



Our product works in three steps. First, the user pricks their finger with a lancet. Next, the user would press their finger against the filtration mesh, which is on top of the test strip. The mesh is removed and a drop of the TMB, horseradish peroxidase, and glucose oxidase solution is placed onto the test strip. After five minutes, there will be a color ranging from pale blue to intense blue. Lastly, the user will take a picture using the mobile app which will give an estimate of the user's blood glucose level.

There were five design criteria: keeping low-cost, sustainable, easy to use, safe, and culturally sensitive.

Tables 2 is a cost analysis of the test solution. The costs are scaled down to costs per mg or mL of solution.

Table 2: Cost Analysis

	Cost per bottle	Cost per mg/mL	Units per bottle
TMB (1mg)	\$41.80	\$0.04	
GO (1mg)	\$45.10	\$0.64	10000
HRP (1mg)	\$122.59	\$0.73	25000
Ethanol (1mL)	\$159.90	\$0.04	
3mg of TMB/5mL of ethanol	\$0.13	\$0.21	\$0.34
1mg of GO/5mL of deionized water	\$0.64		\$0.64
3mg of HRP/5mL of deionized water	\$2.20		\$2.20

In Table 3, the costs from Table 2 are projected to the costs of estimated amounts of the solution per test strip, and this is extrapolated to larger time spans.

Table 3: Projected Costs

	Cost
15ml of test solution	\$3.18
1ml of test solution	\$0.21
1 strip	\$0.001
1 day	\$0.003
1 month	\$0.098
1 year	\$1.159

Table 3 illustrates that a single strip costs less than a cent to make, and that over the span of an entire year, the cost of the solution will be roughly one dollar. There is no additional cost to download the (free) mobile application, provided that the user has access to a mobile phone and a one-time Internet connection. Together, the initial cost \$0.01 is much lower than that of a glucometer, and the cost of the solution, at less than a cent per test strip, fits the design goal of less than one cent and is much less expensive than current test strips.

Ease of use is a category that can use some improvement. The product has many components to function properly, and we have not come up with a solution to distribute it as one product, because the solution will degrade when exposed to air and the mesh is reusable. The app is another component that a user has to learn to use. The goal is that with sufficiently thorough instructional manuals, a user should be able to follow the steps efficiently.

Due to the chemicals that we chose, TMB, horseradish peroxidase, and glucose oxidase, it was sustainable and safe to use. If there is any skin contact or eye contact, the chemicals can be thoroughly washed out with water. Also, since there was very little chemicals used per strip, the test strips are sustainable and can be thrown into the trash after use.

When designing our product, we made sure that we conducted enough research about Kampala so that we could understand people different from us and serve their community better. Since there is a lack of medical facilities in Kampala, the wait times are usually long. They would be giving up a day of work in order for them to check the blood glucose levels. This is why we decided to create something that they could use in their own homes instead of travelling to a medical center.

LABORATORY TEST PLANS AND RESULTS

After deciding on the solution we will pursue, a protocol was created so that each step of the process was laid out. At our time in the lab there were three major stages, which were testing in test tubes, testing on paper, and refining our process for testing. This allowed for us to make sure that nothing was wrong with the chemicals themselves and that they were being used correctly before testing them on paper.

First, we needed to make glucose solutions. The concentrations created followed those that a diabetic would experience (DiabetesAdmin, 2015) (See Table 4).

Table 4: Glucose Concentrations

Concentration of Glucose	Standing of blood glucose level
70mg/dl of deionized water	Lower End of Normal for Fasting
130mg/dl of deionized water	Higher End of Normal for Fasting
150ml/dl of deionized water	Lower End of Normal after a meal
230ml/dl of deionized water	Higher End of Normal after a meal

Then, we decided to test the Tetramethylbenzidine(TMB)-Horseradish peroxidase(HRP) reaction in test tubes to make sure the colors presented by the TMB were correct. Concentrations of TMB, HRP, and Glucose Oxidase (GO) were made (Bergmeyer, 1974) (See Table 5).

Table 5: Chemical Concentrations

Chemical	Concentration
Tetramethylbenzidine (TMB)	3mg/5ml of Ethanol
Horseradish Peroxidase (HRP)	3mg/5ml of Deionized water
Glucose Oxidase (GO)	1mg/5ml of Deionized water

We tested the solutions by using the 70mg/dl concentration of glucose and adding each of the other chemicals into the solution in a 1:1:1:1 ratio. The first test turned out to be blue (Figure 8) which is the right color after the reaction but this was found to be due to the fact that the test tube was closed right after the chemical were added. When not closed the color turned out to be orange (See Figure 9).

Figure 8: Solution with cap closed right after all chemicals were added**Figure 9: Solution with cap left open**

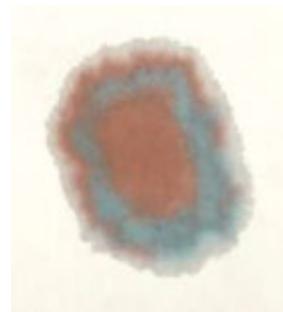
After realizing the effect of leaving the test tube open, we decided to test the color of the solution based on time. Leaving the test tubes open for 5 minutes still gave the solution a blue color (Figure 10) so timing was not a problem as long as it was below 5 minutes.

Figure 10: Solutions for when caps of test tube were closed 5 minutes after chemicals were added: First test (left), Third test (right)



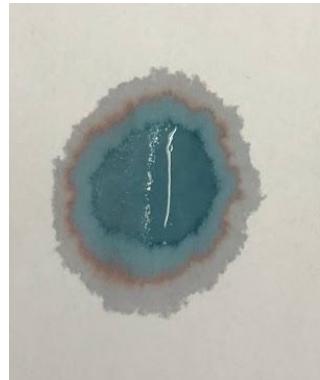
Now knowing that we are using the chemicals correctly, we moved on to creating the test strip. We combined the separate TMB, HRP and GO solutions together in a 1:1:1 ratio to create the test solution which will be put into our product. To create the strip we first added the test solution onto printer paper. Upon the first test, we saw the blue color as expected but what wasn't expected was the red color because the tests in the test tube never showed a red color (Figure 11).

Figure 11: First test with TMB with TMB on the paper first



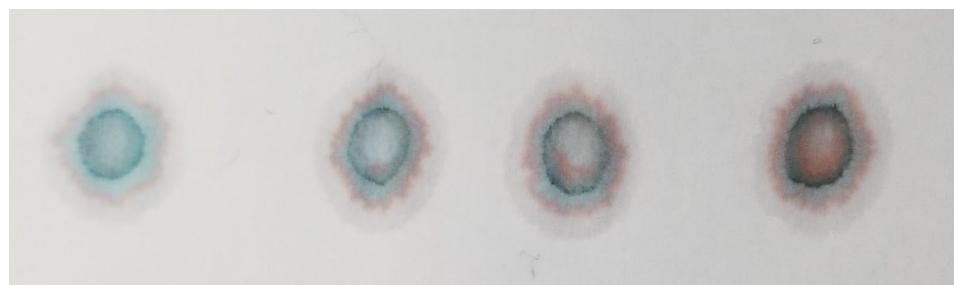
To decrease the amount of red in the color we decided to compare testing with TMB on the paper first (Figure 11) and glucose on the paper first (Figure 12) and we concluded that the best outcome was from the glucose on the paper first because it had the most amount of blue.

Figure 12: Glucose on the paper first



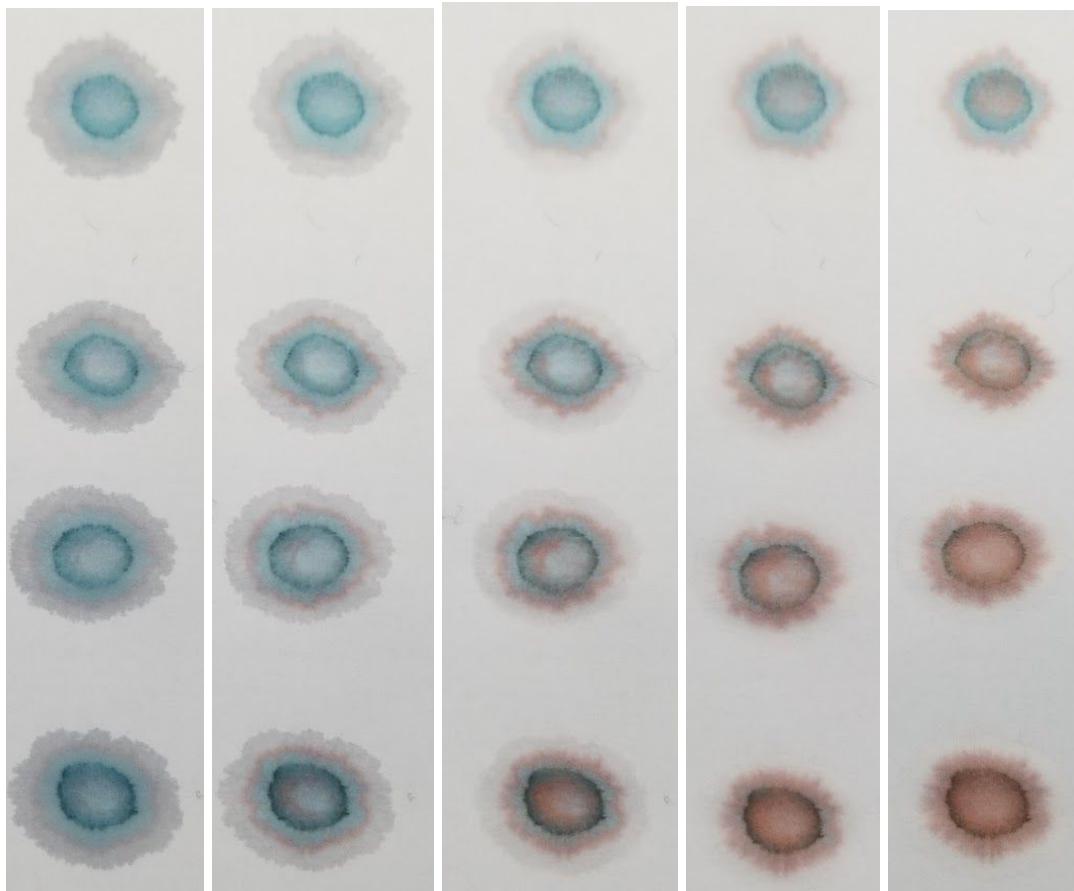
After choosing to start with glucose on the paper first, we tested with different amounts of glucose and the test solution. The tests with the bigger amounts lead to a larger amount of paper used because more of the solutions were soaked in. This was not ideal because the colors spread out too much. $5\mu\text{L}$ of both the glucose and the test solution was optimal as it conserved paper and spread to only a small area (Figure 13).

Figure 13: $5\mu\text{L}$ of Both Glucose and Test Solution: 70mg/dl, 130mg/dl, 150mg/dl, 230mg/dl concentration of glucose (left to right)



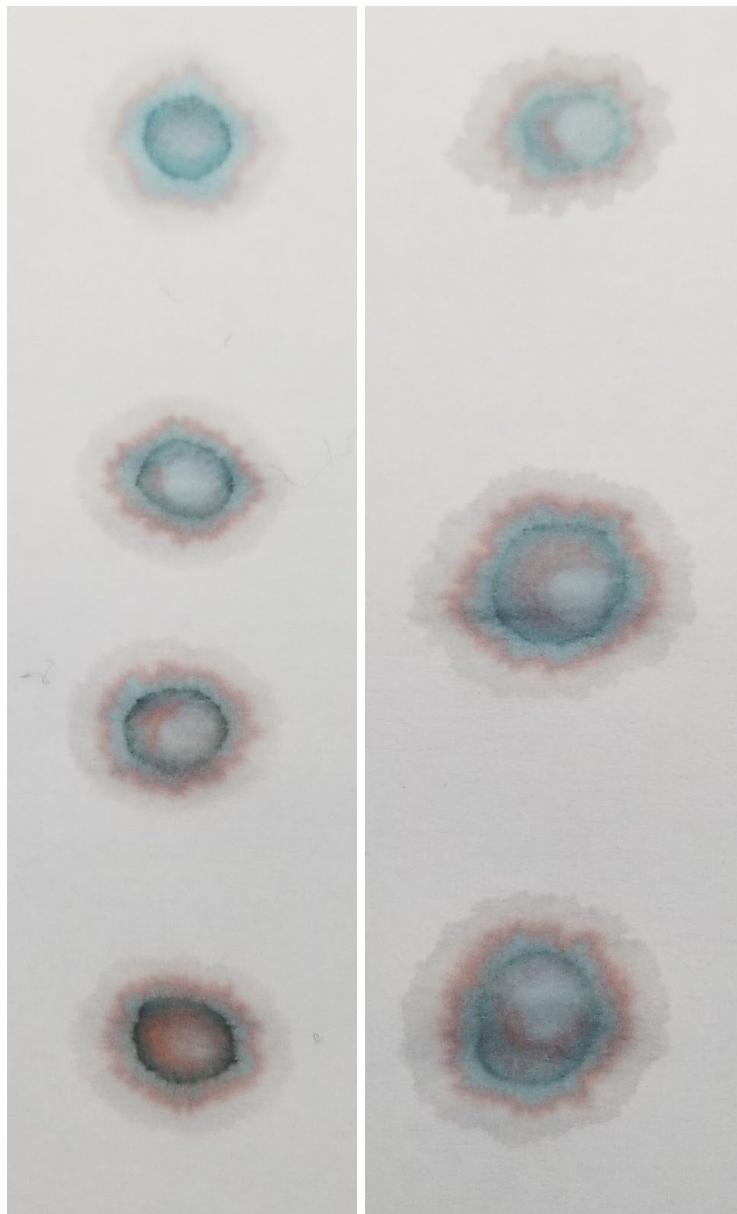
After finding the right amount to test, we had to test at what point should the diabetic take their reading. We took picture of the solutions at 1 minute intervals from 1-5 minutes (See Figure 14).

Figure 14: 5 μ L of Both Glucose and Test Solution at 1 minute intervals from 1-5 minutes (left to right): 70mg/dl, 130mg/dl, 150mg/dl, 230mg/dl concentration of glucose (Top to bottom)



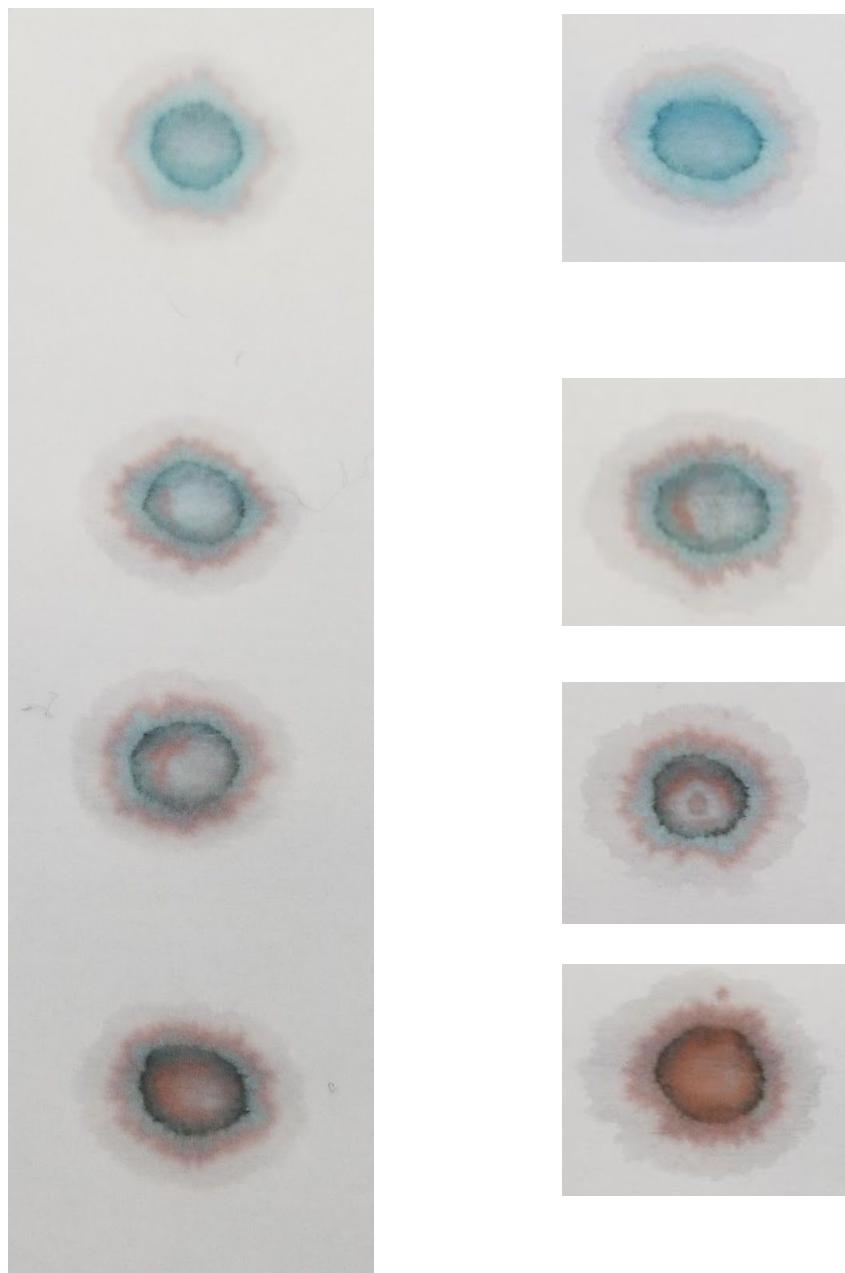
The 3 minute mark turned out have the best variation with both the blue and red color so it was chosen as the marking point of when to take the reading. We did further testing to make sure the tests was consistent we made Figure 13 the basis for our further tests. Glucose solutions with concentration 90mg/dl, 170mg/dl, and 190mg/dl were created to test how accurate of a reading you can get just by looking at the color (See Figure 15).

Figure 15: Comparison of basis glucose concentrations (left) with 90mg/dl, 170mg/dl, and 190mg/dl (top to bottom) glucose concentration (right)



It can be clearly seen that the 90mg/dl one goes between 70mg/dl and 130mg/dl while the 170mg/dl and 190mg/dl go between the 150mg/dl and 230mg/dl so the concentrations in between don't really have a problem but when you get close to the basis concentrations it can be hard to tell (see Figure 16).

Figure 16: Comparison of basis glucose concentrations (left) with another sample with the same concentrations (right) 70mg/dl, 130mg/dl, 150mg/dl, and 230mg/dl (top to bottom)



In the end the prototype was accurate to a certain degree because the closer you got to the basis concentrations the harder it was to tell what your concentration was but at these points the worst case scenario should be taken into account because if you are near the low or high end you are close to not being in the safe range so precautions should be taken no matter what. Further

testing would need to be done to make the prototype more accurate and also further testing would need to be done to see if the prototype could handle the temperature in Kampala Uganda as the test solution needs to be refrigerated and the temperature in the air could affect the test. Storage life of the test solution needs to also be tested because TMB is known to degrade over time.

The TMB and Horseradish Peroxidase chemical reaction produces a color change ranging in the blue tones. Since blood contains a red pigmentation from hemoglobin, the addition of blood into the otherwise blue chemical reaction drastically changes the expected color as shown in Figure 17.

Figure 17. Solutions Mixed With Goat Blood



Therefore, a mesh designed to filter out the red blood cells was created from the polymer polycaprolactone (PCL). PCL was doused in acetic and formic acid for 24 hours to form a polymer solution. This solution was put into a syringe and placed into the handmade electrospinning machine in the IA Lab. Aluminum foil was placed onto the mantle of the electrospinning machine to catch the filament. The electrospun machine is designed to slowly push the syringe at a constant rate to slowly force out the polymer solution. The machine is connected to a 25,000 volt power supply which is used to convert the polymer solution into scattered filament. The random scatters of filament form together to form the red blood cell

mesh. The procedure to make the electrospun fibers were completed by Professor Weiser. An electrospun fiber mesh created in 60 minutes is shown in Figure 18.

Figure 18. Electrospun Fiber Mesh (60 minutes)



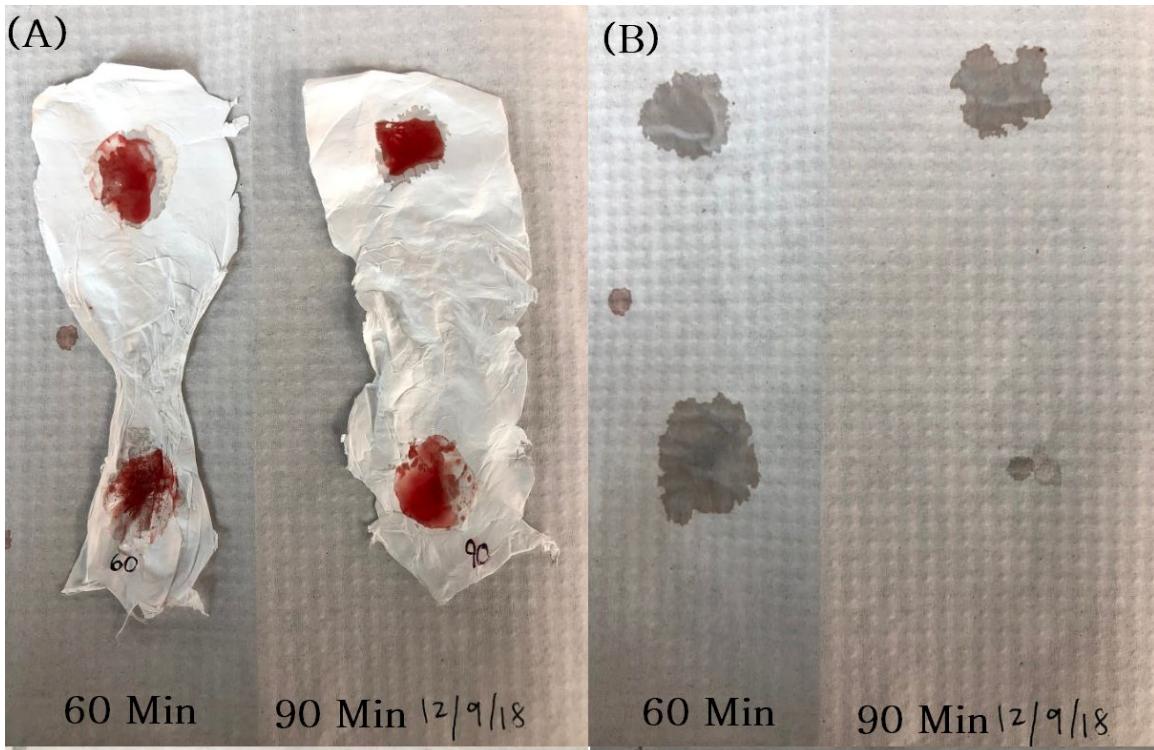
There were two factors taken into consideration when creating the electrospun fiber mesh: time and resistance. The longer the polymer solution was placed into the electrospinning machine, the thicker the resulting mesh and more resistant. However, the resulting mesh is also more narrow due to the additional layers of filament. Electrospun fibers have diameters in the nanometers whereas red blood cells have diameters of approximately 2 to 8 micrometers. It is unknown if the electrospun fiber mesh would filter out everything, not just the red blood cells, if additional layers of filament were added.

Considering time constraints, two electrospun fiber meshes created in 60 minute and 90 minutes were procured and used for initial testing. Due to issues with procuring blood, testing was significantly delayed. Initially, we wanted to use human blood but there were IRB concerns. Then, we wanted to use synthetic human blood but there were time constraints. As a result, goat blood was used to test.

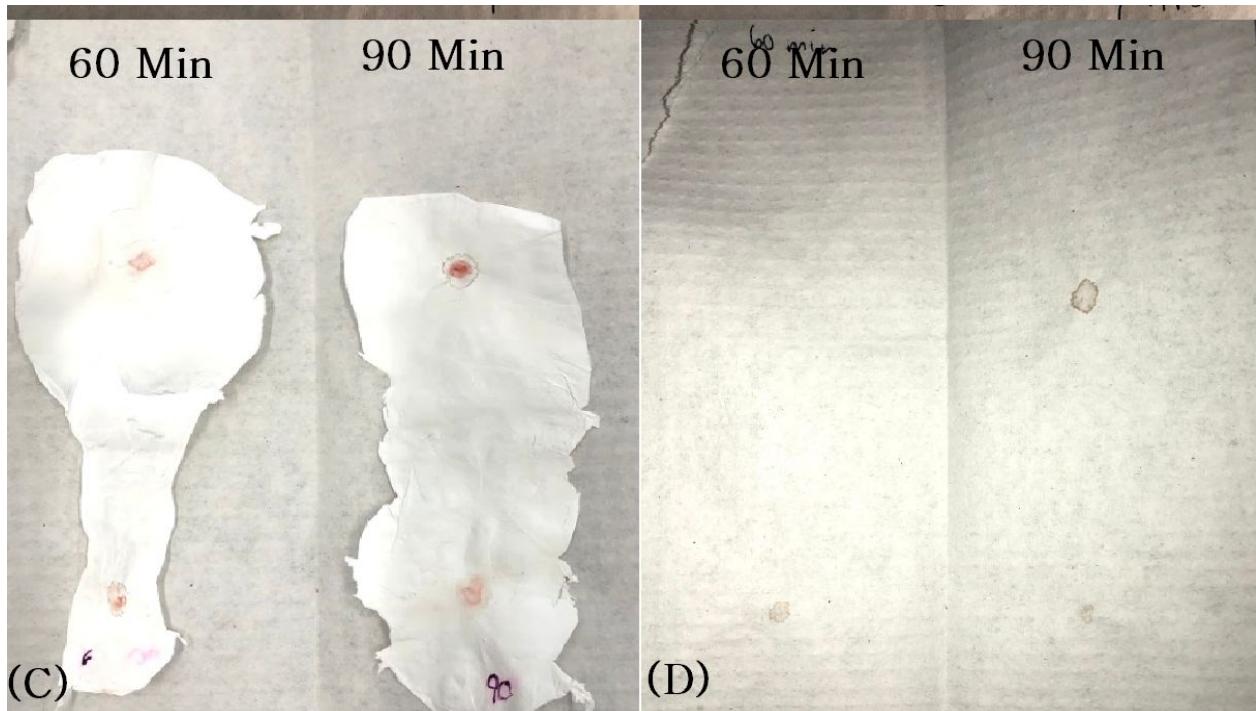
A large amounts of goat blood was used to test if the blood could be filtered, as shown in Figure 19. The upper two squares in Figure 19 A and B show the filtration of goat blood by waiting for

four minutes. The latter two squares show the filtration of goat blood by pushing a certain amount of blood using a finger. This is to mimic the actual procedure of diabetics pricking their finger with a lancet before placing it down on the filtration mesh.

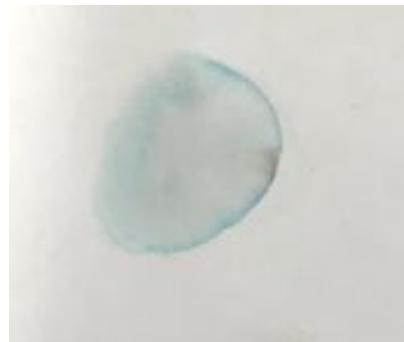
Figure 19. Filtration of 200 μ l of Goat Blood



As shown above, the filtration was successful for 200 μ l of goat blood. Within four minutes, the blood would naturally filter. Pushing the blood through for the mesh created in 60 minutes produced better results since more blood was filtered and the time spent to push was drastically shorter than the time spent on waiting. Although the pushing trial for the 90 minute mesh was worse than all the other results, more trials done and a more forceful push showed that the 90 minute mesh could attain the same results as a 60 minute mesh.

Figure 20. Filtration of 50 µl of Goat Blood

To mimic diabetic usage of the filtration mesh, 50 µl of goat blood was tested. As shown in Figure 20D, there were no splotches in the upper square of the 60 minute mesh which means even after four minutes of waiting, nothing was filtered out. In contrast, the 90 minute mesh was able to filter out some blood. Nevertheless, the trials performed when pushing the blood onto the filtration mesh of both the 60 minute and 90 minute mesh worked.

Figure 21. Filtered Goat Blood and Chemical Solution Result

The electrospun mesh was largely successful. It was tested in conjunction with the chemical solution as shown in Figure 21. The filtered goat's blood was filtered onto copy paper and a drop of the chemical solution was added in a 1:1:1 ratio of TMB: horseradish peroxidase: glucose oxidase. Multiple trials were performed and all of them resulted in the blue-ish color after five minutes.

BILL OF MATERIALS

The total allowed budget for the section was \$450. Our team spent \$201.01 on orders.

Table 6. Bill of Materials

Chemical	Model/CAS #	Part description	Supplier	Quantity	Cost
Tetramethylbenzidine (TMB)	MFCD00007748/54827-17-7	Redox indicator that can react with hydrogen peroxidase	Sigma-Aldrich	1g	\$41.80
Horseradish Peroxidase (HRP)	MFCD00071339/9003-99-0	Enzyme needed in the TMB and hydrogen peroxidase reaction	Sigma-Aldrich	25kU	\$122.59
Glucose Oxidase (GO)	MFCD00131182/9001-37-0	Reacts with glucose to create gluconic acid and hydrogen peroxide	Sigma-Aldrich	5kU	\$22.55
Glucose ($C_6H_{12}O_6$)		Sugar	Amazon	500g	\$8.07
Goat blood		Used to test the filter for filtering out of RBCs	L Aladdin Poultry	~1.5qt	~\$10.00

Electrospun Fiber Mesh		Filters out RBC	Professor Weiser		~\$0.01
Total					~\$205.02

ETHICAL CONSIDERATIONS

When coming up with a solution to any problem, it is important to remain moral, which is why one of our main agendas was to be ethical. Throughout the whole engineering design process, our team's actions and intentions followed the NYSPE Code of Ethics for Engineers ("Code of Ethics for Engineers", 2018).

Since our problem statement was focused in Kampala, we decided it was best to conduct research on that area to get an understanding of what is moral and accepted in their culture. Also, in order to get a true understanding of the scope of the project, we talked to people who went to Kampala to work with the medical centers. We were able to ask questions to people who first handedly experienced what it was like to live in Kampala.

After understanding the problem that we needed to solve, we began brainstorming and designing. During this process, we wanted a product that was safe for public use. As a result, we eliminated any chemicals that we did not find the material safety data sheet for or had little information to how safe it was, such as 5,6-Dimethylphenanthroline (Fe complex) ($C_{14}H_{12}N_2$) and 2,2'-Bipyridine (Fe complex) ($C_{10}H_8N_2$). This limited our list of chemicals to TMB, horseradish peroxidase, and glucose oxidase so that is what we decided to move forthwith.

In addition, while testing, all data were recorded to make sure that none of our data were forged. It was important that we were honest in order to serve the best interest of the public. We did not omit any facts during the whole engineering process and none of the information was misrepresented. All of our data were recorded and plotted on a graph with a logarithmic regression. All the results of the blood glucose level on the app were based on many experiments.

In the future, for marketing the product, we plan to be honest and issue public statements in a truthful and objective manner. As the code of conduct for engineers goes, we would include all

relevant information in reports and be as truthful and straightforward as possible. This would ensure that we do not deceive the public and that they would trust the colorimetric test strips.

SAFETY

In any engineering project, safety is a major concern. Safety concerns on the preliminary designs, implemented chemical design, and testing procedures were noted throughout the entirety of this course and design of the colorimetric test strip.

The colorimetric test strip was chosen as the basis of our preliminary design. Many different indicators such as those containing metal oxides were eliminated due to potential toxicity to the environment and user. The chemical reaction selected consist of TMB and Horseradish peroxidase. Although both substances are classified as non-hazardous, ingestion, skin contact, and eye contact with these chemicals are to be thoroughly washed with water. To ensure safety, the design should be kept out of a child's reach. Therefore, as long as the chemicals are properly used for glucose regulation, the test strips are safe to use.

The test strips are an invasive strategy to measuring blood glucose level. Blood must be used on the test strip for proper glucose measurement. This usage of blood is a large potential hazard but can be alleviated with the proper protocol. Firstly, the amount of blood necessary for the functioning of the colorimetric test strip can be lessened by increasing the amount of chemical indicator on the test strip. Secondly, the blood is filtered through the filtration mesh and the mesh is removed before any chemical addition to prevent cross-contamination. Although red blood cells can be washed from the filtration mesh with tap water, chemicals cannot. Later placement of an open wound with a mesh with potential chemical residues is a serious safety hazard. To prevent this, proper instructions on how to use the strips will be outlined and preferably, demonstrated to the diabetics in Kampala. It would be better if patient education is spread throughout Kampala to raise awareness, provide practice to lessen mistakes of using the test strips, and thereby lessen risks of biocontamination.

The design prototype was created and tested in laboratory settings with supervisors in proximity. A draft of the laboratory procedure and all relevant SDS sheets were procured and sent to

Professor Savizky for safety approval. Chemical testing done in the Kanabar Lab were under the supervision of Professor Jajuvensic and proper chemical rules were followed. Chemicals that needed refrigeration such as glucose oxidase were properly refrigerated after usage. The production of the red blood cell filtration mesh through electrospinning was done in the IA Lab, under the supervision of Professor Weiser. Animal blood was used as a substitute for human blood during the red blood cell filtration tests. All chemicals and materials were properly labelled, sealed, and stored to avoid contamination and safety hazards.

PROJECT ONLINE DELIVERABLES

Link to website and video: <https://theregulators.github.io/>

Link to final presentation: <https://goo.gl/PH2ayu>

The website was created as soon as the solution was narrowed down to the colorimetric test strip, and relevant content was added throughout the development of the product. The most significant improvements and additions to the site were made during the week of midterm and final presentations. The website was developed using the React Javascript framework, and its design was intended to be navigationally intuitive and minimalistic. All content on the website, including documents and media, are original content generated from this project.

After the solution was created and refined, we began the process of making a video to inform consumers and suppliers of the product we made. The video was made at the end of the term using clips and pictures taken throughout the semester. The video was stitched together using iMovie.

CONCLUSIONS AND FUTURE CONSIDERATIONS

The finished product, while still a rough prototype, showed a color change roughly corresponding to change in blood glucose levels. While not as precise as the traditional glucometer and test strips, it is a viable means of rough estimation of blood glucose levels and would be of good use for those living in developing nations, such as Uganda. The color change that the glucose oxidase-TMB-HRP solution produced would be separated into three categories: low, medium, and high, which was represented by a light blue, medium blue, and dark blue-red color respectively. This would be enough to let a diabetic know approximately what their blood glucose level was. While the app was not as effective in precisely reading the exact blood glucose level from the color change produced by the test strip, it was still fully constructed and with some modifications, further testing, and more time, would definitely be able to produce more valid results.

The entire process was done ethically; no results were forged. Diabetes is a serious issue and any mismanagement could result in serious injury or possibly death. Therefore, calculations were done precisely and with the utmost care. The project was also done with the goal of helping people in developing nations, so it was made to be as cost-effective as possible, to a reasonable degree of accuracy. The cost analysis showed that the price of a strip averaged out to be less than a cent per unit. This was considered to be a big success and would surely help those in Kampala. Additionally, the product would be packaged safely in an airtight bottle which would prevent the decay of the chemicals inside. With diabetes already being such a serious disease, it was important that the chemicals in the strip would not be harmful to the patient.

While the project appeared to be overall successful—safely and inexpensively measuring blood glucose level in a consistent manner—there were many areas open for future research and improvements to the design. Some of the major future considerations are listed below.

For portability reasons, it would be a good idea to work on the combination of all of the parts. The current design consists of many separate components, which would be difficult to distribute and confusing to the end user. Distributing the solution combined with the strip may be a better solution. A way to extend the shelf life of the solution is also an important consideration—storage of the chemical solution in refrigerated amber-colored glass bottles provides a shelf life of roughly one year. This is additional work for the user and therefore not ideal.

In terms of the mobile application, while a large improvement over the 2017 group's analysis algorithm, there are several improvements that can be made to improve the color analysis. More research into the colors and patterns corresponding to different blood glucose levels is necessary to determine accurate parameters for color analysis. Future research into machine learning to find these parameters, as well as ways to take into account lighting and placement of the item, would be very beneficial to the algorithm. The current estimate of $\pm 30\text{mg/dL}$ variation for the app algorithm only applies to a single lighting condition (and worse with changes of lighting or shadows), and the running time of the algorithm takes 10 to 20 seconds on an average Android tablet; it is hopeful that machine learning can be used to improve both of these statistics.

Currently, the mobile application is somewhat barebones and does not implement any storage or data analysis of past BGL measurements. It is possible to create a tab of the app that displays past glucose measurements and sets a goal for daily sugar intake so that a patient could track their daily intake and know how much more sugar they could consume for the day, much like apps such as My Fitness Pal. The about page should be updated with more captivating and intuitive how-to visuals, especially for Kampalans who cannot read English; better yet, there should be multiple translations of the text, to the other languages most often spoken in Kampala, that can be switched between in the app.

The test chemical's concentrations were not properly tested to find the most optimal and cost effective levels. The current concentrations were based on values for R&D assays and such are most likely higher than necessary. In the future, the concentrations can be tested to find the

lowest amount of each reagent possible while still keeping the reliability and actual function of the chemical mixture.

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We would also like to thank Carolina Biological Supply Company for answering our questions about blood and for Sigma Aldrich for providing materials used.

Additionally, we would like to thank the 2017 Section-E EID group, G Cubed Solutions, for allowing us to build off of the idea of colorimetric strips.

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APPENDIX I: MOBILE APP CODE

The overall concept for the mobile application is outlined in the Design Documentation, Section III. The mobile application was written in Java for Android, using the Android Studio IDE, but the concepts can be extended to other platforms. Only snippets of code relevant to the image processing will be provided below. Minor visual changes and comments may have been modified for presentation purposes. The full app code is open source and available on GitHub at <https://github.com/theregulators/regulators-android>.

I. UI Thread Controller

The code shown in Snippet 1 is that running on the main (UI) thread. This thread calls the drawing function, and already has the time-intensive task of drawing the camera input to a `TextureView` every frame. The image analysis takes a long time, so to prevent lockups, a secondary thread is created when the image processing is taking place. A flag (`parseBitmapLock`) is set whenever image processing begins and unset when it finishes, in order to prevent multiple image processing events to overlap, causing larger processor strain.

A bitmap of the camera input is sent to `ColorDetection.getColor()` (stage one), which returns the average color of the chosen cluster (discussed in the Design Documentation). This color is then sent to `BGLDetermination.colorToBGL()` (stage two). When the processing is complete, a request is sent back to the UI thread to update the BGL reading.

Snippet 1. UI Thread Controller (ScanFragment.java)

```
public volatile static boolean parseBitmapLock = false;
public volatile static String bglTextViewText = "---";
private void parseBitmap() {
```

```
// lock while running to avoid processor strain
if(ScanFragment.parseBitmapLock) {
    Toast toast = Toast.makeText(getContext(),
        "An analysis is already in progress!",
        Toast.LENGTH_SHORT);
    toast.show();
    return;
}
bglTextView.setText("Analyzing...");

new Thread(new Runnable() {
    @Override
    public void run() {
        // set lock flag
        ScanFragment.parseBitmapLock = true;
        // get bitmap
        Bitmap bitmap = textureView.getBitmap();
        if(bitmap == null) return;
        int width = bitmap.getWidth();
        int height = bitmap.getHeight();
        int[] pixels = new int[width * height];
        bitmap.getPixels(pixels, 0, width, 0, 0, width, height);
        for(int i = 0; i < 100; i++) {
            int j = pixels[i];
        }
        // perform stage 1
        VectorRGB averageColor =
            ColorDetection.getColor(pixels, width, height);
        // perform stage 2
        double bgl = BGLDetermination.colorToBGL(averageColor);
        // write output to UI
        bglTextViewText = "" + (Math.round(bgl * 10.0) / 10.0);
        getView().post(new Runnable() {
            @Override
            public void run() {
                bglTextView.setText(bglTextViewText);
            }
        });
        // remove lock
        ScanFragment.parseBitmapLock = false;
    }
}).start();
}
```

The snippet above uses a helper class for colors, `VectorRGB`. This class was implemented as shown in Snippet 2. (It includes some functions from the first iteration of the image analysis that are not used in the current design. The original design included more work with vectors and projections, which may also be used in future iterations of the current design.)

Snippet 2. `VectorRGB` Helper Class (`VectorRGB.java`)

```
public class VectorRGB {
    public double r;
    public double g;
    public double b;
    public VectorRGB(double r, double g, double b) {
        this.r = r;
        this.g = g;
        this.b = b;
    }
    public VectorRGB(int packedInt) {
        this.setColor(packedInt);
    }
    public VectorRGB(int[] componentArray) {
        this.r = componentArray[0];
        this.g = componentArray[1];
        this.b = componentArray[2];
    }
    public void setColor(int packedInt) {
        this.r = Color.red(packedInt);
        this.g = Color.green(packedInt);
        this.b = Color.blue(packedInt);
    }
    public double dot(VectorRGB v2) {
        return r*v2.r + g*v2.g + b*v2.b;
    }
    public double norm() {
        return Math.sqrt(r*r + g*g + b*b);
    }
    public VectorRGB negate() {
        return new VectorRGB(-r, -g, -b);
    }
    public VectorRGB add(VectorRGB v2) {
        return new VectorRGB(r+v2.r, g+v2.g, b+v2.b);
    }
    public VectorRGB subtract(VectorRGB v2) {
```

```

        return this.add(v2.negate());
    }
    public double distanceTo(VectorRGB v2) {
        return this.subtract(v2).norm();
    }
    public VectorRGB timesScalar(double k) {
        return new VectorRGB(r*k, g*k, b*k);
    }
    public VectorRGB projOn(VectorRGB v2) {
        return v2.timesScalar(this.dot(v2) / Math.pow(v2.norm(), 2));
    }
    public VectorRGB ortProjOn(VectorRGB v2) {
        return this.subtract(this.projOn(v2));
    }
    public String toString() {
        return String.format("Vector RGB R: %f G: %f B: %f", r, g, b);
    }
    public int toColorInt() {
        int a = 255;
        return (a & 0xff) << 24 | ((int) r & 0xff) << 16 | ((int) g &
0xff) << 8 | ((int) b & 0xff);
    }
}

```

II. Color Detection (Stage One)

The description of the color detection code in Snippet 3 is outlined in the Design Documentation.

Snippet 3. Color Detection (ColorDetection.java)

```

public class ColorDetection {
    private static class Pixel {
        public int x;
        public int y;
        public Pixel(int x, int y) {
            setPos(x, y);
        }
        public void setPos(int x, int y) {
            this.x = x;

```

```
        this.y = y;
    }
}

private static class PixelCluster {
    public int pixelCount;
    public VectorRGB color;
    public List<Pixel> pixelList = new ArrayList<>();
    public PixelCluster(int r, int g, int b) {
        color = new VectorRGB(r, g, b);
    }
    public void addPixel(Pixel pixel) {
        pixelList.add(pixel);
        pixelCount++;
    }
}

// main color analysis function
public static VectorRGB getColor(int[] bitmap, int width, int height) {
    // step 1: initializing pixel clusters
    PixelCluster[][][] pixelClusters = new PixelCluster[16][16][16];
    int i, j, k, x, y;
    for(i = 0; i < 16; i++) {
        for(j = 0; j < 16; j++) {
            for(k = 0; k < 16; k++) {
                pixelClusters[i][j][k] = new PixelCluster(i << 4, j << 4, k << 4);
            }
        }
    }
    // step 2: filling pixel clusters
    VectorRGB color = new VectorRGB(0);
    for(y = 0; y < height; y++) {
        for(x = 0; x < width; x++) {
            color.setColor(bitmap[y * width + x]);
            int thresholdR = (int) color.r >> 4;
            int thresholdG = (int) color.g >> 4;
            int thresholdB = (int) color.b >> 4;
            Pixel pixel = new Pixel(x,y);
            pixelClusters[thresholdR][thresholdG][thresholdB]
                .addPixel(pixel);
        }
    }
}
```

```
// step 3: analyzing pixel clusters
int lowThresholdCount = width * height / 1000;
int highThresholdCount = width * height / 2;
int thresholdNum = 0;
List<PixelCluster> chosenClusters = new ArrayList<>();
for(i = 0; i < 16; i++) {
    for(j = 0; j < 16; j++) {
        for(k = 0; k < 16; k++) {
            // get pixel cluster
            PixelCluster currentPixelCluster = pixelClusters[i][j][k];
            // filter out clusters with too few pixels
            if(currentPixelCluster.pixelCount < lowThresholdCount ||
currentPixelCluster.pixelCount > highThresholdCount) {
                // filter condition 1
                continue;
            }
            // check "jump" method
            int xAvg = 0;
            int yAvg = 0;
            for(Pixel clusterPixel : currentPixelCluster.pixelList) {
                xAvg += clusterPixel.x;
                yAvg += clusterPixel.y;
            }
            xAvg /= currentPixelCluster.pixelCount;
            yAvg /= currentPixelCluster.pixelCount;
            if(Math.abs(xAvg - width/2) > width/4 ||
Math.abs(yAvg - height/2) > height/4) {
                // filter condition 2
                continue;
            }
            double error = 0;
            for(Pixel clusterPixel : currentPixelCluster.pixelList) {
                error += Math.sqrt(Math.pow(clusterPixel.x - xAvg, 2) +
Math.pow(clusterPixel.y - yAvg, 2));
            }
            double relativeError = error /
                currentPixelCluster.pixelCount;
            if(relativeError > 150) {
                // filter condition 3
                continue;
            }
            if(k >= i && k >= j && chosenClusters.size() < 4) {
                chosenClusters.add(currentPixelCluster);
            }
        }
    }
}
```

```

        }
    }
}
VectorRGB avgBlue = new VectorRGB(0, 0, 0);
int totalCount = 0;
for(PixelCluster pixelCluster : chosenClusters) {
    totalCount += pixelCluster.pixelCount;
    avgBlue = avgBlue.add(new VectorRGB(pixelCluster.color.r,
        pixelCluster.color.g,
        pixelCluster.color.b).timesScalar(pixelCluster.pixelCount));
}
if(totalCount != 0) {
    avgBlue = avgBlue.timesScalar(1.0 / totalCount);
}
return avgBlue;
}
}

```

III. Color Analysis (Stage Two)

The blood glucose level determination is also described in the Design Documentation. The functions `rToBGL()`, `gToBGL()`, and `bToBGL()` are the inverse functions of the three calibration trendlines in Figure 2.

Figure 4. Blood Glucose Level Determination from Color (BGLDetermination.java)

```

public class BGLDetermination {
    final static private VectorRGB colorStart =
        new VectorRGB(255, 0, 255);
    final static private VectorRGB colorEnd =
        new VectorRGB(255, 255, 0);

    // these coefficients of determinations and functions
    // are experimentally determined
    // see the calibration curves for more information
    private static double rToBGL(double r) {
        return Math.exp((112.041-r)/13.921) * 10;
    }
}

```

```
private static double gToBGL(double g) {
    return Math.exp((159.955-g)/28.059) * 10;
}
private static double bToBGL(double b) {
    return Math.exp((165.499-b)/28.447) * 10;
}
private static double rR2 = 0.624163;
private static double gR2 = 0.853277;
private static double bR2 = 0.887773;

public static double colorToBGL(VectorRGB color) {
    double rBGLGuess = rToBGL(color.r);
    double gBGLGuess = gToBGL(color.g);
    double bBGLGuess = bToBGL(color.b);
    double weightedBGLGuess = (rBGLGuess * rR2 + gBGLGuess * gR2 +
bBGLGuess * bR2) / (rR2 + gR2 + bR2);
    return weightedBGLGuess;
}
}
```

Project Overview: Glucose Colorimetric Paper Test Strips

Contributors: P. Baccarella, C. Chen, J. Lam, V. Wang, A. Leong, E. Yasharpour

Primary Contacts: chen34@cooper.edu, leong2@cooper.edu

Background:

Diabetes is the group of diseases characterized by excessive blood glucose levels due to the body's inability to produce insulin or the lack of proper usage of insulin. Since diabetes is an incurable and chronic disease, daily blood glucose checkups are vital in ensuring well-being and safety. However, it is difficult for many diabetics in developing countries to manage their disease because there are no means to inexpensively and effectively measure their blood glucose levels. Currently, the most prevalent method is to use a glucometer with one-time-use test strips.

Glucometers range from \$40 to \$60¹ and individual test strips cost between \$0.40 to \$2.00². Type II diabetics who are not on oral medication are recommended to test blood sugar levels at least once a day, and Type I diabetics may need to test up to six to ten times per day³. This financial constraint is especially dire in countries like Uganda, where the average income in Kampala, its largest city and second wealthiest district by GDP per capita, is roughly \$300 per month⁴.

Proposed Solution:

Our project is centered on glucose colorimetric paper test strips and focused on improving the visual accuracy of the blood sugar determination through indicator experimentation. When glucose is introduced to the strips, a color change occurs and indicates the relative blood glucose and diabetic status of the user. Glucose oxidase, the primary glucose reagent in glucometers, will be used in these test strips to produce gluconic acid and hydrogen peroxide. We plan to use indicators such as potassium iodide (using the well-known starch-iodide color change), TMB, and 2,2'-Bipyridine (Fe complex); these indicators can all be used to visually differentiate between different levels of hydrogen peroxide, which should be approximately proportional to blood glucose levels. The glucose oxidase and indicator solutions will be distributed in bottles, from which tests can be conducted dropwise onto strips of A4 copy paper. To complement the colorimetric strips, we hope to create a smartphone application that uses camera input and a color analysis algorithm to determine the glucose level (to a reasonable accuracy) based on the color of the strips. The Uganda Bureau of Statistics shows that 86% of 18-30-year-olds own a smartphone and most Kampala households have access to a smartphone so a mobile app is reasonable⁵.

This project is an extension from the first iteration by the 2017 EID group⁶. As an extension to their method, we plan to use a fibermesh membrane to filter out plasma from red blood cells to avoid a red color contamination. We also planned to improve the algorithm to filter out some of the red blood color and lighting by using a small blood sample and white paper as color controls.

¹ <https://www.webmd.com/diabetes/qa/how-much-do-glucose-meters-cost>

² <http://www.diabetesforecast.org/2012/jul/the-cost-of-test-strips.html>

³ <https://www.diabetesselfmanagement.com/blog/type-1-diabetes-vs-type-2/>

⁴ https://moodle.cooper.edu/moodle/pluginfile.php/72961/mod_resource/content/1/DiabetesManagement-IntroPresentation-9-6-18-v1.pdf

⁵ <https://www.ubos.org/onlinefiles/uploads/ubos/2014CensusProfiles/KAMPALA-KCCA.pdf>

⁶ <https://minhtyyufa.wixsite.com/gcubedsolutions>

GLUCOSE MONITORING DEVICE

Peter Baccarella, Amy Leong, Catherine Chen, Vincent Wang, Jonathan Lam, Emily Yasharpour

Objective / Background

Colorimetric test strips for diabetics in
Kampala within constraints of cost,
manufacturability, and user-friendliness

Background



4.2% or 63,297

Diabetic Prevalence and Diagnosed Diabetic Population



\$287.62

Average Household Income

Methodology/Solution

- Colorimetric test strips with emphasis on:
 - Different Enzymes & Indicators
 - Improved Image Processing
 - RBC Separation

Abstraction & Synthesis

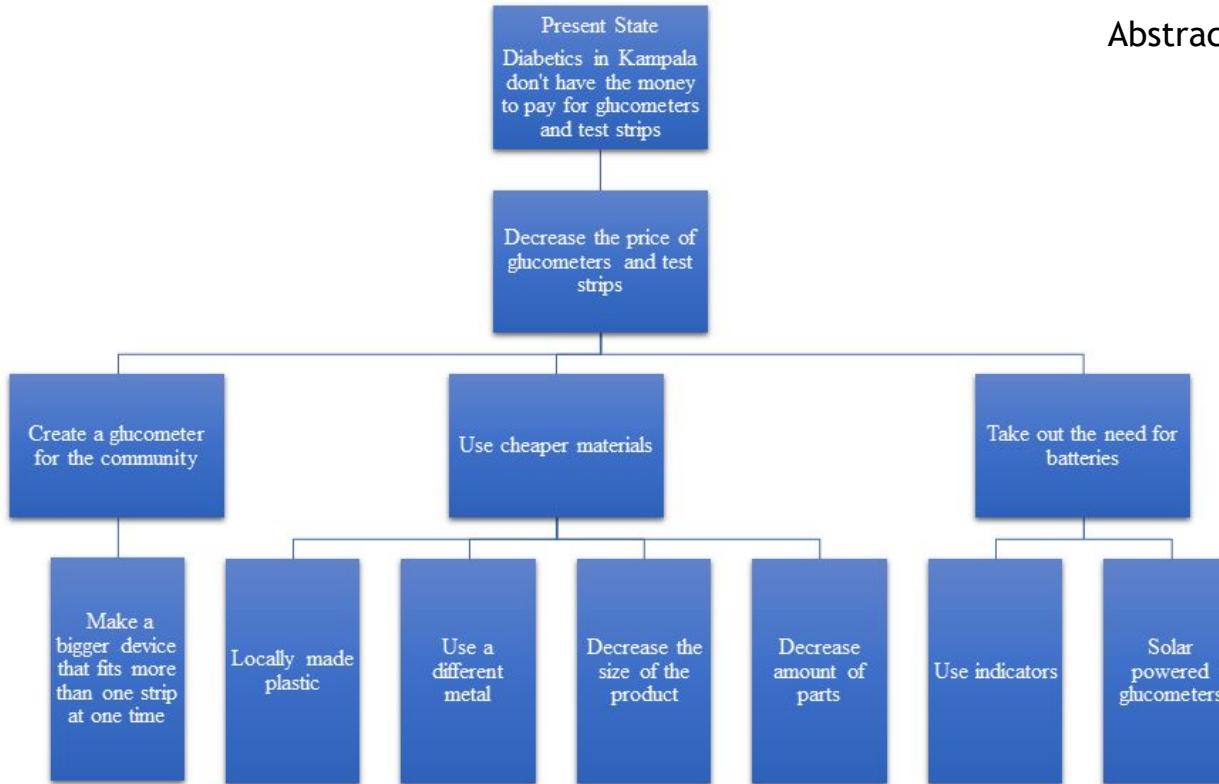


Figure 1A: Duncker Diagram (Present State)

Abstraction & Synthesis

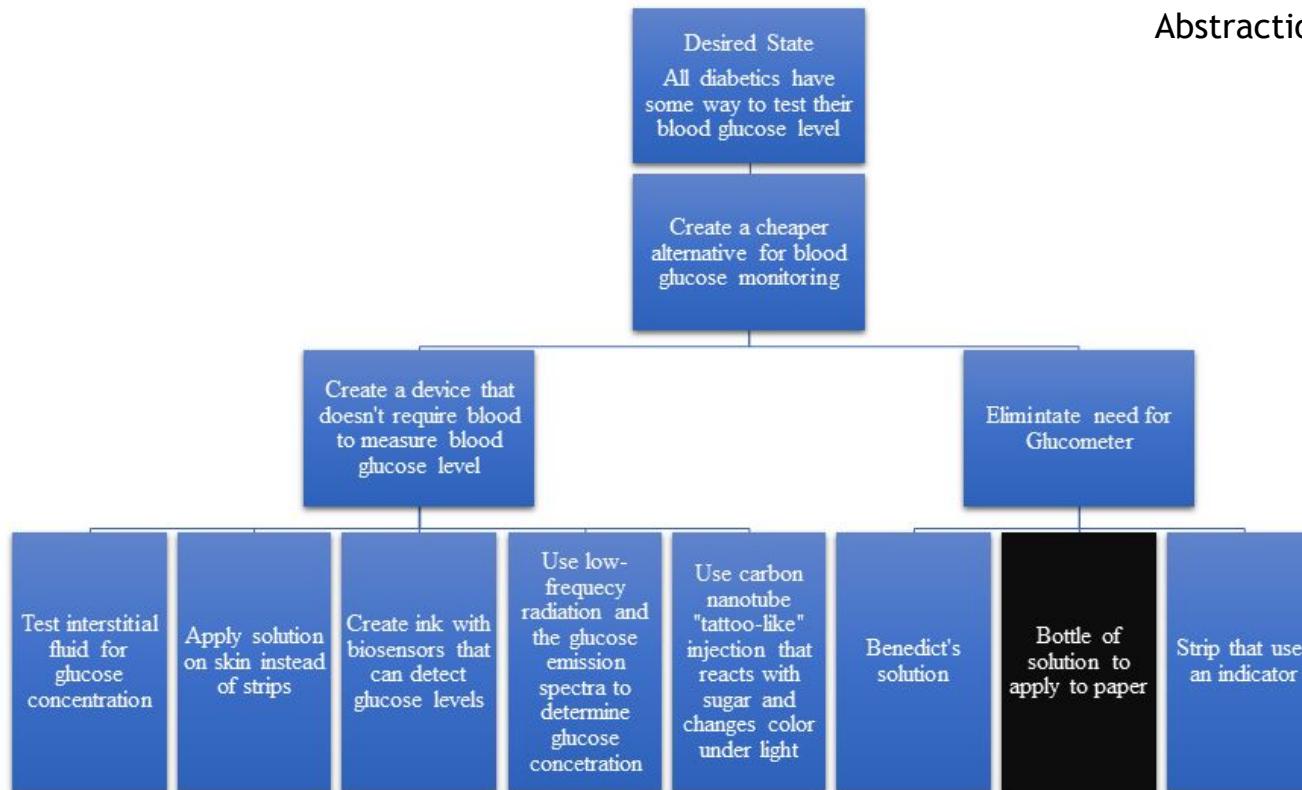


Figure 1B: Duncker Diagram (Desired State)

Proposed Design

Indicators:

- Iodine-starch (control), Redox, Acid/base

Primary chemical reaction:

- Glucose oxidase, Benedict's and Fehling's solution, Yeast

Software:

- Control (eliminate RBC color and lighting)
- Statistical analyses

Proposed Design

Other improvements:

- Glass Fiber Mesh
- Different Papers

Models:

- Glucose solutions
- Marker and paper optical calibration

Occam's Razor

- Reject Glucometer for Test Strips
- Reject Centrifuge for Glass Fiber Mesh

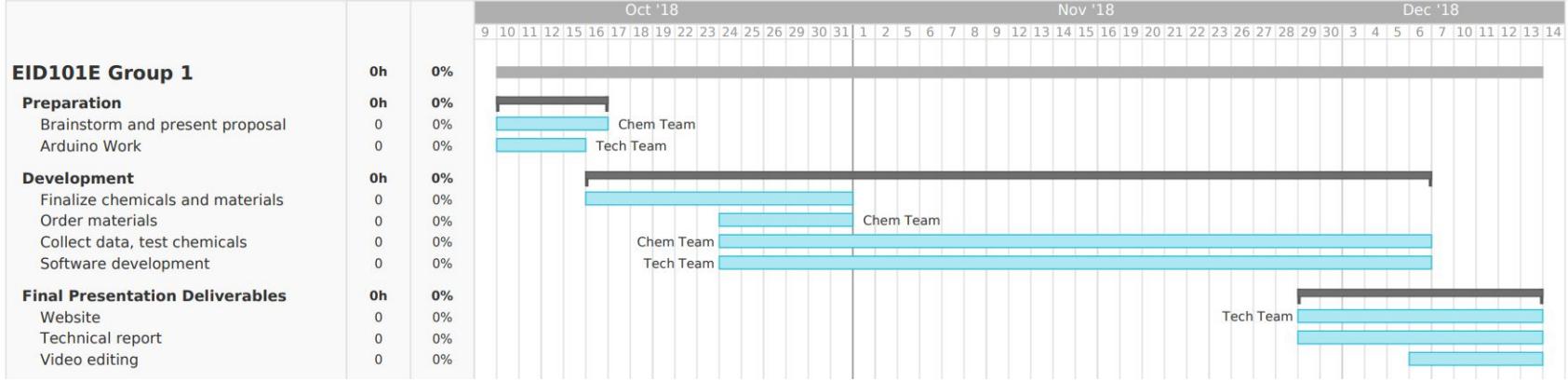


Figure 2.2A: GANTT Chart

Role	People
Leaders / Primary spokespeople	Vincent, Emily, Peter
Note-taking	Amy
Designing, modeling, prototyping (chemicals)	Catherine, Emily, Peter, Vincent
Designing, modeling, prototyping (data analysis and software)	Amy, Jon
Webmaster	Jon, Peter
Technical Report	Jon, Vincent, Catherine, Amy

Figure 2.2B: Primary Responsibility Chart

Challenges

- Finding a non-toxic, low-cost, locally sustainable alternative chemical indicator
- Accurately and reliably analyzing the color to determine blood glucose concentration

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Atkins and Jeppo: Model engineers with rigor and compassion

There are few negative character flaws apparent in Atkins and Jeppo as they invent a bicycle-powered water pump in chapters 17 and 18 of *The Ugly American*. The two characters are very blunt in speech, but they are both high-functioning engineers throughout the entire process, taking careful attention to the success of the design from the planning to idea-pitching to manufacturing to sales. The technical and communication skills required throughout these stages, as well as the passionate desire to fulfill the product, evidence that Jeppo and Atkins are strong role models for engineers and the process a realistic example of the engineering design method.

Because the story is given in a narrative format, the personality of the characters must be inferred through their actions.

A straightforward way of determining the quality of an engineer is to observe how well they follow the principles of engineering design. A good engineer should methodically lay out any major engineering project in the same rigorous manner as in the engineering design process. The following section organizes the relevant actions of the two main engineers into the broad subcategories of the engineering design process, and analyzes the actions in each subgroup as a whole.

A. Needs assessment

At the beginning of chapter 17, Atkins argues with several diplomats about the necessity of building roads. He believes that the major problem at hand is that other, more necessary infrastructure, such as “first, a brick factory. Cheap, easy to run, and it would give them building materials. Second, stone quarries back in the hills … Third, … a model canning plant … Fourth, … run little finger-roads back through the jungle so the coastal people can get to good land” (177-8). At this point, Atkins has already surveyed the Vietnamese “boondocks” (backcountry) and prepared a report based on this experience; he also has prior knowledge with “practical engineering” and “heavy construction” (177). He presents this assessment of the *real* problem at hand. Unfortunately, the diplomats are unwilling to change their assumption that the most important problem at hand is road construction, and Atkins is stubborn. As a result, this engineering project fails, but Atkins does perform a thorough needs assessment.

For the engineering problem of the bicycle, Atkins is given the problem of raising water in Sarkhan by Ambassador MacWhite. The problem (need) is very clear here and Atkins does not evaluate it further.

B. Problem formulation

While Atkins is quick to jump to a potential solution for the water raising problem when he draws out a design for a water pump, he learns what the real problem is: the people of Sarkhan are poor and will not be able to easily have access to the parts common for more developed nations. He knows at the beginning that Sarkhan is a poor nation and that it does not have the industry like in the U.S.; when Emma suggests that he spend some of his own wealth to invest in the modern technology, he refuses because part of the problem is to create a sustainable, local means of manufacturing: he says, “if the pump is going to work at all, it has to be their pump, not mine” (180). Later on, the problem statement is further narrowed when Jeppo informs him about the nature of the bikes in Sarkhan, which are too worn-out after use: this leads to another redesign of the problem statement to use something other than decommissioned bicycles.

Throughout the entire process, Atkins is thinking about the problem with a knowledge of the design specifications firmly in his mind, which allows him to create a feasible design using locally-abundant bamboo, Jeep parts, and in-commission bicycles.

C. Abstraction and synthesis

Atkins is observed breaking the problem down into three steps soon after moving to Sarkhan: “First, it needed cheap and readily available piping” (182), a problem he fixed with bamboo. The second problem was with the pumping mechanism, which he solved by finding the abundance of abandoned military Jeeps. And the third was the source of power, which he discovered through a suggestion by his wife to use bicycles. These were specific, functional blocks that, when the source of their materials was conceived, were synthesized into the complete model.

D. Analysis, reflection, and iterative design

On the first demonstration of the water pump, Jeopo tells Atkins that “[the pump] will not be a sensible machine for [Sarkhan]” (188), and cites the lack of suitable bicycles for the design (because bicycles either are used for transportation or are too damaged to be converted into the power source for these pumps). The two men immediately get to work, brainstorming ways to lower the cost of resources (such as only using the necessary part of the bike), and settle on a method that uses bikes but does not force deconstruction of the bike, and thus allowing ordinary working bikes to power the pump. At the end of the story, the two engineers are pictured arguing over another modification to the bike. They are not afraid to make improvements to the original design of the pump based on a noticeable flaw.

C. Implementation

The manufacture of the product is carried out very smoothly, most likely due to the previous experience of Atkins in construction. A warehouse is promptly rented out, workers are hired, and a sales plan is devised as soon as eight models are constructed. Because of the locally-reproducible design and fair working conditions, construction is not hindered at all. A final step in the implementation is to spread the knowledge of the pump’s construction throughout Sarkhan, which serves as a form of documentation and dissemination of the knowledge, encouraging other engineers to construct and improve on the pump.

Throughout the entire engineering process, Atkins (and Jeopo when he is introduced to the project) remains very professional and demonstrates various aspects of good engineers: being open to new ideas (such as the use of the bicycle as power); having sufficient technical, mathematical, and scientific knowledge (to create an efficient pump); working fairly in teams and have a proper amount of argumentative discourse (“they were the only times that the Surkhanese had ever seen one of their own kind arguing fairly and honestly, and with a chance of success, against a white man” (193)); and being knowledgeable of worldly problems (Atkins attempts to aid the foreign nations Vietnam and Surkhan). The latter is perhaps the most important: Atkins feels obliged to help others, with the best interest of the locals in mind, as opposed to others with a monetary or political mission (such as the diplomat’s narrow-minded vision to build roads when that is not the best decision). And Jeopo and the workers have a personal stake in the situation simply because they are Surkhanese. Jeopo goes as far as saying

that “neither I nor [Atkins] shall license or patent the idea of the pump” (192) so that the idea can help as many people as possible, and that their engineering motive is not a purely economic one. With Atkins’ compassion and the Sarkhans’ personal interest in the solution, the engineers are driven to create a quality, feasible solution that could be easily manufactured and distributed to the areas of need in Sarkhan; the bicycle-powered water pump meets all of these criteria.

The main downside with viewing Atkins and Jeppo as “the engineering profession at its best” is that their communication skills are not refined: Atkins displeases the diplomats at the beginning and Jeppo is very blunt towards the headman. While both of them are experienced and have reason to be stubborn, being able to communicate openly and non-argumentally (and compromise towards a solution) with clients and employers is an important skill in being an engineer. However, it appears as though Atkins is attempting to improve his communication skills by learning from Emma.

Works Cited

Lederer, William J, and Eugene Burdick. *The Ugly American.*, 1958. Print.

Case History: Jeopo-Atkins Company in Sarkhan

Project Overview

The terrain in Sarkhan is hilly, and raising water from the rivers to the hillside paddies is difficult work. The common method of raising water is by using dip lifts, which requires many hours of work per day to water the fields. The technology for advanced powered pumps is not available in many of the rural regions of Sarkhan.

The Problem

The process of lifting water makes villages high above water and those with multiple levels of fields spend a large amount of time and effort raising water for their fields. For example, the village of Chang ‘Dong has eight levels of paddies and has remained poor because of the inefficiency of bringing water to all of the levels. Because of the hilliness and lesser wealth in the countryside of Sarkhan, either importing materials or completed pumps from abroad is impractical; therefore, a solution to increase the efficiency of raising water must be locally manufactured and sustainable.

The Solution

A manual bicycle-powered water pump was designed to fit all of the criteria. Piping is to be constructed of locally-abundant bamboo. Pistons and cylinders from abandoned military-authority jeeps, common around the villages of Sarkhan, are used for the suction mechanism of the pump. Human-powered bicycles power the pump. At first, a specially-converted bicycle was connected directly to the pump; a change in the design allows any working bicycle to be placed in a bamboo rack and power the machine. The construction of such a machine only requires parts that can be found locally (bamboo, jeep parts, and bicycles) and is not very difficult to manufacture with common construction tools.

The Result

24 pumps were made in the first batch in only six weeks, without any hindrances and adhering to the design. These were displayed by the engineers as samples to other communities in Sarkhan. Future deliverables will include informative pamphlets describing the design of the pump to allow construction by other engineers.

Benefits

The bicycle pump greatly helped the first community it was delivered to (Chang ‘Dong) by lifting in “a few minutes … more water than [they] could lift by [their] old methods in five hours of work.” In addition, the current design uses working bicycles, a common tool for transportation, as a source of power (without affecting its ability to transport people). This both frees up time for farmers to perform other tasks and reduces the amount of effort and strength necessary to lift water.

Farmers who are in desperate need of help lifting water may receive a pump and pay back the cost over a three-year loan. This allows for immediate aid to some farmers who are experiencing more severely the problem addressed.

Project Overview: The Regulators: Glucose Colorimetric Paper Test Strips

Contributors: P. Baccarella, C. Chen, J. Lam, V. Wang, A. Leong, E. Yasharpour

Primary Contacts: chen34@cooper.edu, leong2@cooper.edu

Background:

Diabetes is the group of diseases characterized by excessive blood glucose levels due to the body's inability to produce insulin or the lack of proper usage of insulin. Since diabetes is an incurable and chronic disease, daily blood glucose checkups are vital in ensuring well-being and safety. However, it is difficult for many diabetics in developing countries to manage their disease because there are no means to inexpensively and effectively measure their blood glucose levels.

Currently, the most prevalent method is to use a glucometer with one-time-use test strips.

Glucometers range from \$40 to \$60¹ and individual test strips cost between \$0.40 to \$2.00². Type II diabetics who are not on oral medication are recommended to test blood sugar levels at least once a day, and Type I diabetics may need to test up to six to ten times per day³. This financial constraint is especially dire in countries like Uganda, where the average income in Kampala, its largest city and second wealthiest district by GDP per capita, is roughly \$300 per month⁴.

Proposed Solution:

Our project is centered on glucose colorimetric paper test strips and focused on improving the visual accuracy of the blood sugar determination through indicator experimentation. When glucose is introduced to the strips, a color change occurs and indicates the relative blood glucose and diabetic status of the user. Glucose oxidase, the primary glucose reagent in glucometers, will be used in these test strips to produce gluconic acid and hydrogen peroxide. We used TMB, an indicator used to visually differentiate between different levels of hydrogen peroxide, which should be approximately proportional to blood glucose levels. The glucose oxidase and indicator solutions will be distributed in bottles, from which tests can be conducted dropwise onto strips of A4 copy paper. To complement the colorimetric strips, we created a mobile application that uses camera input and a color analysis algorithm to determine the glucose level (to a reasonable accuracy) based on the color of the strips. The Uganda Bureau of Statistics shows that 86% of 18-30-year-olds own a smartphone and most Kampala households have access to a smartphone so a mobile app is reasonable⁵.

This project is an extension from the first iteration by the 2017 EID group⁶. As an extension to their method, we created a fibermesh membrane to filter out plasma from red blood cells to avoid a red color contamination. We also planned to improve the algorithm to filter out some of the red blood color and lighting by using a small blood sample and white paper as color controls.

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³ <https://www.diabetesselfmanagement.com/blog/type-1-diabetes-vs-type-2/>

⁴ https://moodle.cooper.edu/moodle/pluginfile.php/72961/mod_resource/content/1/DiabetesManagement-IntroPresentation-9-6-18-v1.pdf

⁵ <https://www.ubos.org/onlinefiles/uploads/ubos/2014CensusProfiles/KAMPALA-KCCA.pdf>

⁶ <https://minhtyyufa.wixsite.com/gcubedsolutions>

Addendum: Notes on the App

The mobile app makes it easy for a user to determine blood glucose level from the test strip: the user points the camera at the image, and clicks the “Analyze” button. The device camera stream will be shown with a guiding marker in the app. A brief how-to guide in the app to help users.

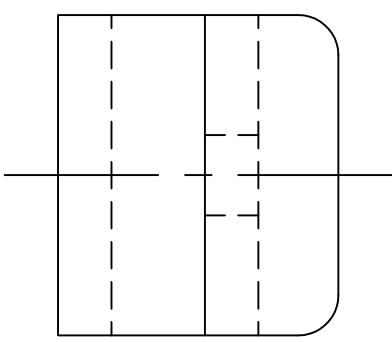
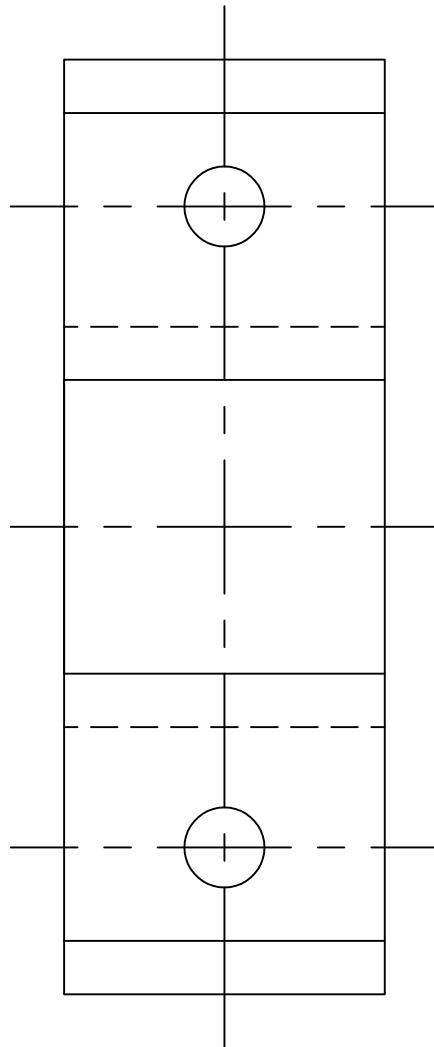
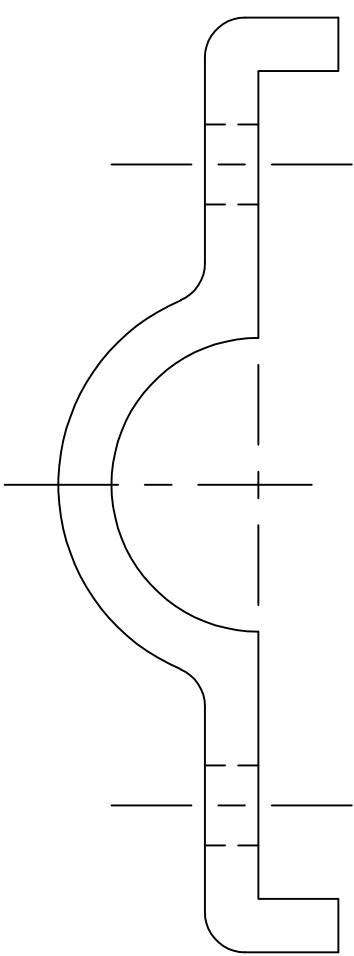
The color detection is a set of heuristics determined by trial and error. The major steps were threshold all of the pixels into clusters (i.e., breaking down the 2^{24} color space down to 2^{12} clusters), and filtering out clusters based on number of pixels (too few would indicate an insignificant splotch, such as a speck of dust, and too large might indicate a background color), center (the center of the clustered pixels should be near the center of the camera input), error using the “jump method”⁷, and color (the dark blue ring was determined to be the best indicator of color, and thus the algorithm biased dark and primarily-blue clusters). The few clusters that remained would be averaged (weighted averaged based on number of pixels per cluster), and the R, G, and B values of this cluster would be put through the inverse trend lines generated by the model (see answer to (2)) to guess at the blood glucose level. The three estimates (one for R, G, and B) would be averaged (weighted based on R^2) to get a final BGL determination. This offers results better than the ones from last year’s app because it does not require any user input and can capture more complex patterns (i.e., the rings of color).

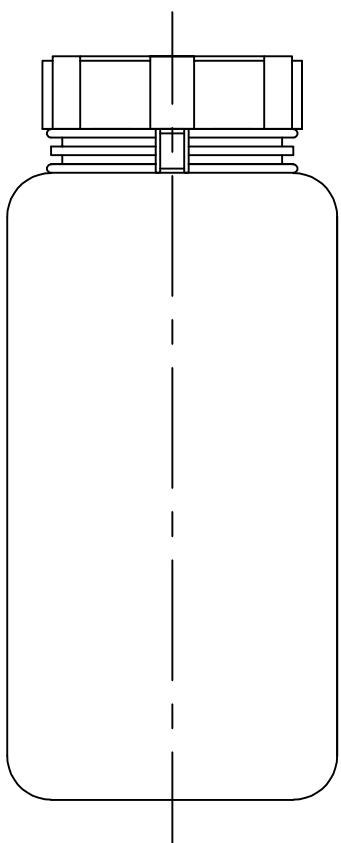
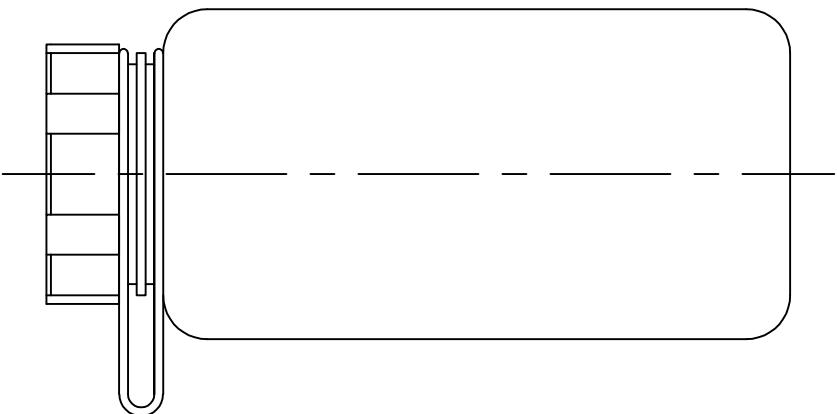
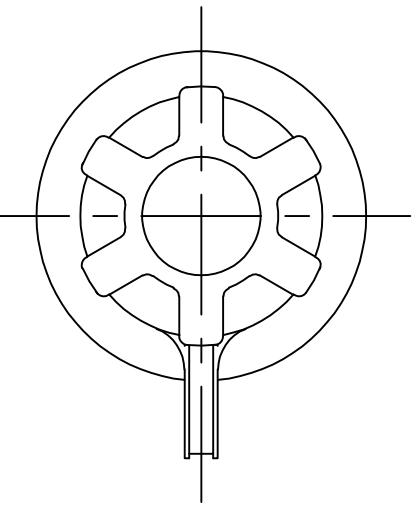
The calibration "trials" involved running the heuristic filtering on the samples, and plotting the final cluster against BGL concentration. A trend line was created for each color. (A polynomial trend line worked best, but its end behavior did not make sense; the close-behind logarithmic models seemed more reasonable). Unsurprisingly, the trend line for the blue component was strongest, indicating that the difference between the blue could most reliably be used to determine BGL.

The concentrations of the samples for calibration were known. When the heuristics are performed on these samples, there is some variation. If used correctly and lighting is consistent, the variation in readings of the same sample varied by up to roughly $\pm 30\text{mg/dL}$. While this may seem like a wide range of error, diabetics' blood sugar levels can range far greater⁸, so it should still be a useful metric. With further experimentation, however, it is expected that the the algorithm should improve and variation should decrease, and user error and lighting will be better accounted for.

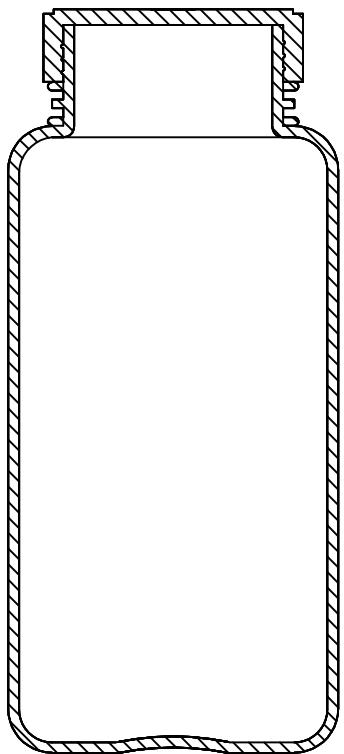
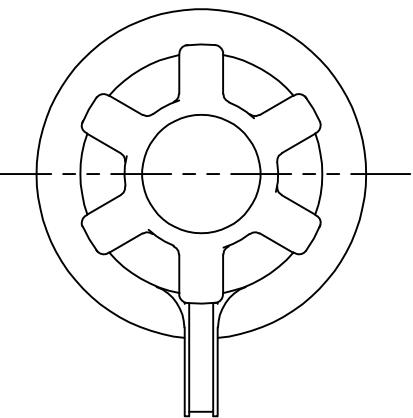
⁷<https://blog.algolia.com/how-we-handled-color-identification/>

⁸<https://www.joeniekrofoundation.com/stroke-2/3685/attachment/diabetes-blood-sugar-chart/>



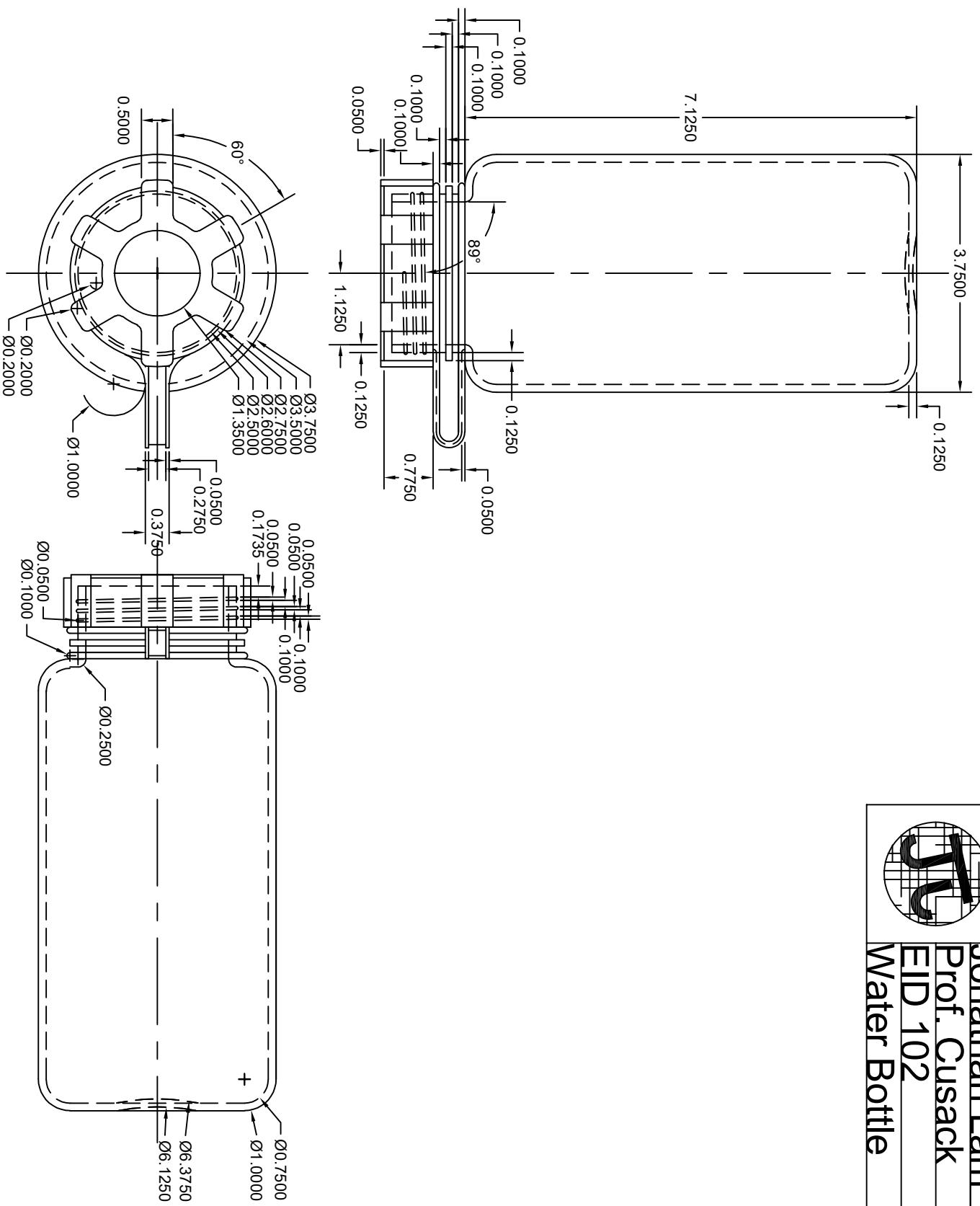


	Jonathan Lam Prof. Cusack EID 102 Water Bottle
--	---



Jonathan Lam
Prof. Cusack
EID 102
Water Bottle

Jonathan Lam
Prof. Cusack
EID 102



6

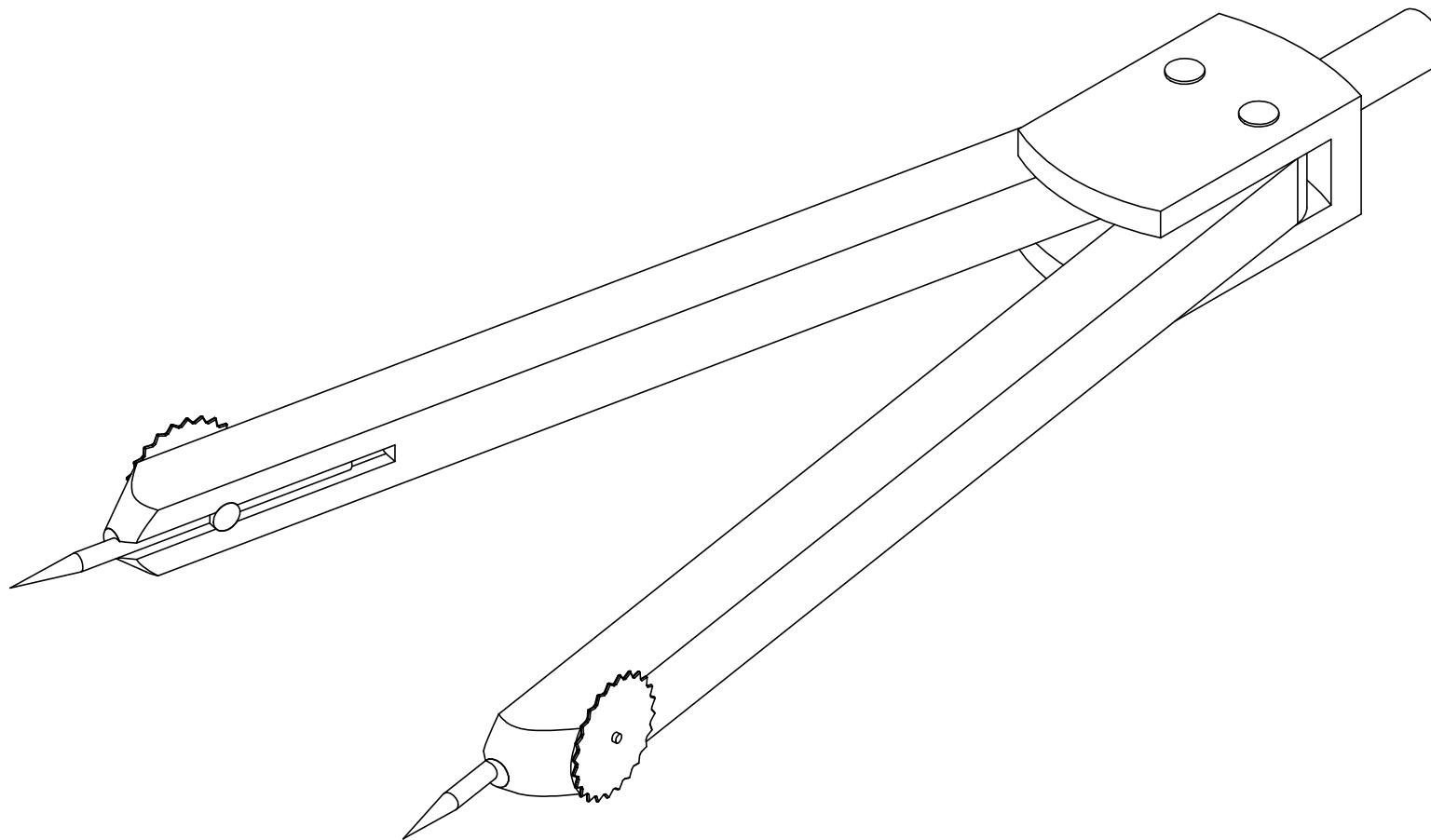
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4

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1



UNLESS OTHERWISE SPECIFIED:
DIMENSIONS ARE IN MILLIMETERS
SURFACE FINISH:
TOLERANCES:
LINEAR:
ANGULAR:

FINISH:

DEBURR AND
BREAK SHARP
EDGES

DO NOT SCALE DRAWING

REVISION

DRAWN NAME SIGNATURE DATE

11/8/18

CHK'D

APPV'D

MFG

Q.A.

MATERIAL:

DWG NO.

WEIGHT:

SCALE:1:8:1

TITLE:

Divider

Assembly

A4

SHEET 1 OF 1

6

5

4

3

2

1

6

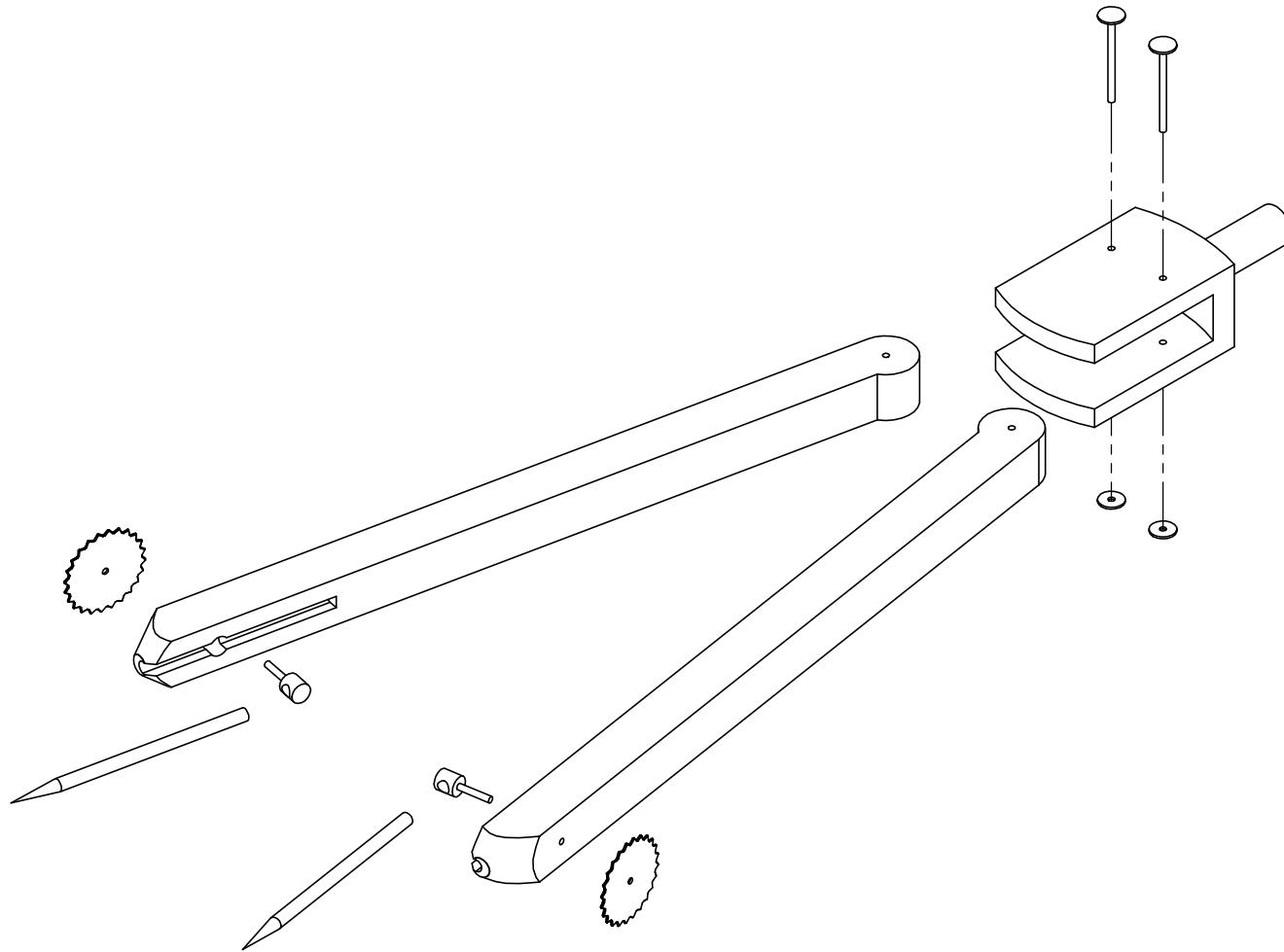
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1



UNLESS OTHERWISE SPECIFIED:
DIMENSIONS ARE IN MILLIMETERS
SURFACE FINISH:
TOLERANCES:
LINEAR:
ANGULAR:

FINISH:

DEBURR AND
BREAK SHARP
EDGES

DO NOT SCALE DRAWING

REVISION

DRAWN	NAME	SIGNATURE	DATE		
CHK'D					
APPV'D					
MFG					
Q.A.				MATERIAL:	

TITLE:

Divider

DWG NO.

Exploded Assembly

A4

WEIGHT:

SCALE:1:2:1

SHEET 1 OF 1

6

5

4

3

2

1

6

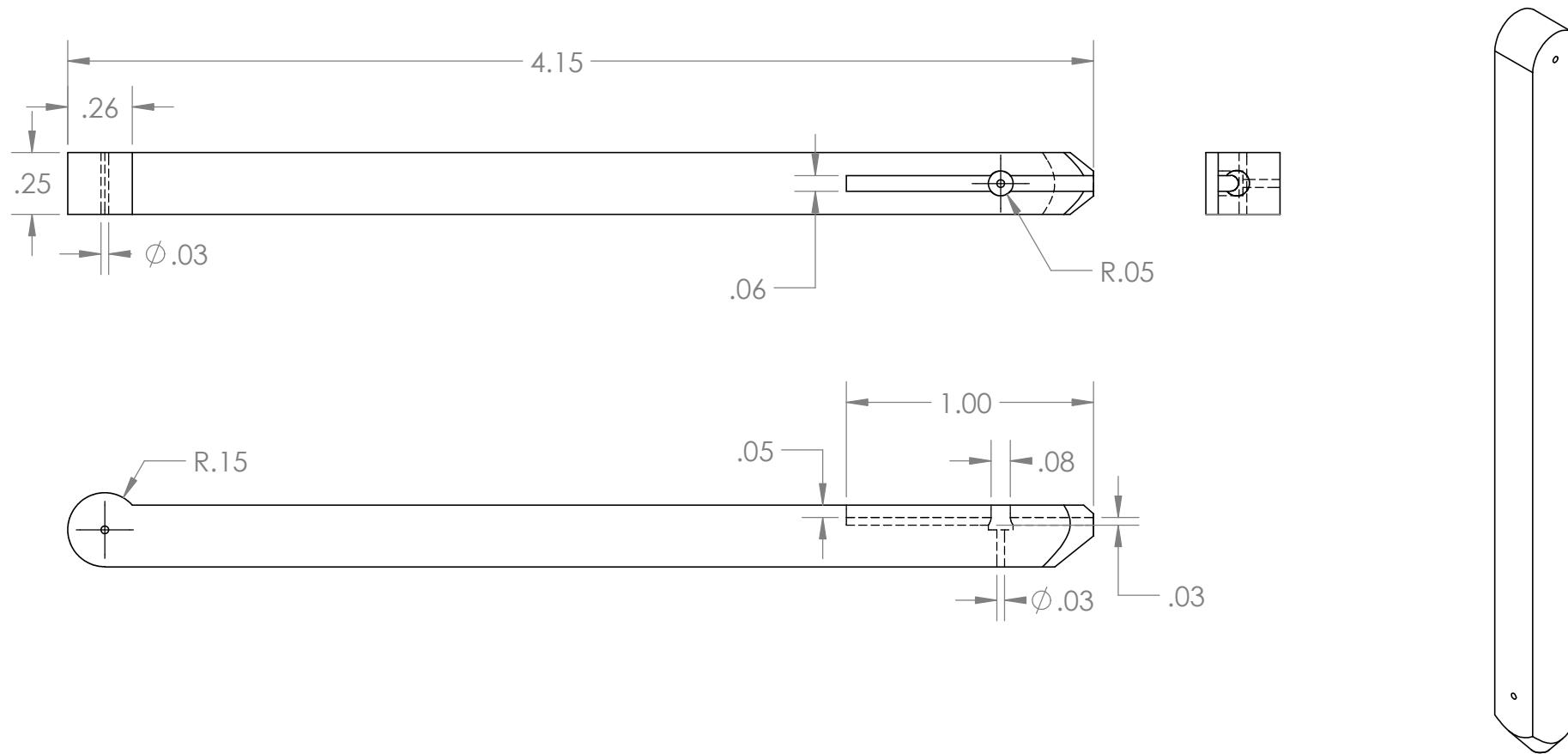
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UNLESS OTHERWISE SPECIFIED: DIMENSIONS ARE IN MILLIMETERS SURFACE FINISH: TOLERANCES: LINEAR: ANGULAR:			FINISH:			DEBurr AND BREAK SHARP EDGES	DO NOT SCALE DRAWING	REVISION			
DRAWN	NAME	SIGNATURE	DATE								
CHK'D											
APPV'D											
MFG											
Q.A.				MATERIAL:			DWG NO.				
				WEIGHT:			SCALE:1:3:1	SHEET 1 OF 1			
TITLE: Divider Arm											
A4											

6

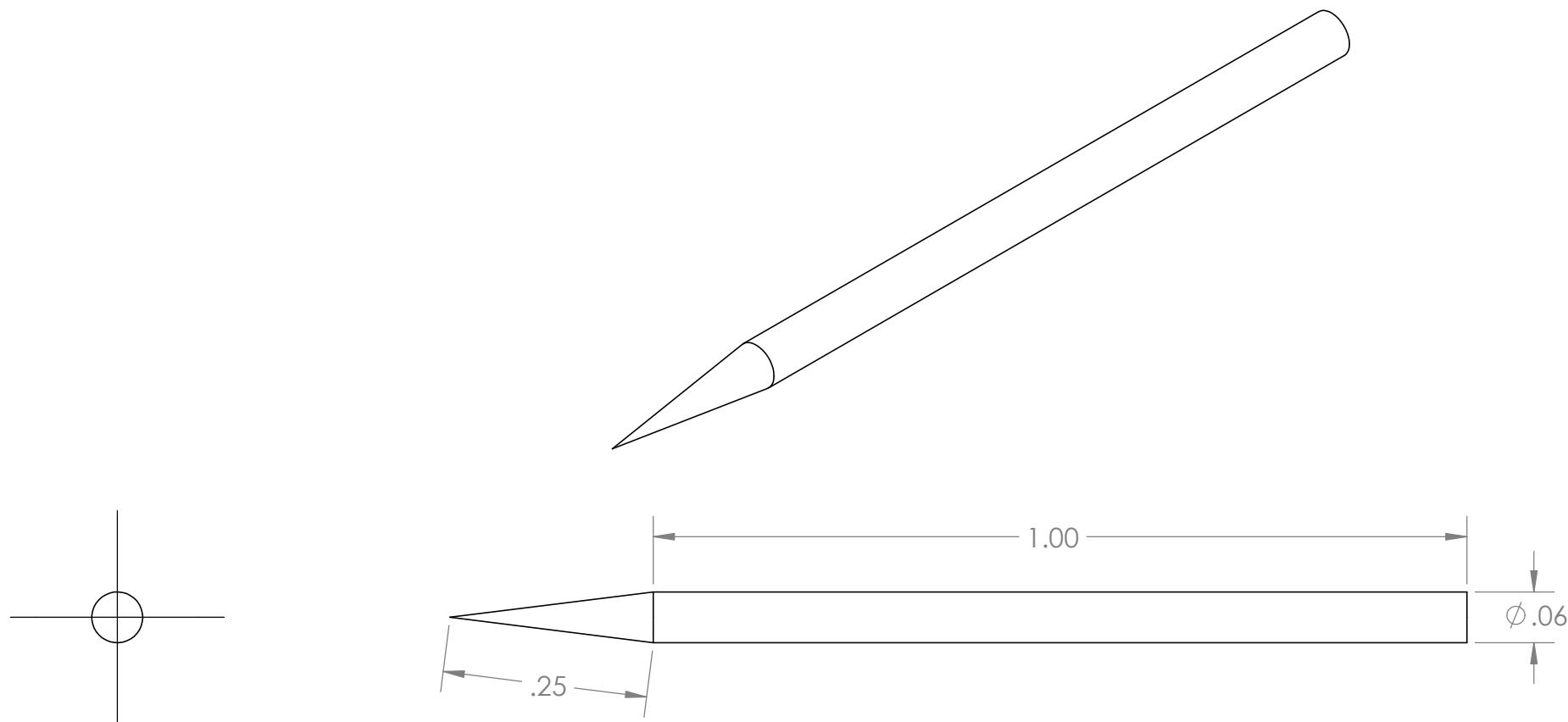
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UNLESS OTHERWISE SPECIFIED: DIMENSIONS ARE IN MILLIMETERS SURFACE FINISH: TOLERANCES: LINEAR: ANGULAR:				FINISH:		DEBurr AND BREAK SHARP EDGES	DO NOT SCALE DRAWING	REVISION
DRAWN	NAME Jonathan Lam	SIGNATURE	DATE 11/8/18					
CHK'D								
APPV'D								
MFG								
Q.A.				MATERIAL:			DWG NO.	
				WEIGHT:			SCALE:5:1	

Divider

Needle

A4

6

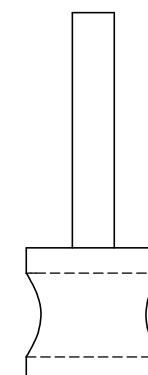
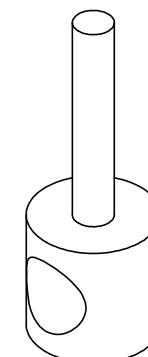
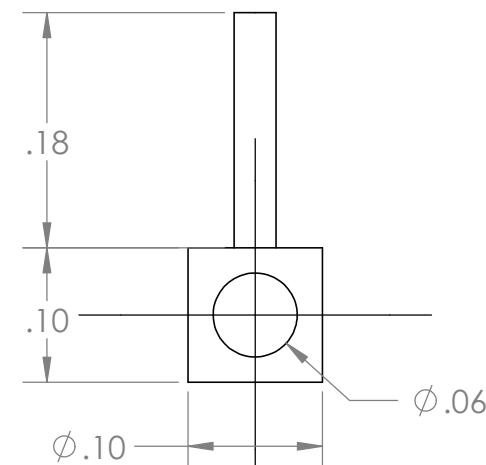
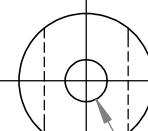
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UNLESS OTHERWISE SPECIFIED:
DIMENSIONS ARE IN MILLIMETERS
SURFACE FINISH:
TOLERANCES:
LINEAR:
ANGULAR:

FINISH:

DEBURR AND
BREAK SHARP
EDGES

DO NOT SCALE DRAWING

REVISION

	NAME	SIGNATURE	DATE		
DRAWN	Jonathan Lam		11/8/18		
CHK'D					
APPV'D					
MFG					
Q.A.				MATERIAL:	

TITLE:

Divider

Needle Holder

A4

3

2

1

6

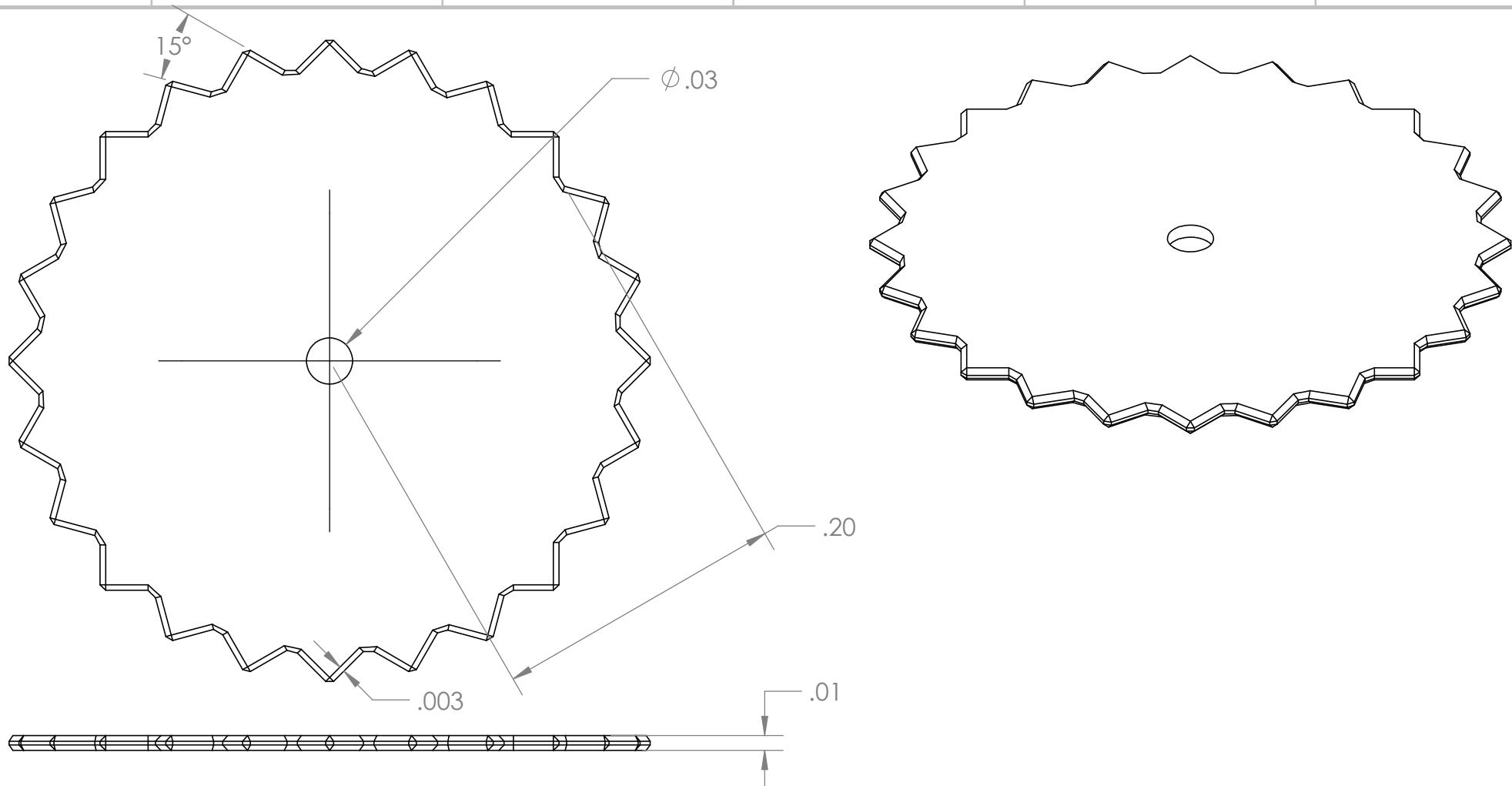
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4

3

2

1



All chamfers are $.003$ in.
Each tooth is identical
and offset by 15deg .

UNLESS OTHERWISE SPECIFIED: DIMENSIONS ARE IN MILLIMETERS SURFACE FINISH: TOLERANCES: LINEAR: ANGULAR:				FINISH:	DEBURN AND BREAK SHARP EDGES	DO NOT SCALE DRAWING	REVISION
DRAWN	NAME Jonathan Lam	SIGNATURE	DATE 11/8/18				
CHK'D							
APP'D							
MFG							
Q.A.				MATERIAL:			
						DWG NO.	
						Needle Holder Nut	A4
				WEIGHT:		SCALE:10:1	
							SHEET 1 OF 1

6

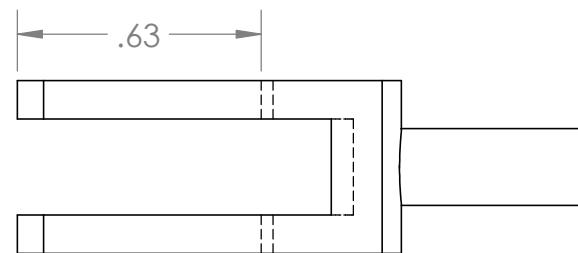
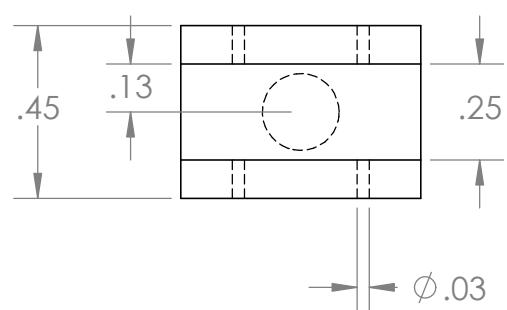
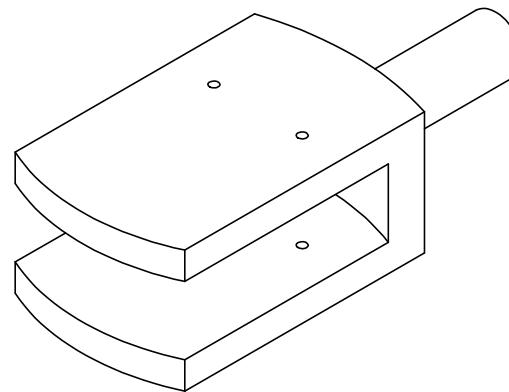
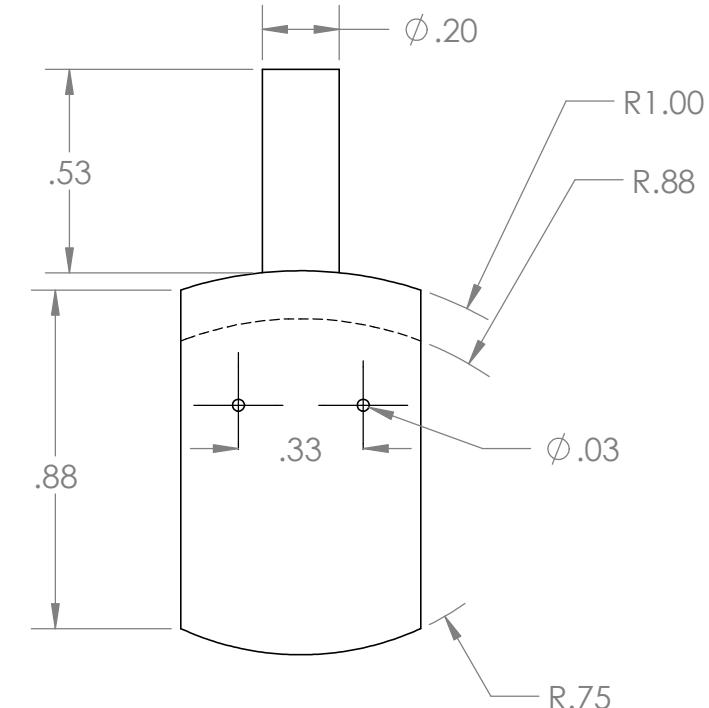
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UNLESS OTHERWISE SPECIFIED:
DIMENSIONS ARE IN MILLIMETERS
SURFACE FINISH:
TOLERANCES:
LINEAR:
ANGULAR:

FINISH:

DEBURR AND
BREAK SHARP
EDGES

DO NOT SCALE DRAWING

REVISION

	NAME	SIGNATURE	DATE	
DRAWN	Jonathan Lam		11/8/18	
CHK'D				
APPV'D				
MFG				
Q.A.				

MATERIAL:

DWG NO.:

Top Connector

A4

WEIGHT:

SCALE:2:1

SHEET 1 OF 1

6

5

4

3

2

1

6

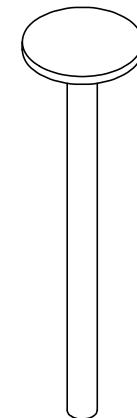
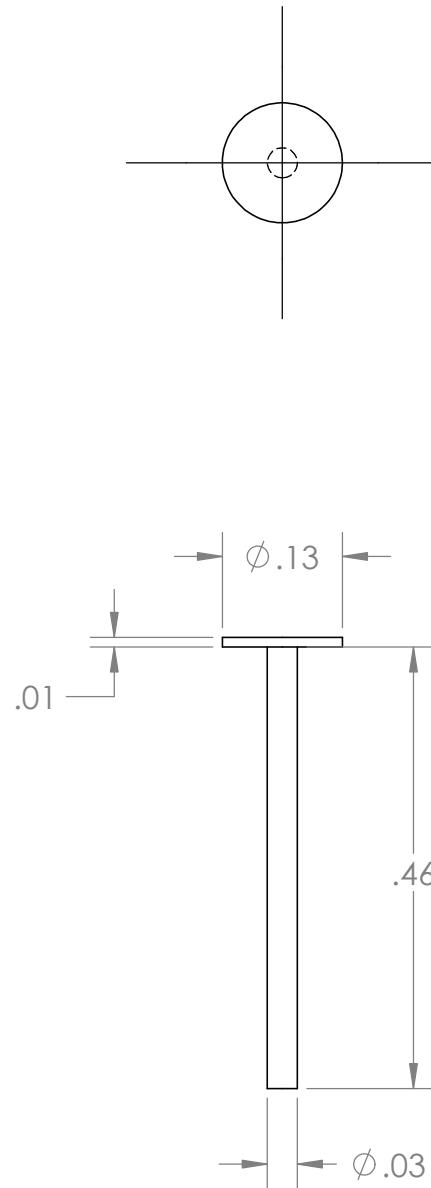
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UNLESS OTHERWISE SPECIFIED: DIMENSIONS ARE IN MILLIMETERS SURFACE FINISH:				FINISH:	DEBURR AND BREAK SHARP EDGES	DO NOT SCALE DRAWING	REVISION
DRAWN	NAME	SIGNATURE	DATE				
CHK'D							
APPV'D							
MFG							
Q.A.				MATERIAL:		DWG NO.	
						SCALE:5:1	
				WEIGHT:			

TITLE: Divider

Top Bolt

A4

6

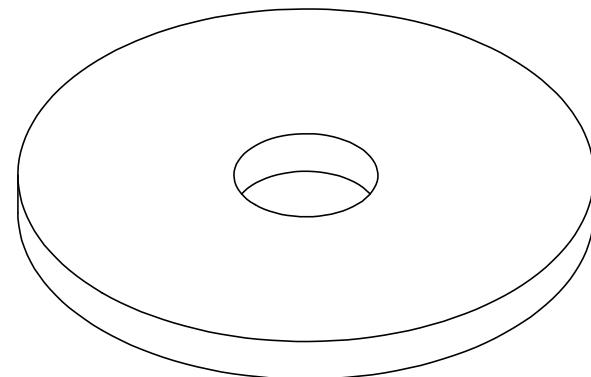
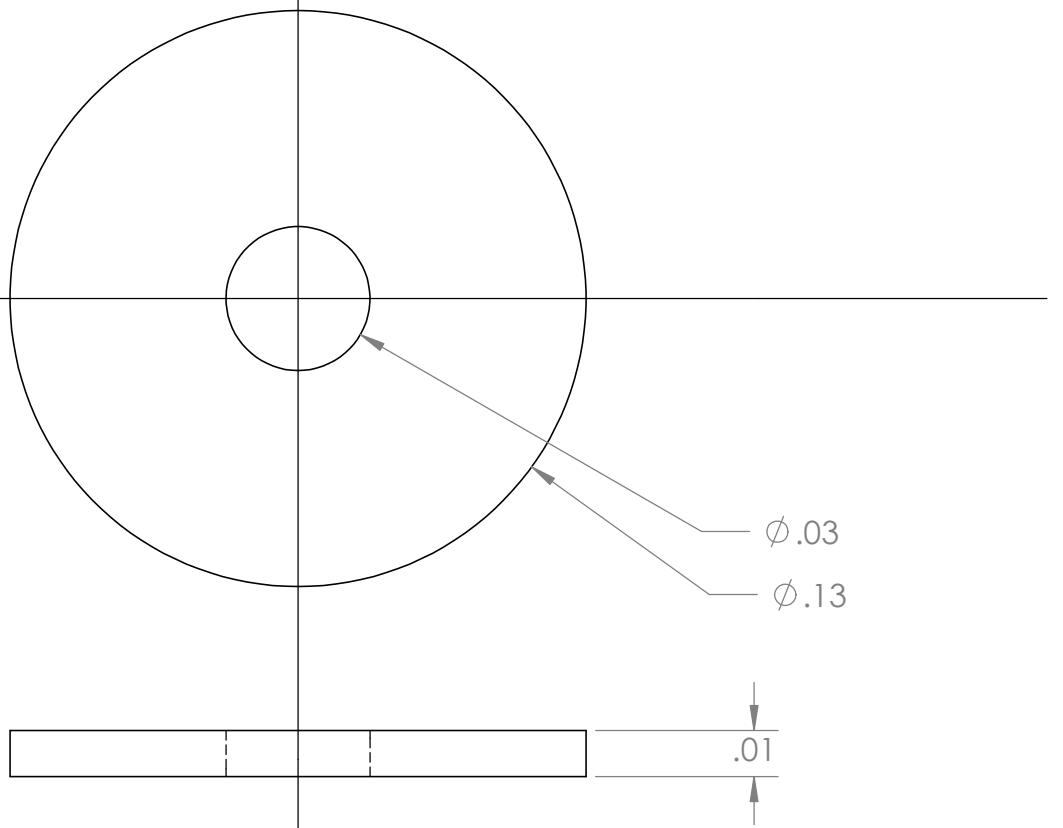
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4

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2

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UNLESS OTHERWISE SPECIFIED:
DIMENSIONS ARE IN MILLIMETERS
SURFACE FINISH:
TOLERANCES:
LINEAR:
ANGULAR:

FINISH:

DEBURR AND
BREAK SHARP
EDGES

DO NOT SCALE DRAWING

REVISION

	NAME	SIGNATURE	DATE		
DRAWN	Jonathan Lam		11/8/18		
CHK'D					
APPV'D					
MFG					
Q.A.				MATERIAL:	
					DWG NO.
					SCALE:24:1
					SHEET 1 OF 1

3

2

1

Divider

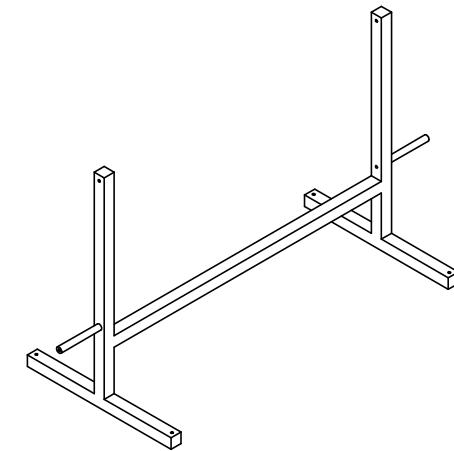
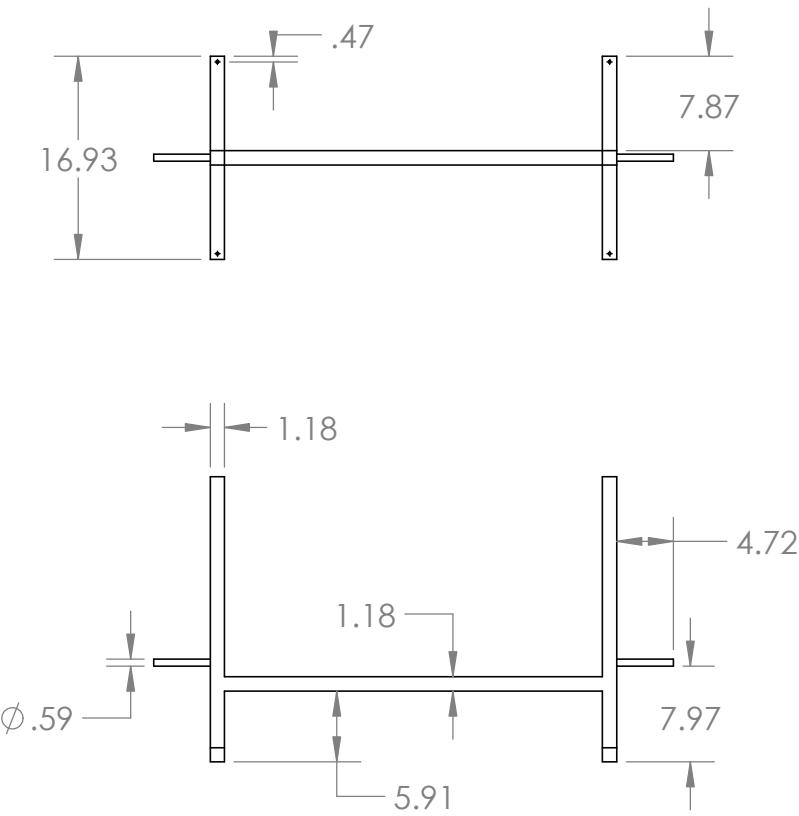
Top Nut

A4

2

1

B



B

A

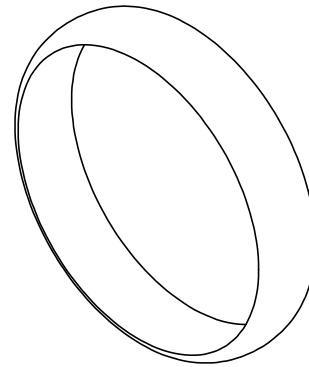
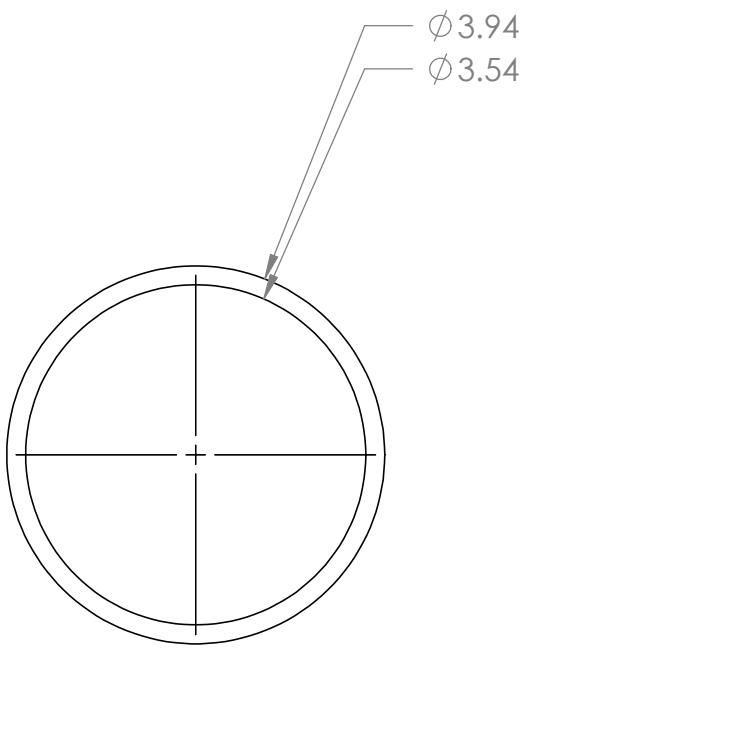
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		INTERPRET GEOMETRIC TOLERANCING PER: MATERIAL		CHECKED	ENG APPR.	MFG APPR.			
		NEXT ASSY							
		USED ON		FINISH		COMMENTS:			
		APPLICATION		DO NOT SCALE DRAWING					
SIZE	DWG. NO.					REV			
A									
SCALE: 1:16		WEIGHT:		SHEET 1 OF 1					

A

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PROHIBITED.

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1



B

B

A

A

		UNLESS OTHERWISE SPECIFIED:			NAME	DATE						
		DIMENSIONS ARE IN INCHES TOLERANCES: FRACTIONAL \pm ANGULAR: MACH \pm BEND \pm TWO PLACE DECIMAL \pm THREE PLACE DECIMAL \pm		DRAWN	Jon L.	11/20/18						
				CHECKED								
				ENG APPR.								
				MFG APPR.								
				Q.A.								
		INTERPRET GEOMETRIC TOLERANCING PER:		COMMENTS:								
		MATERIAL										
NEXT ASSY		USED ON		FINISH								
APPLICATION		DO NOT SCALE DRAWING										

TITLE:

Wheel Tire

SIZE

DWG. NO.

REV

A

SCALE: 1:2

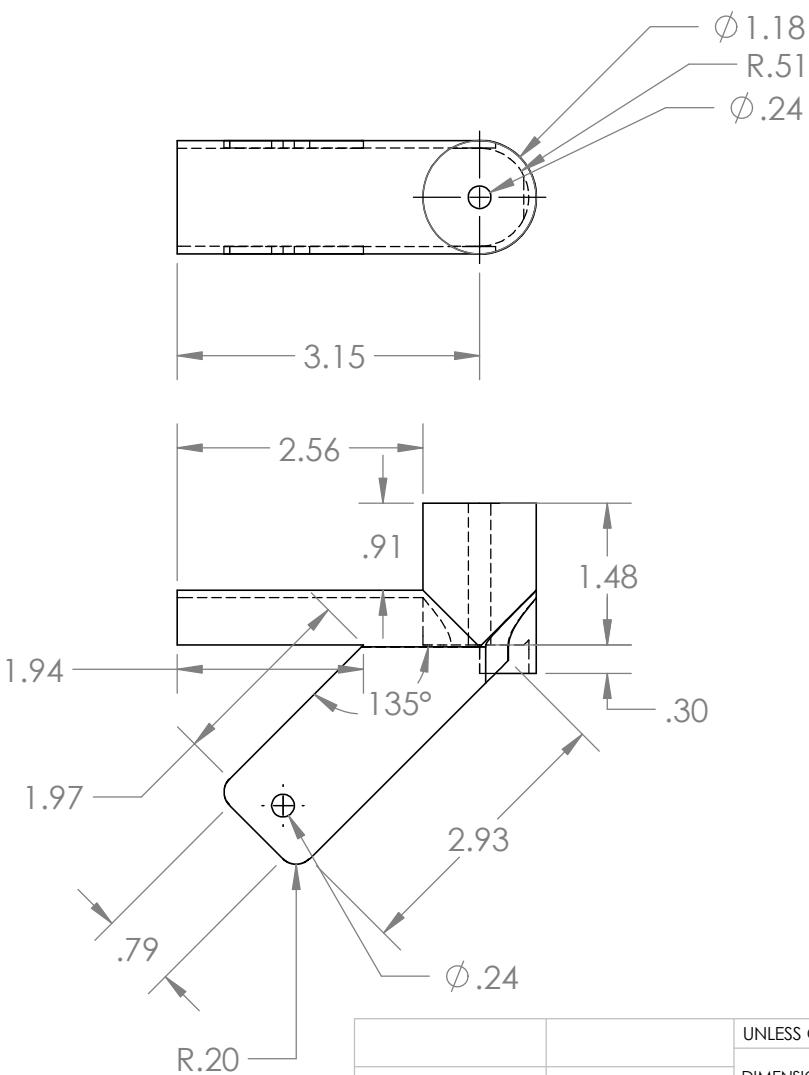
WEIGHT:

SHEET 1 OF 1

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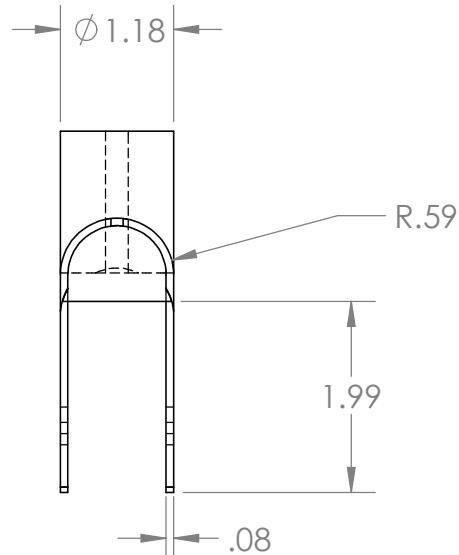
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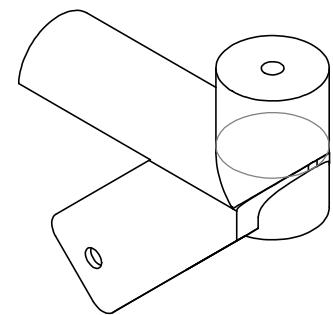


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B

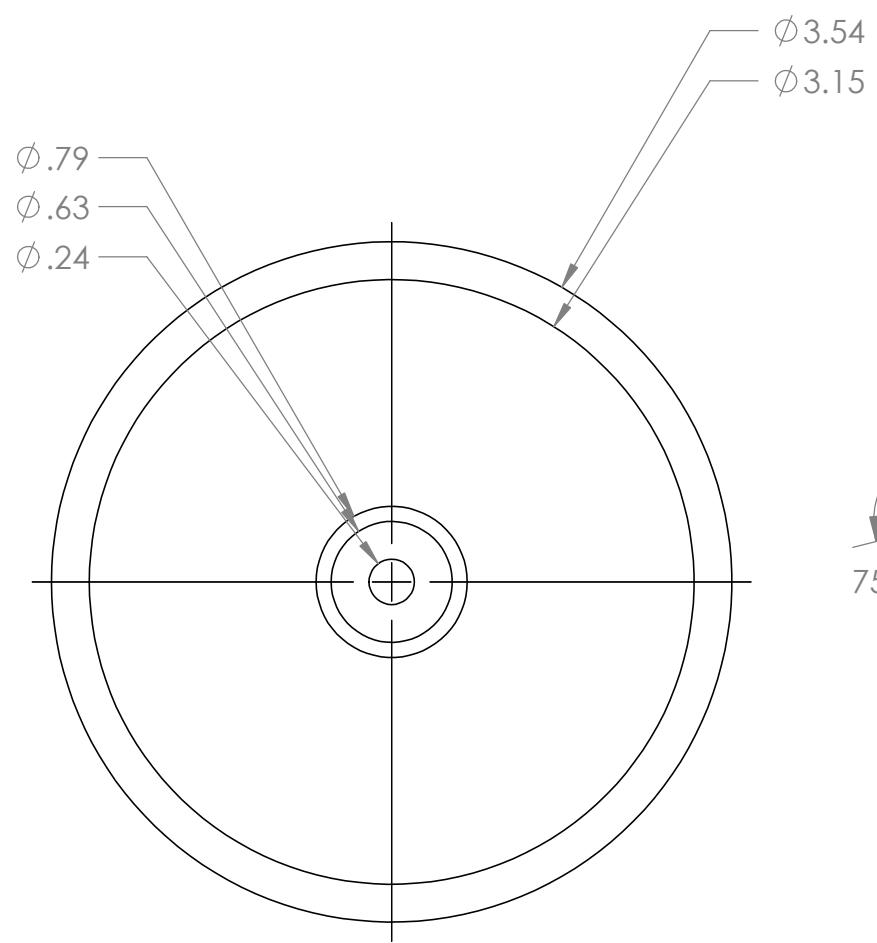


Wheel Holder

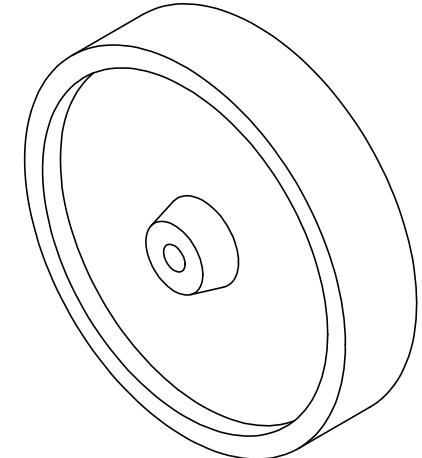
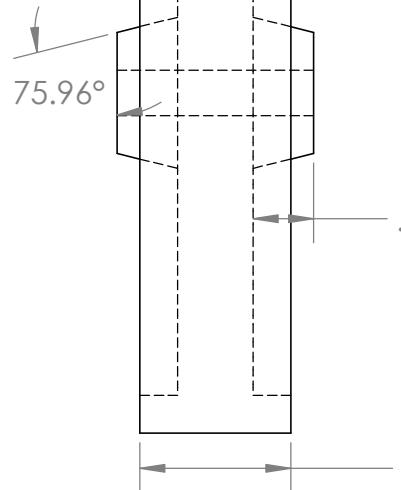
SIZE	DWG. NO.	REV
A		
SCALE: 1:2	WEIGHT:	SHEET 1 OF 1

2

1



.20



B

A

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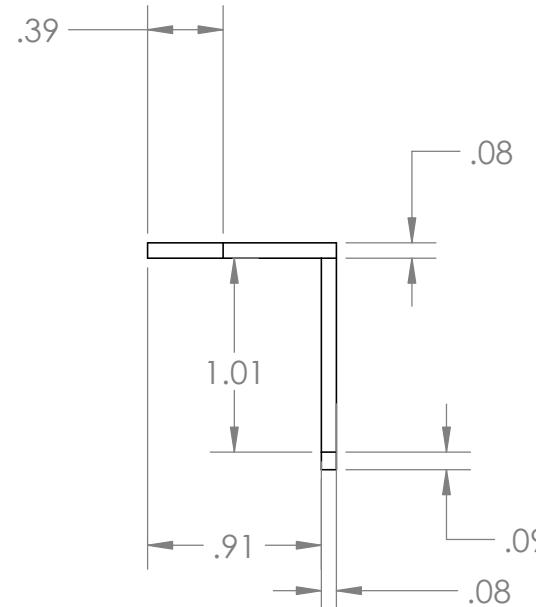
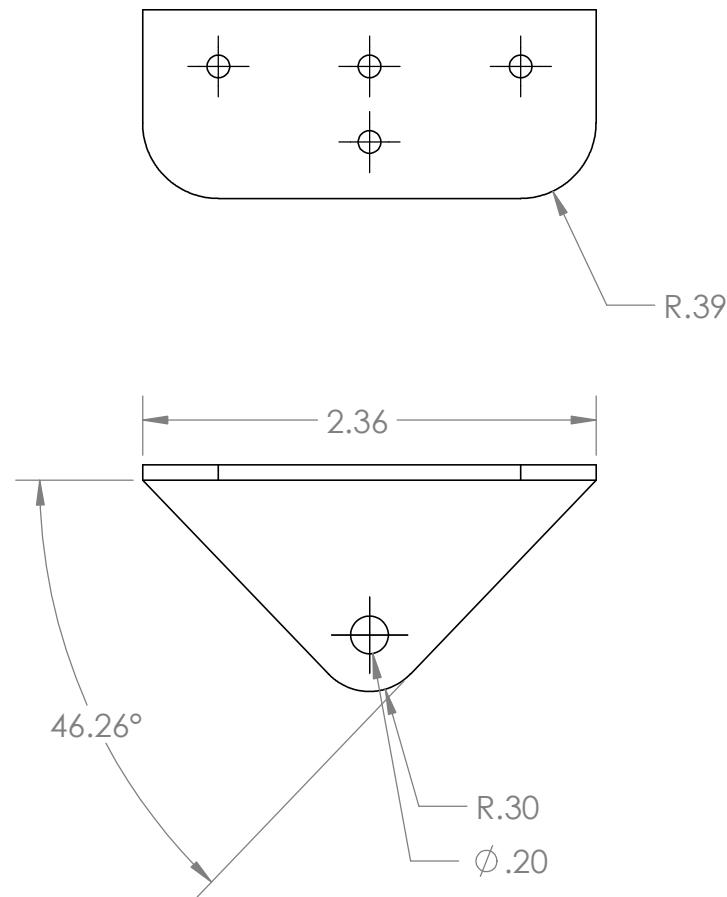
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		DIMENSIONS ARE IN INCHES TOLERANCES: FRACTIONAL ± ANGULAR: MACH ± BEND ± TWO PLACE DECIMAL ± THREE PLACE DECIMAL ±		DRAWN	Jon L.	11/20/18						
		INTERPRET GEOMETRIC TOLERANCING PER:		CHECKED								
		MATERIAL		ENG APPR.								
		NEXT ASSY		MFG APPR.								
		USED ON		Q.A.								
		FINISH		COMMENTS:								
		APPLICATION										
		DO NOT SCALE DRAWING										
				SIZE	DWG. NO.			REV				
				A								
				SCALE: 1:1	WEIGHT:			SHEET 1 OF 1				

1

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All holes 0.12"D unless otherwise specified.



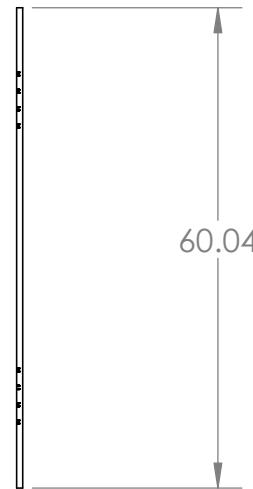
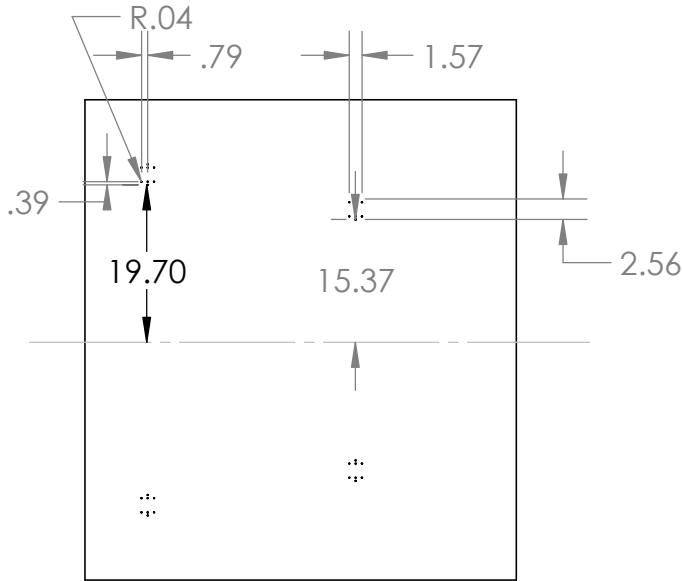
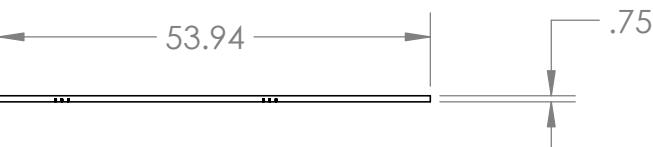
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		INTERPRET GEOMETRIC TOLERANCING PER: MATERIAL		CHECKED	ENG APPR.	MFG APPR.			
		NEXT ASSY							
		USED ON		FINISH		COMMENTS:			
		APPLICATION		DO NOT SCALE DRAWING					
SIZE	DWG. NO.					REV			
A									
SCALE: 1:1		WEIGHT:		SHEET 1 OF 1					

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2

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B



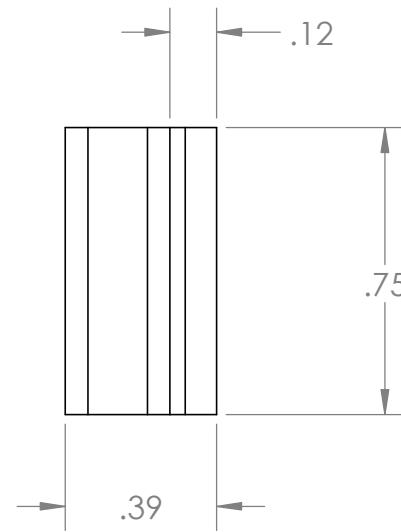
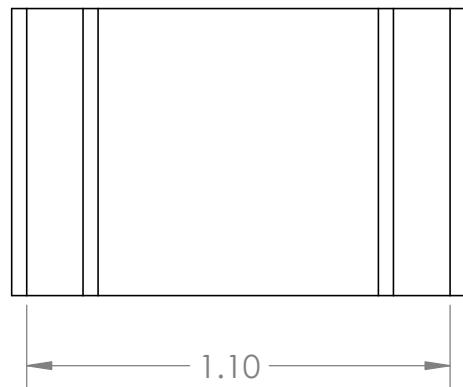
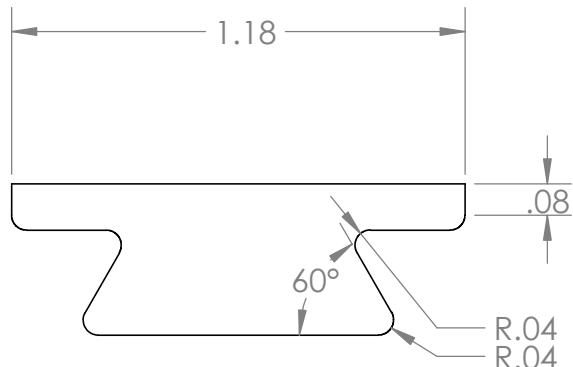
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1

		UNLESS OTHERWISE SPECIFIED:				NAME	DATE	TITLE: Table Top		
		DIMENSIONS ARE IN INCHES TOLERANCES: FRACTIONAL \pm ANGULAR: MACH \pm BEND \pm TWO PLACE DECIMAL \pm THREE PLACE DECIMAL \pm			DRAWN	Jon L.	11/20/18			
		INTERPRET GEOMETRIC TOLERANCING PER: MATERIAL			CHECKED					
		NEXT ASSY		USED ON	FINISH	COMMENTS:				
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								A		
								SCALE: 1:24	WEIGHT:	SHEET 1 OF 1

2

1



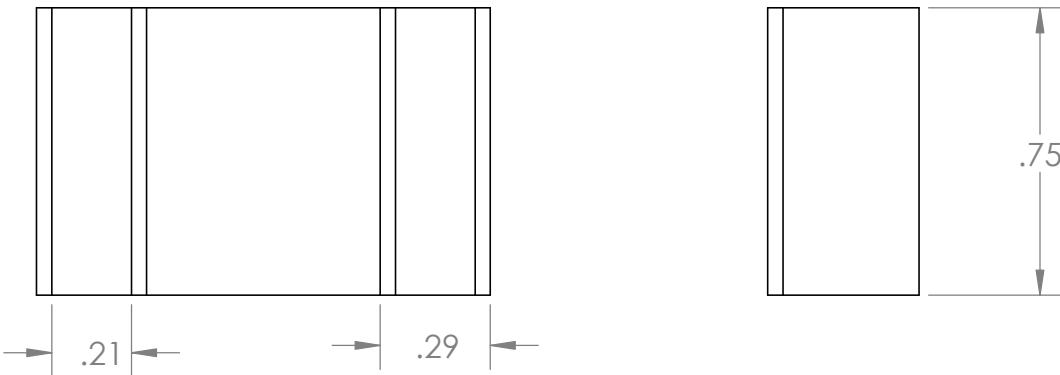
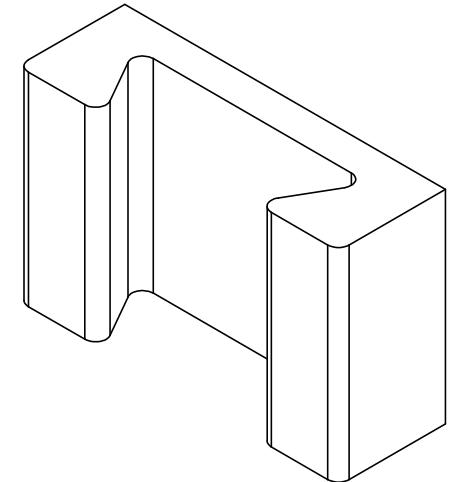
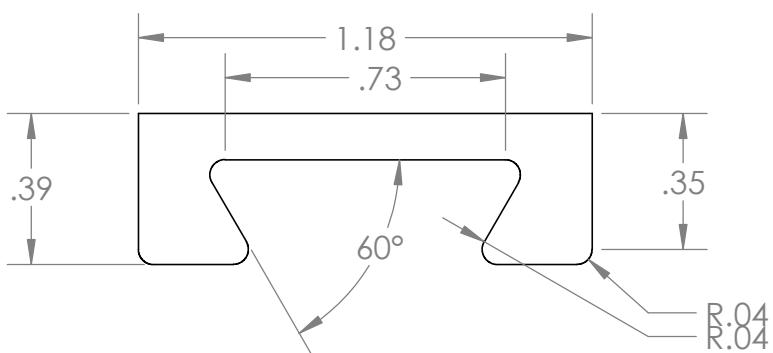
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		UNLESS OTHERWISE SPECIFIED:			
		DIMENSIONS ARE IN INCHES TOLERANCES: FRACTIONAL \pm ANGULAR: MACH \pm BEND \pm TWO PLACE DECIMAL \pm THREE PLACE DECIMAL \pm	DRAWN	Jon L.	11/20/18
		INTERPRET GEOMETRIC TOLERANCING PER: MATERIAL	CHECKED		
			ENG APPR.		
			MFG APPR.		
			Q.A.		
		COMMENTS:			
NEXT ASSY	USED ON	FINISH			
APPLICATION		DO NOT SCALE DRAWING			

SIZE	DWG. NO.	REV
A		
SCALE: 2:1	WEIGHT:	SHEET 1 OF 1

2

1

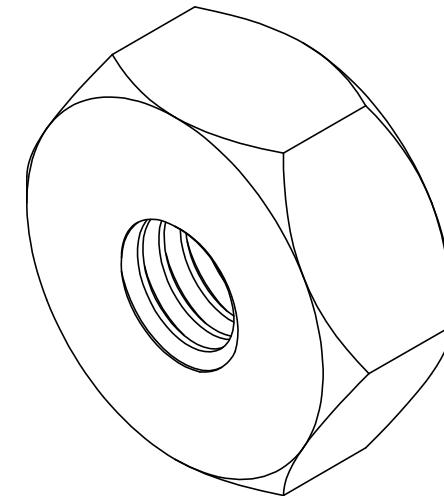
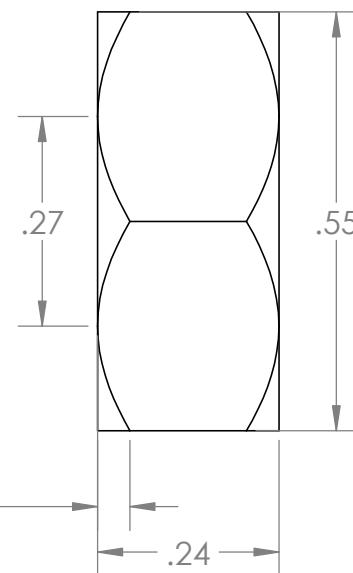
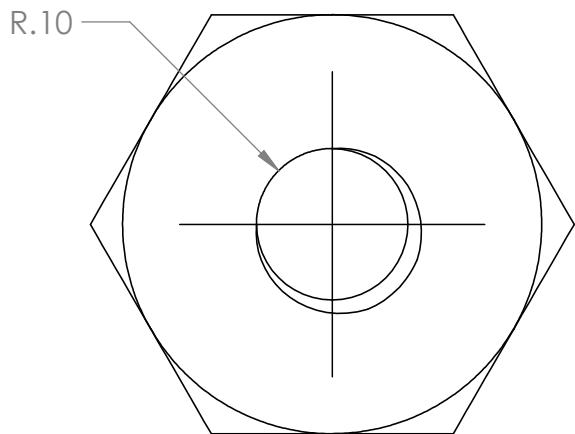
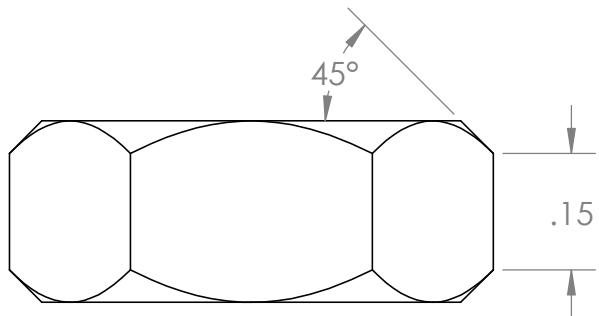


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		INTERPRET GEOMETRIC TOLERANCING PER: MATERIAL		CHECKED	ENG APPR.	MFG APPR.			
		NEXT ASSY							
		USED ON		FINISH		COMMENTS:			
		APPLICATION		DO NOT SCALE DRAWING					
SIZE	DWG. NO.					REV			
A									
SCALE: 2:1		WEIGHT:		SHEET 1 OF 1					

2

1



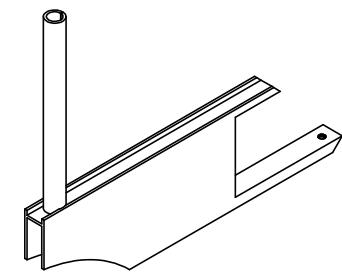
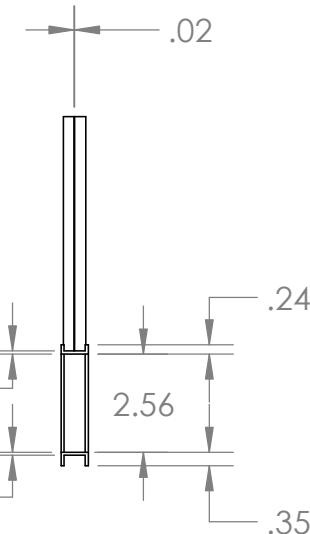
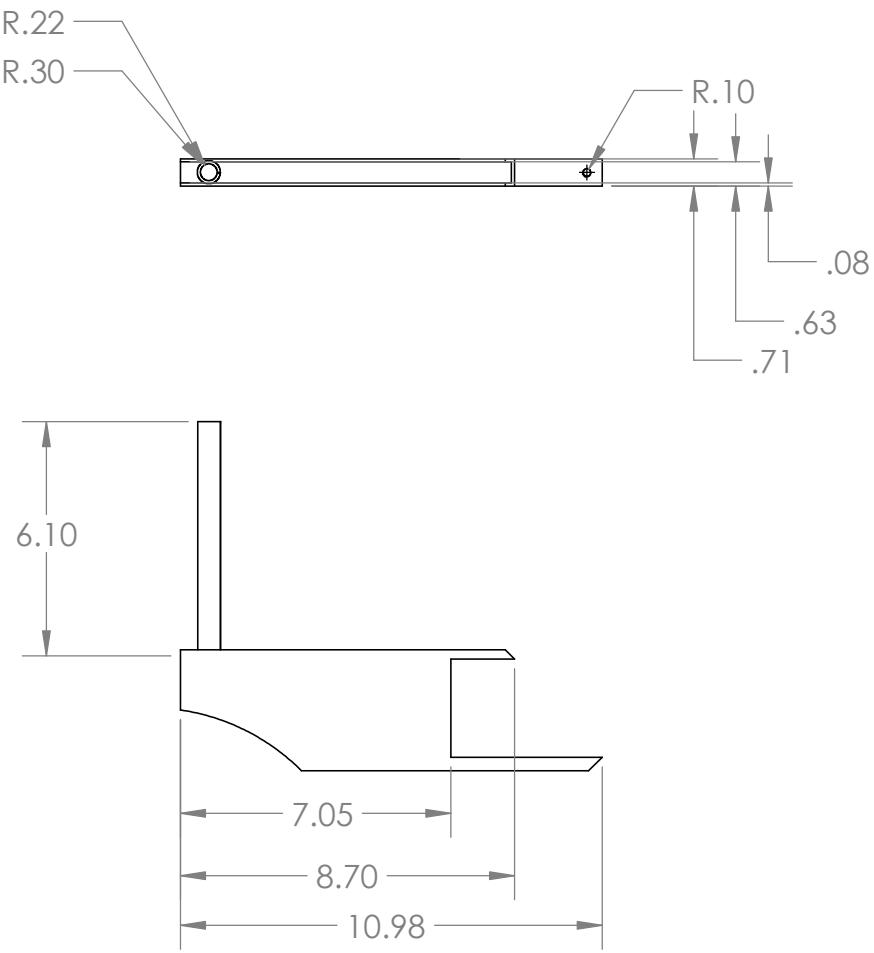
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		UNLESS OTHERWISE SPECIFIED:		DRAWN CHECKED ENG APPR. MFG APPR. Q.A.	NAME DATE	TITLE: Nut
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		INTERPRET GEOMETRIC TOLERANCING PER: MATERIAL				
NEXT ASSY	USED ON	FINISH				
APPLICATION		DO NOT SCALE DRAWING				
SIZE	DWG. NO.					REV
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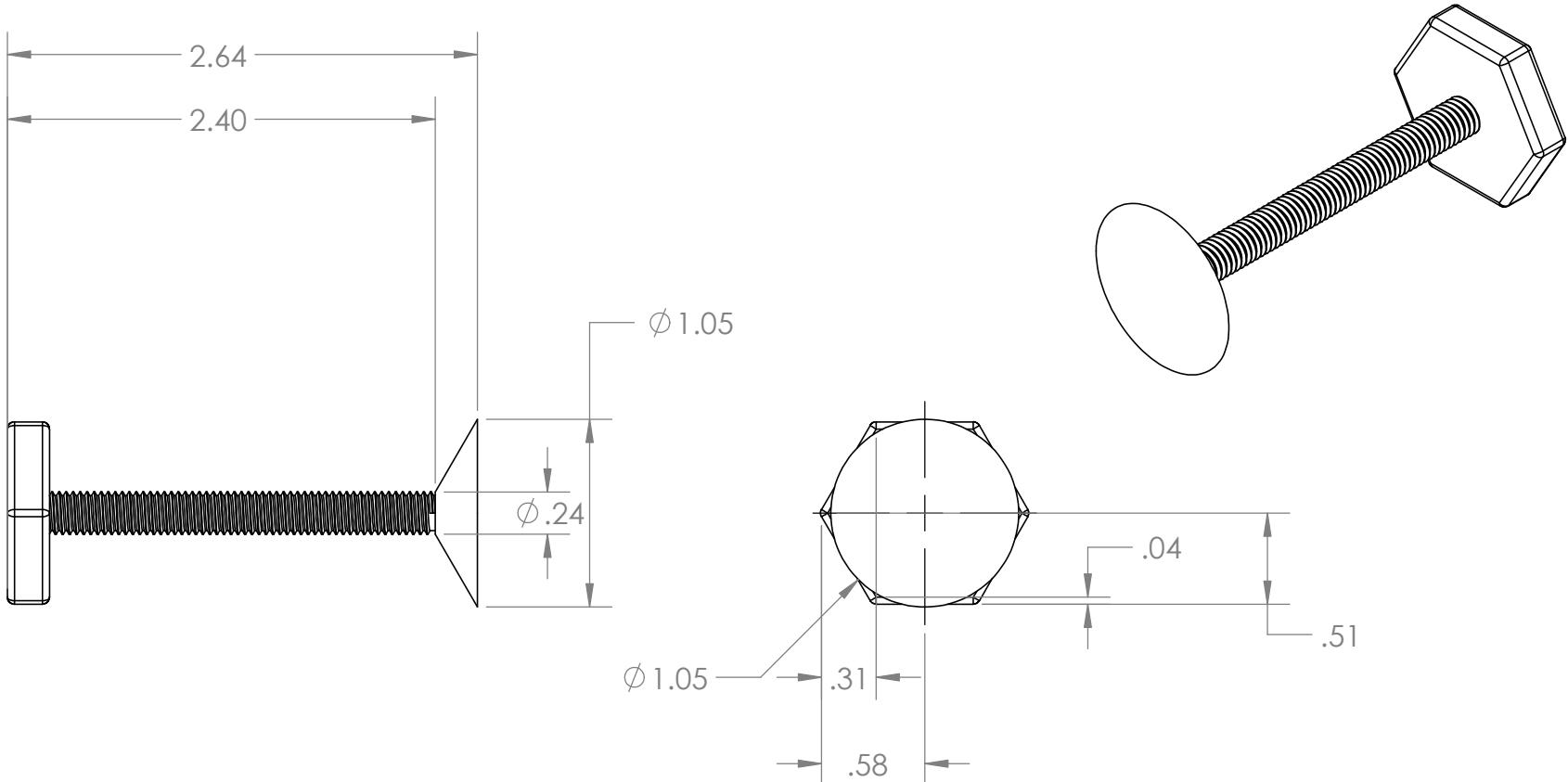
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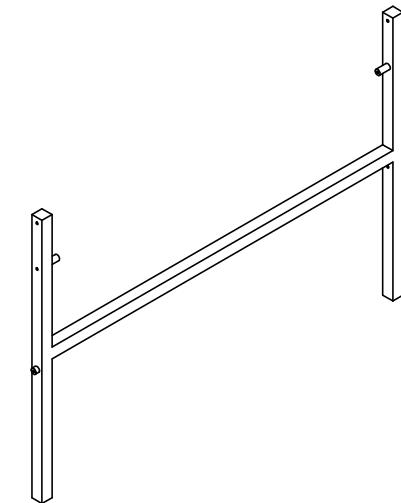
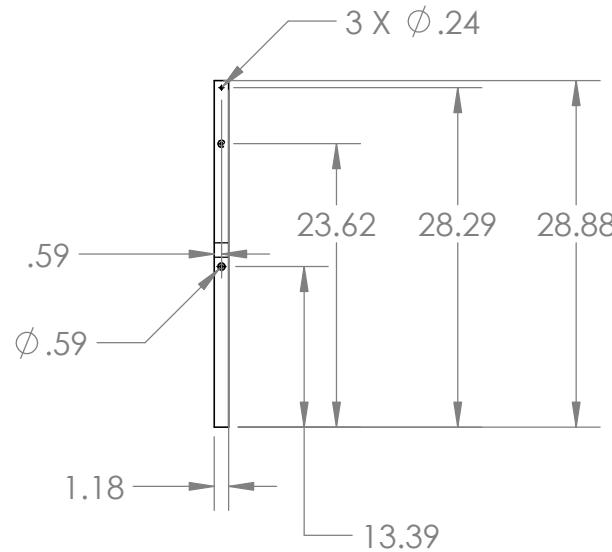
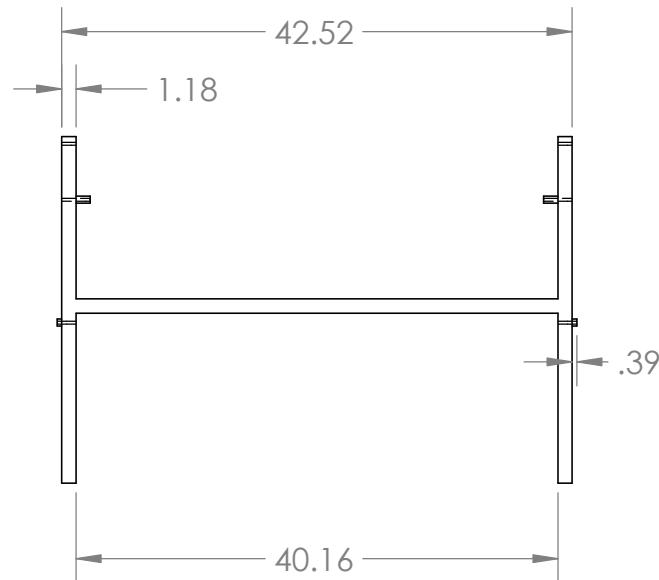
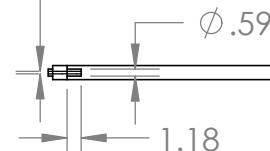
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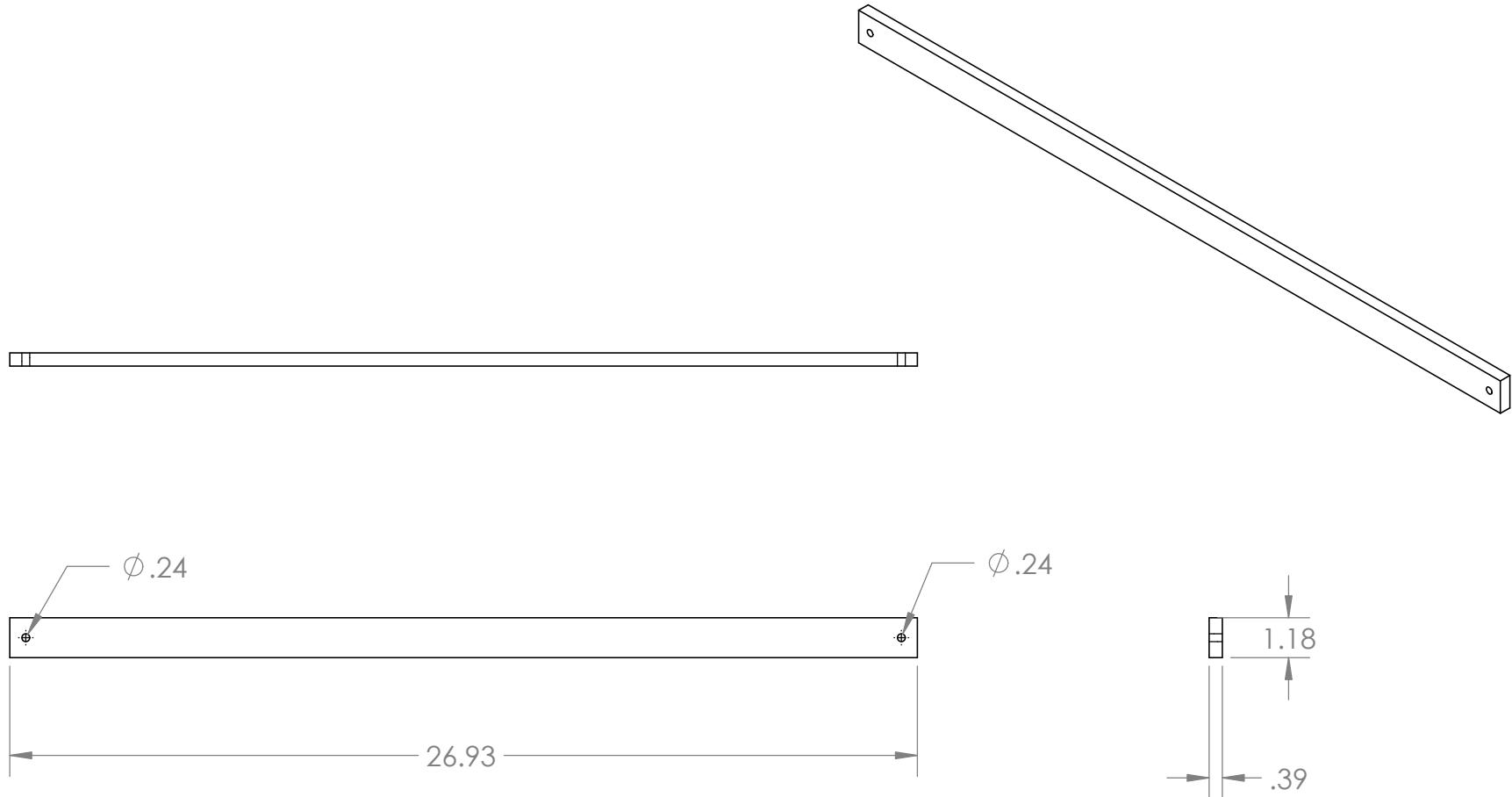
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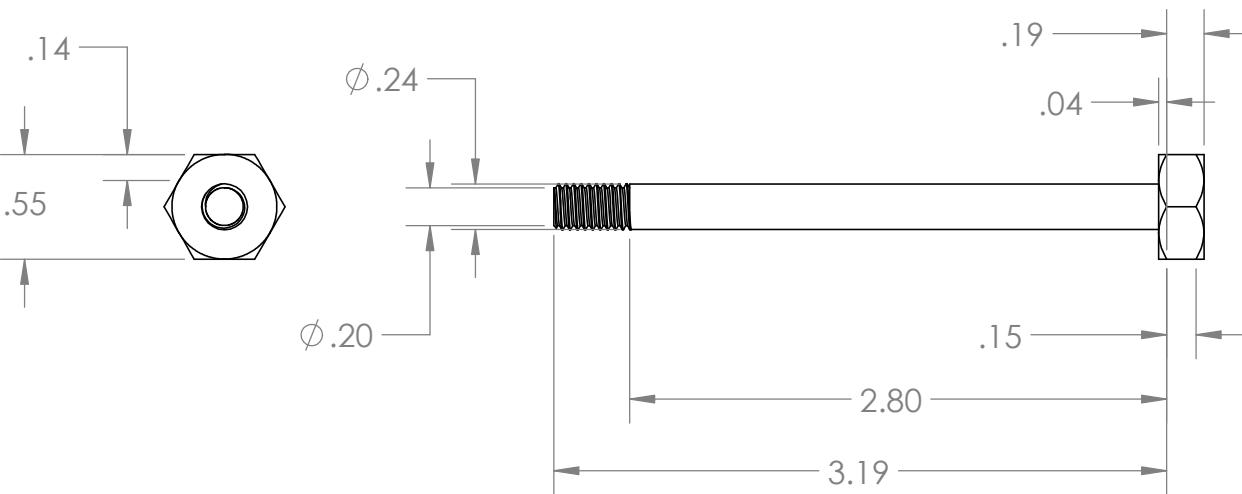
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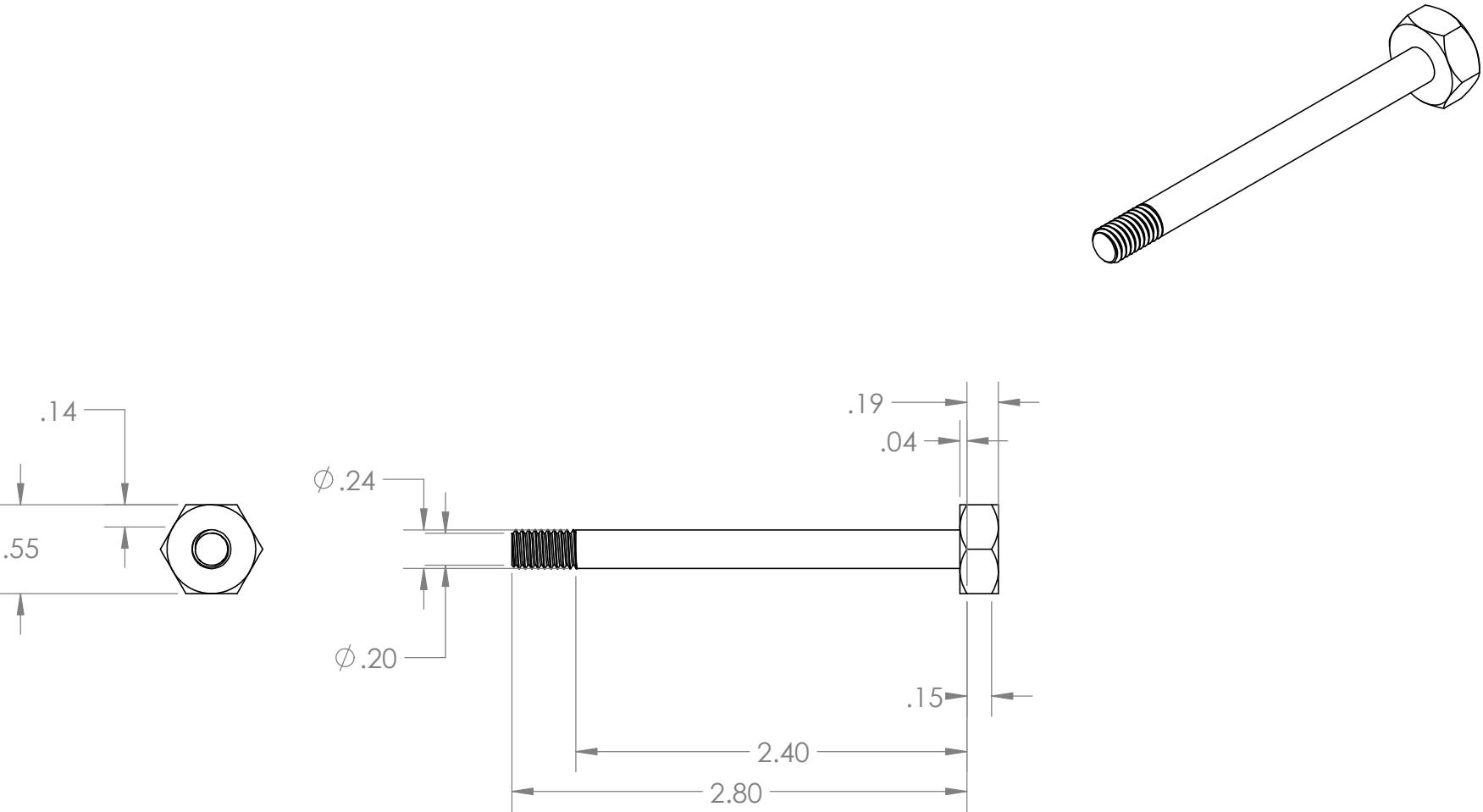
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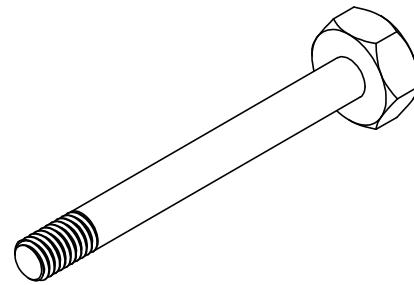


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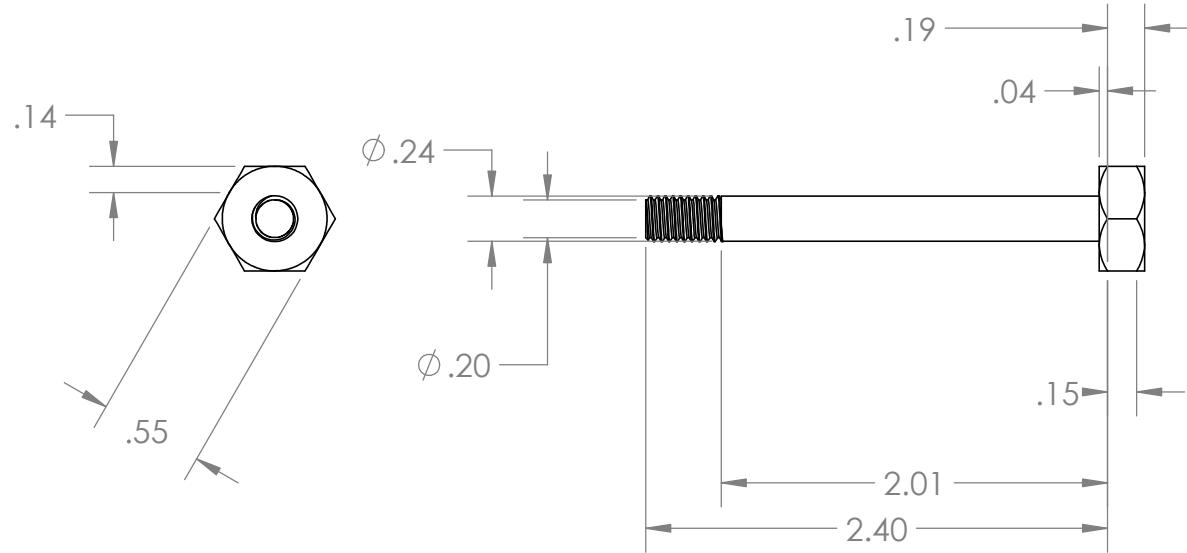
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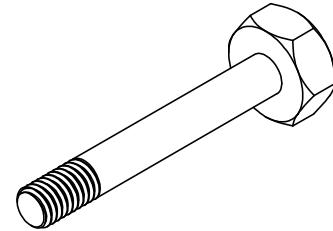
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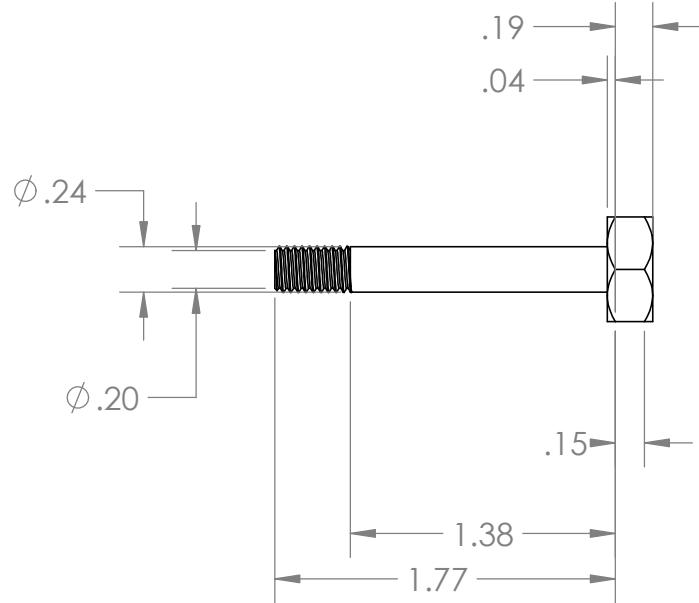
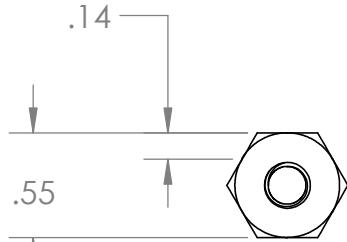
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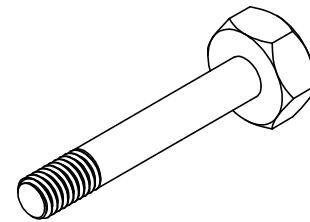
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NEXT ASSY	USED ON	FINISH									
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SIZE	DWG. NO.	A 34mm Bolt					REV				
SCALE: 1:1	WEIGHT:	SHEET 1 OF 1									

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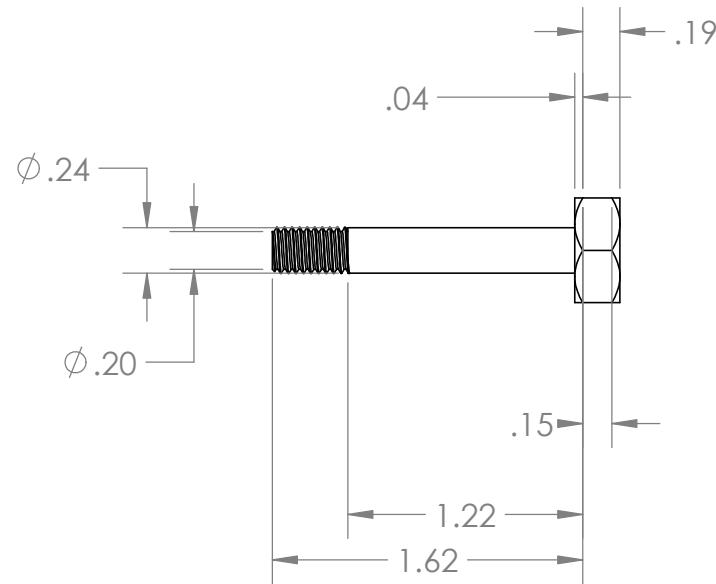
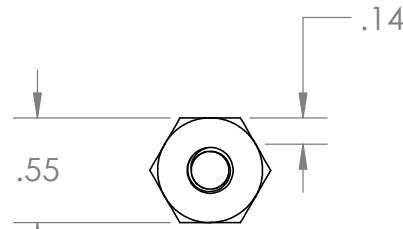
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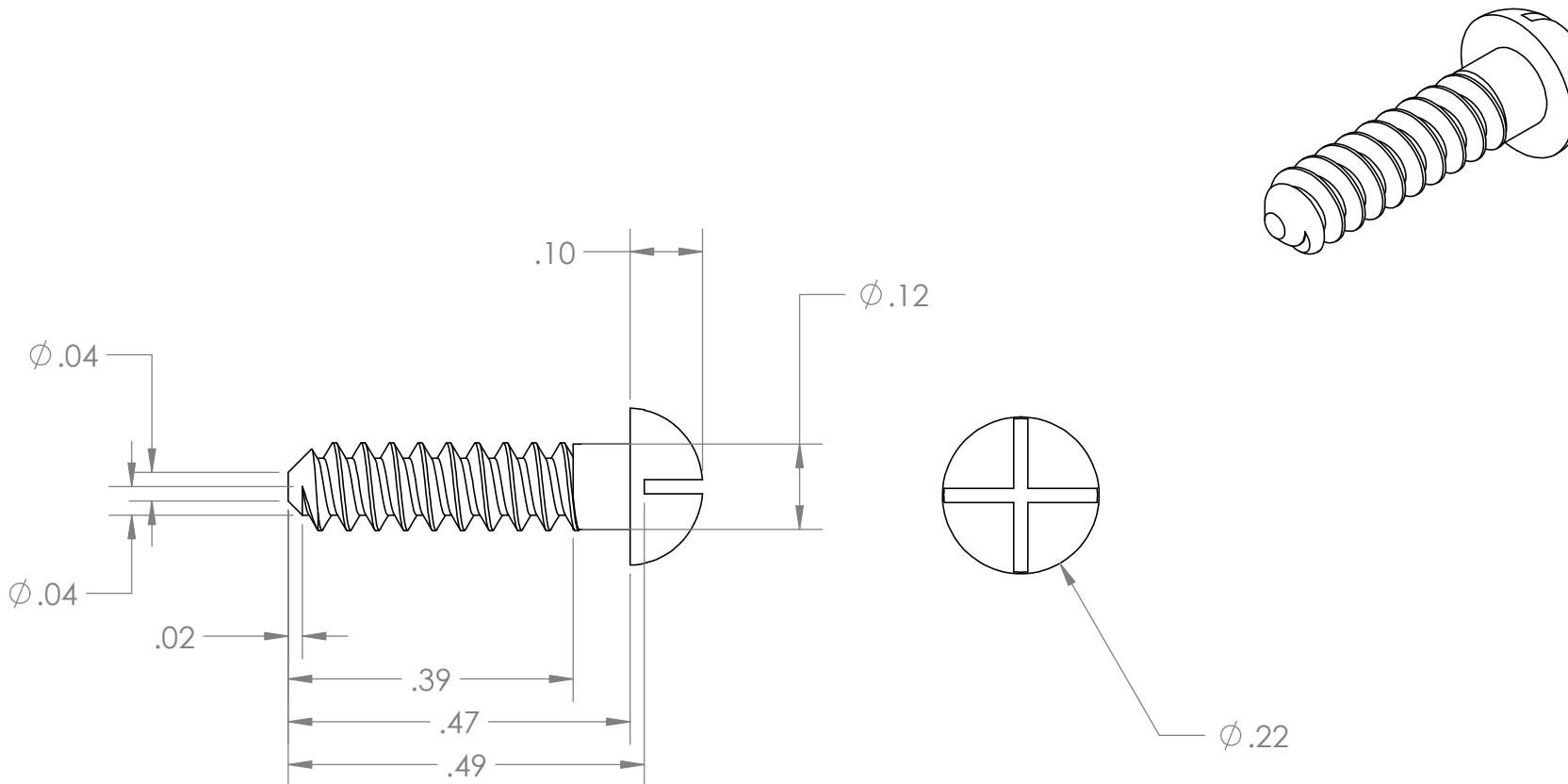
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SCALE: 1:1	WEIGHT:	SHEET 1 OF 1									

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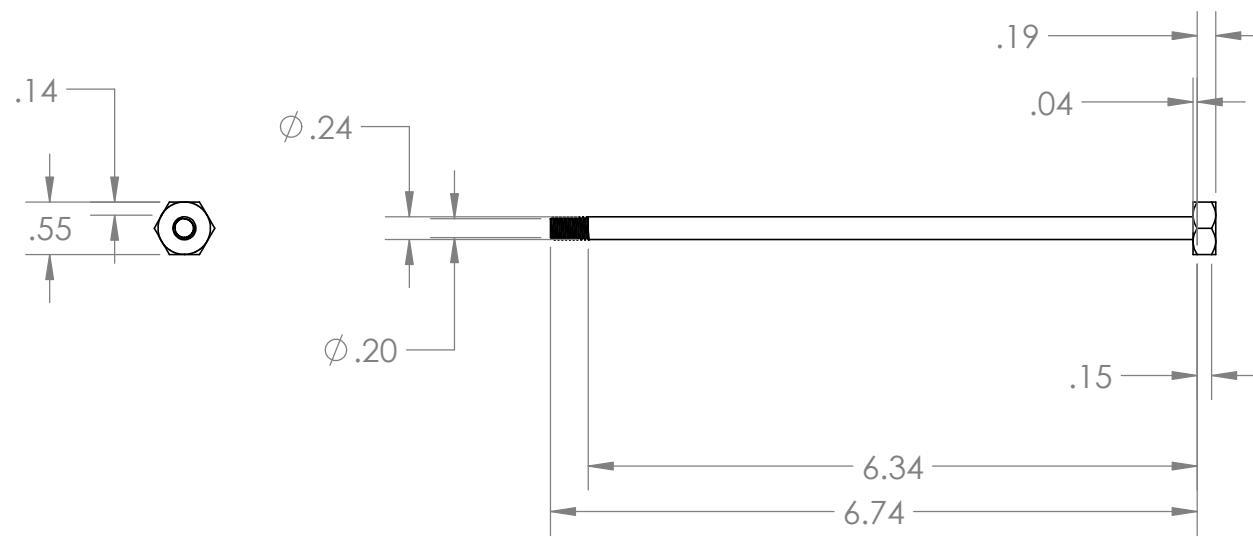
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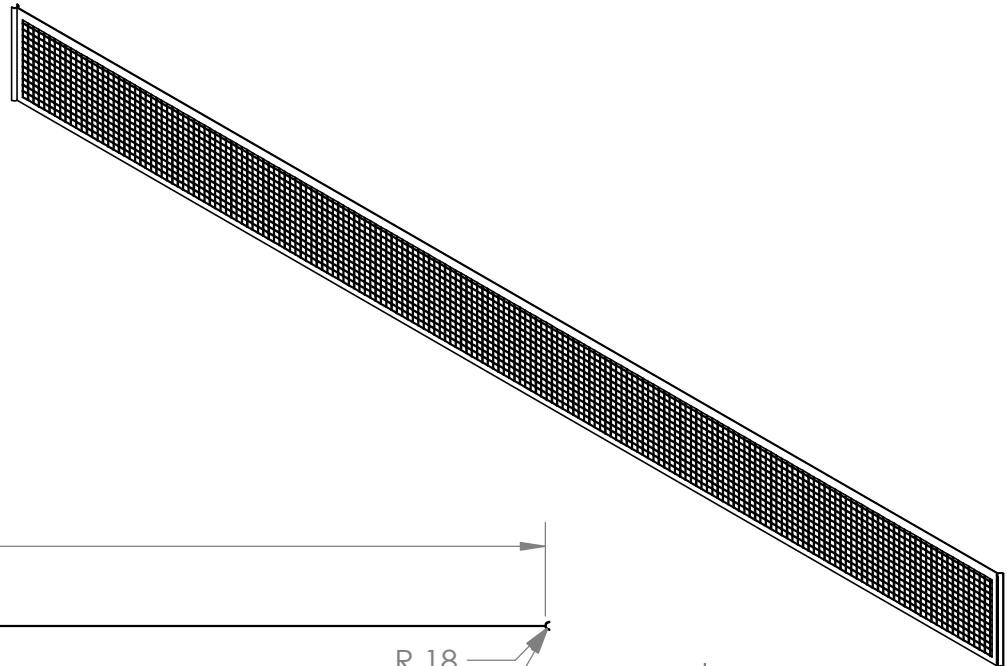
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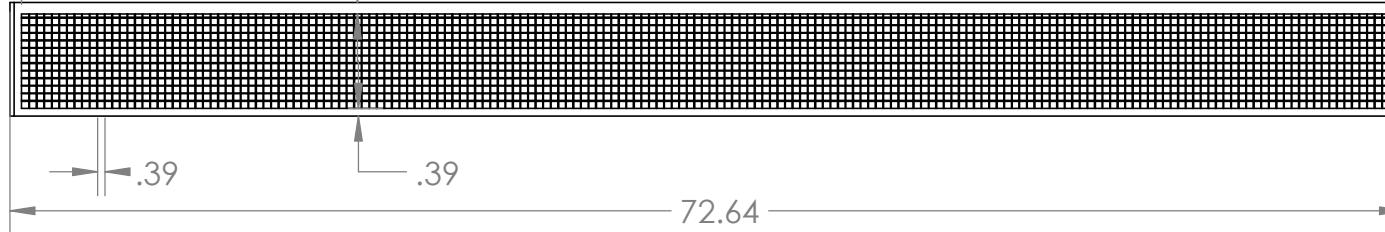
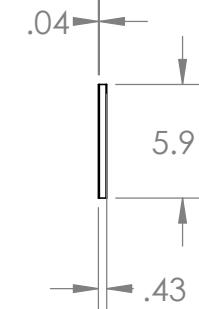
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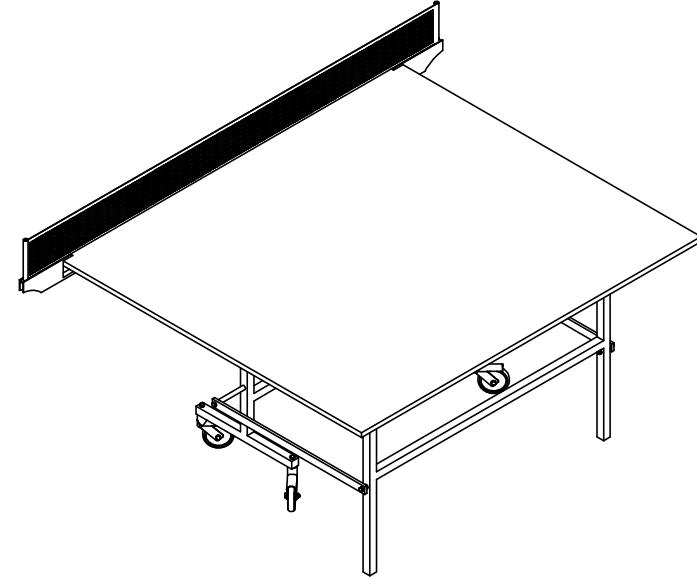
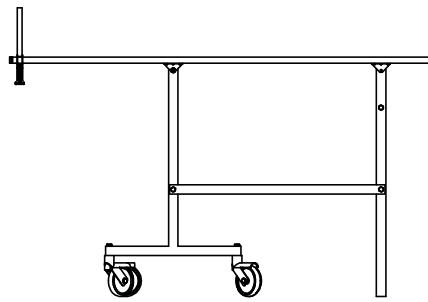
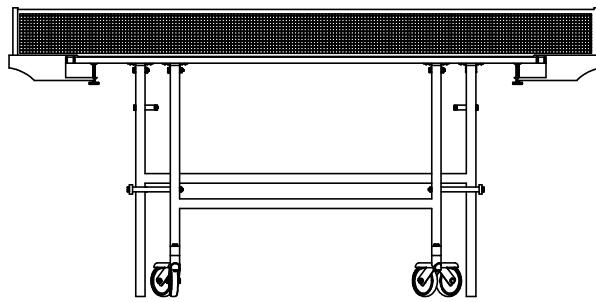
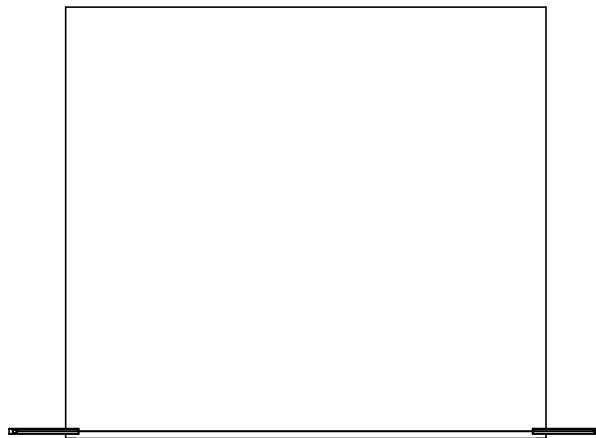
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Half Table Solid Lines

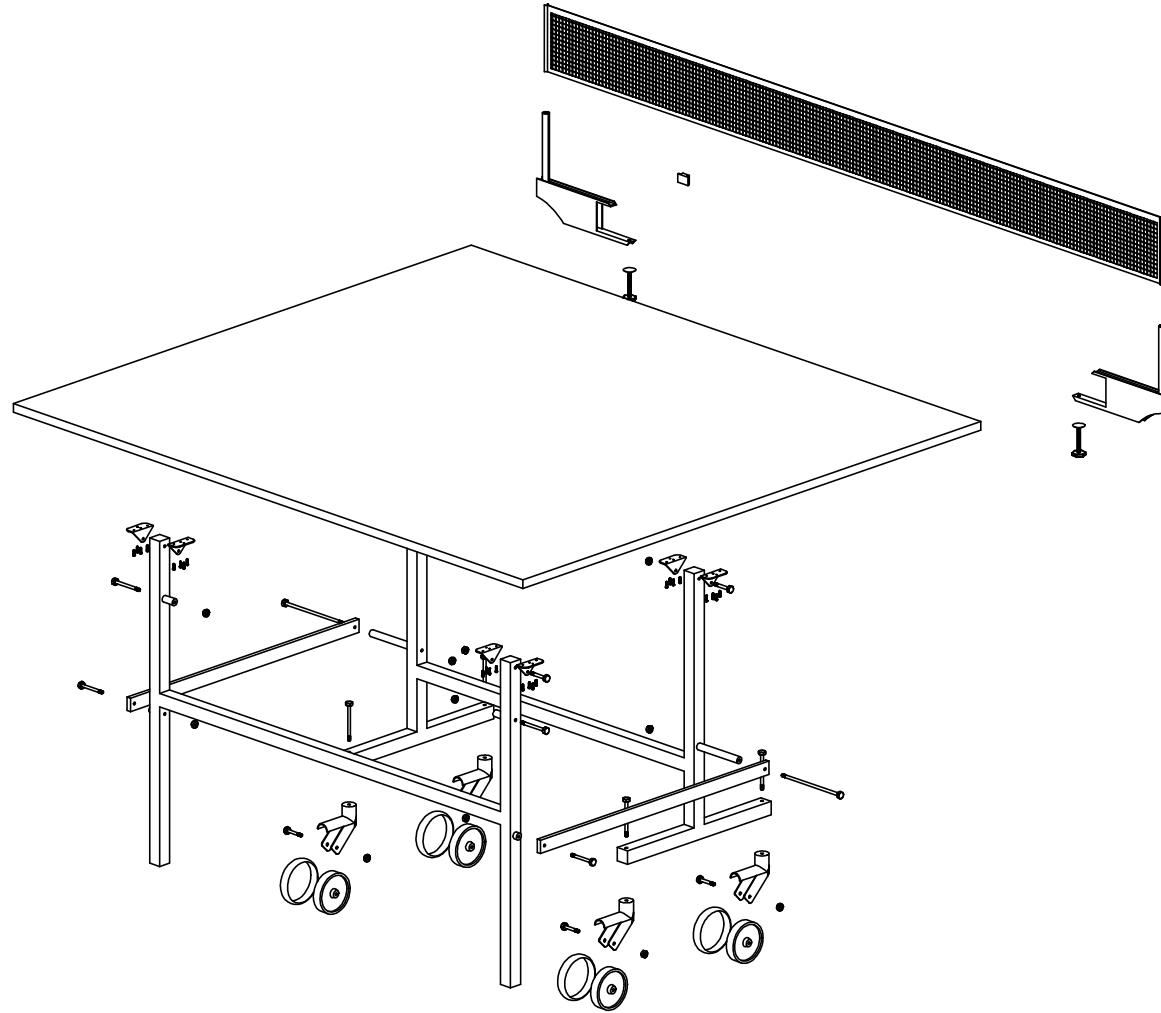
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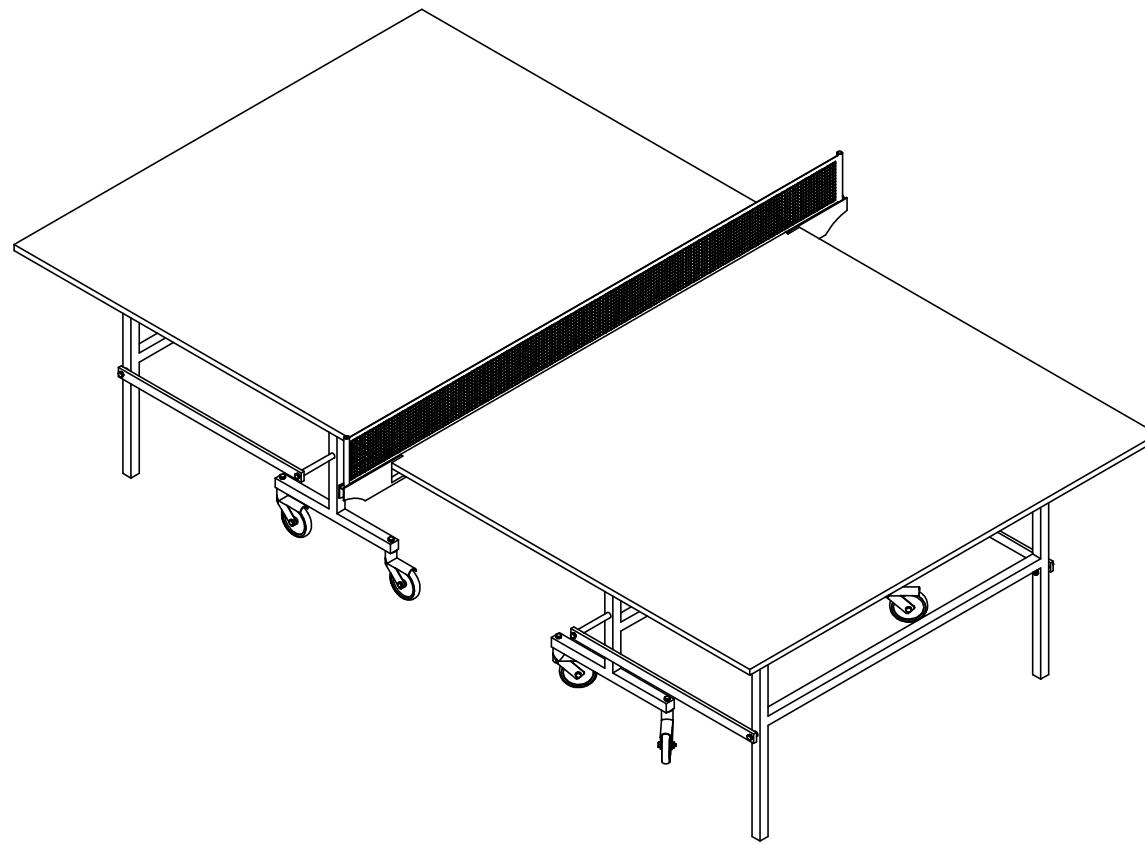
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APPLICATION		DO NOT SCALE DRAWING			

Ping Pong Table
 TITLE:
Full Table Solid Lines

SIZE	DWG. NO.	REV
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SCALE: 1:20	WEIGHT:	SHEET 1 OF 1

Jonathan Lam

Professor Germano

HSS1B

29 October 2018

Spending Strength and Bending Gender

The fundamental unit of the popular programming paradigm known as object-oriented programming is the object, an abstract representation of some real-world entity with both “state” and “behavior.” “State” or “data” members of the object define its attributes; “behavior” or “function” members define its actions. The classic example is a bicycle: every bicycle object is associated with descriptive data (brand, make, year, color) as well as actions (pedal, brake, change gear, use bell).

The classic bicycle example becomes confusing if the two types of members exchange roles. Perhaps it makes some sense that to pedal, to brake, to change gear, and to use a bell are valid attributes of a bike (i.e., these functions define a bicycle), but the switch from data members to function members is more unclear. What does it mean for make or color to be a function of a bicycle? A function member, like a data member, is still innate to an object—items are defined by their functional purpose—but also much more ephemeral.

The programming example is an analogy to the role of gender on the planet Winter in Ursula K. Le Guin’s science-fiction fantasy novel *The Left Hand of Darkness*. A person on Winter is not born with a binary gender, but are instead androgynous: only clearly exhibiting a (previously indeterminate) binary gender during kemmer (estrus). In Spanish, the difference between a woman in our world (terra) and theirs (Gethen or Winter) is the difference between

saying “soy una mujer” and “estoy una mujer”; namely, “I am a woman” versus “I am [in the state of] a woman,” the latter definitely absurd and incorrect in our understanding of gender. But to the Karhidians and Orgoreynians of Winter, gender is most surely a function of a person, temporarily defining their body and mind. The general absence of gender for the Gethenians is a result of the harsh natural circumstances, but it is balanced with the quasi-controllable gender-like functions of kemmer and dothe.

There is a clear biological difference between men and women on terra. Men are (generally) more able to lift heavier manual loads. Women are physically adapted to carry and tend for babies as all female mammals are. The societal roles of the two genders are deep parts of a person’s identity because of their physical definitions. While men are by no means confined to physical labor nor women to domestic, child-rearing activities, their biological function gives an undeniable advantage. This is the same idea as “comparative advantage” from an economic perspective: the term “refers to an economy's ability to produce goods and services at a lower opportunity cost than trade partners” (“Comparative Advantage”); less effort is put into achieving certain tasks by one gender or the other purely by natural reasons. Men and women become specialized, and society becomes streamlined (this is one merit of delegation, of not sharing everything).

This most objective, economic view might make the impression that permanent gender is a useful construct of society (as it is for all mammals and intelligent creatures, including the rest of the Ekumen), and that the loss or lack of gender as an inherent part of one’s identity for the Gethenians is perhaps a harmful mutation of random natural selection, as an investigator initially notes (Le Guin, 89). Gethenian androgynes, normally sexually neutral but able to express female

or male sexuality during kemmer, are perhaps even more confusing than hermaphrodites such as snails, for there is an uncertainty every time one goes into kemmer (at least biologically, without the use of gender-forcing drugs). In the former and the latter, there is the certainty of being one of two sexes, or of being both at once. In the latter two, there is more of an equality between the two roles, and if a humanoid, intelligent species of hermaphrodites did exist, the society they would exist in would likely be similar to one of the Gethenians. In either case, lack of the basic societal specialization between man and woman would make a hermaphroditic society similarly technologically slow-paced as Gethen.

But the people of Winter would still have their third, latent state that spans the majority of their lifetimes. A Gethenian is never certain which gender he will naturally assume during kemmer; he can only be certain that he *will* assume a gender, and that most of his life will be spent in some intermediate state between the two binary designations. A certainty of an uncertainty.

But this uncertainty of gender doesn't have a negative effect on the world—after all, they have no preconception of a world with binary genders. The Gethenians set up kemmerhouses to isolate the behavior from the rest of society. The confusion of sex resolves itself in kemmerhouses by shielding society's eyes from the kemmerers,

At the beginning of the novel, Estraven is—or rather, is characterized as by Genly as—a powerful man, “one of the most powerful men in the country … lord of a Domain and lord of the Kingdom, a mover of great events” (5). While Genly insists on using male pronouns for consistency, there is the strong sense of male-ness by the terran connotation of lords with men, and men with power. But during Genly’s rescue mission, Estraven becomes almost a couple with

Genly, resting between maternal and romantic figure. Genly, however, remains a man biologically (as dictated by nature) and in his mindset. Estraven's gender here is a response to his relationship with Genly.

Usually, the call, the invocation of such a response, would be another Gethenian going into kemmer, but Genly's pervertedness is a constant signal. Undoubtedly this makes many Gethenian feel very uncomfortable around him; for them, it is unnatural to sustain high levels of one gender or the other.

Nature's call is something natural and unavoidable. Unlike human males, who can avoid the pains of reproduction and can therefore safely assume long positions in office, all Gethenians are susceptible to the physical burden. King Argaven is no exception; his pregnancy, and the militarization of Karhide under the surrogate king, is a result of this natural responsibility.

There are, however, ways and reasons to meddle with sexual orientation. Drugs are used in Orgoreyn to force a specific gender, to effect kemmer, or to alleviate it; the latter two are much like sexual performance and birth control drugs in common use today. Gaum attempts to seduce Estraven in an attempt of political siding with the aid of such drugs (153). During a Handdarata foretelling ceremony, there is always a male pervert that keeps a kemmering Gethenian aroused throughout the ceremony. There is also a small proportion of the Gethenians who are perverts by hormone imbalances, so Genly's sexual situation is not totally alien (albeit looked down upon).

Gethenians are average in stature and strength in comparison to humans; Genly, an average male, is taller and stronger than they are. There is no equivalent to the constantly raised levels of testosterone that give men their strength.

In times of need, however, Gethenians trained by the Handdarata can push past the boundaries of typical human strength using “dothe” strength. Imagine being able to sustain superhero-level strength for up to a day—only to be balanced afterwards by a much longer rest period, or thangen. Like kemmer, the male-ness is made up for in short, intense bursts, this time of strength rather than manliness.

What purpose does this adaptation serve for the Gethenians? As the investigator noted, “burden and privilege are shared out pretty equally; everybody has the same risk to run or choice to make” (93), citing the burden of childbearing and the privilege of free males. She also notes the absence of rape and the planet-wide lack of division and war. This is based on the premise stated earlier that women are physically disadvantaged by their reproductive function and men advantaged without such a need, emphasizing that this is the single most important difference between men and women; eliminating this difference, in the investigator’s eyes, eliminates the great natural inequality of sex.

But there is another factor—and this too is noted by the investigator, but with respect to war—more grave than any other of Winter: namely, winter weather itself. Winter is a cold and unforgiving barrier. Efficiency and technical dominance do not matter in a land where the elements guard prisons and dictate travelling routes; rather, the goal is survival. Gethenians cannot afford to have half of the race carry the burden of reproduction; kemmer allows every individual to carry children, and thus has a higher capacity for reproduction rate. And men, while stronger than women, use much more energy and have a smaller percentage body fat, so they are worse-equipped to endure cold weather; a mixture between the two genders provides a balance between physical longevity and performance. If Gethen’s situation is considered in such a way,

their physical adaptations (which would be inefficient on a planet with better living conditions) become well-justified.

While Gethenians spend most of their time sexually latent and with average strength, kemmer and dothe are equally important. They are natural power-ups for use during rituals and emergencies. They are a way for Gethenians to semi-consciously control gender and strength, turning these aspects into functions of a person, a way for them to interact with each other using the construct of gender.

Differing physical circumstances define the role of gender in different societies societies. Our terran culture is like our sun, a red giant burning bright and fast, doomed to expand and wither in five billion years. The society on Winter is like that of a red dwarf, which can last ten trillion years. The dwarf star is cooler and dimmer, but there's still a warm fire within.

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Spending Strength and Bending Gender: Revisions to the First Draft

Cover Letter to the Second Draft

You (Prof. Germano) left a very interesting question at the end of my essay that seemed so fundamentally relevant to and absent in my essay: why, if this totally foreign system of androgyny had its benefits, natural selection (or practical societal norm) would not have led to some similar system elsewhere. Along with that was a note that the OOP analogy at the beginning was abandoned. This was really a nice combination (if intentional; if not then coincidence?) and helped establish another facet of the claim: that, while economical, the androgynous way of living does feel quite like programming (which clashes with many Terrans' love of free-form free-dom, and is only overpowered by a dire need to survive). This makes a more developed conclusion.

The paragraph in which Estraven was introduced was not set up well—there was no transition. In this draft, I tried to make a clear distinction between the previous talk of the nature of kemmer as an “active” function to also a “passive” function (i.e., response, reaction) that drives a large part of Gethenian culture. This also connects the idea of gender as a response (passive function) to the harsh climate more clearly to the central claim.

Unfortunately, I spent very little time on this revision because of a high volume of pre-Thanksgiving homework and midterms, so there were no substantial changes except the two mentioned above and marked grammatical fixes. Hopefully this version is a little more connected and interesting than the first draft.

Jonathan Lam

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HSS1B

14 November 2018

Spending Strength and Bending Gender

The fundamental unit of the popular programming paradigm known as object-oriented programming is the object, an abstract representation of some real-world entity with both “state” and “behavior.” “State” or “data” members of the object define its attributes; “behavior” or “function” members define its actions. The classic example is a bicycle: every bicycle object is associated with descriptive data (brand, make, year, color) as well as actions (pedal, brake, change gear, use bell).

The classic bicycle example becomes confusing if the two types of members exchange roles. Perhaps it makes some sense that to pedal, to brake, to change gear, and to use a bell are valid attributes of a bike (i.e., these functions define a bicycle), but the switch from data members to function members is more unclear. What does it mean for make or color to be a function of a bicycle? A function member, like a data member, is still innate to an object—items are defined by their functional purpose—but also much more ephemeral.

The programming example is an analogy to the role of gender on the planet Winter in Ursula K. Le Guin’s science-fiction fantasy novel *The Left Hand of Darkness*. A person on Winter is not born with a binary gender, but is instead androgynous: only clearly exhibiting a (previously indeterminate) binary gender during kemmer (estrus). In Spanish, the difference between a woman in our world (Terra) and theirs (Gethen or Winter) is the difference between

saying “soy una mujer” and “estoy una mujer”; namely, “I am a woman” versus “I am [in the state of] a woman,” the latter definitely absurd and incorrect in our understanding of gender. But to the Karhidians and Orgoreynians of Winter, gender is most surely a function of a person, temporarily defining their body and mind. The general absence of gender for the Gethenians is a result of the harsh natural circumstances, but it is balanced with the quasi-controllable gender-like functions of kemmer and dothe.

There is a clear biological difference between men and women on Terra. Men are (generally) more able to lift heavier manual loads. Women are physically adapted to carry and tend for babies as all female mammals are. The societal roles of the two genders are deep parts of a person’s identity because of their physical definitions. While men are by no means confined to physical labor nor women to domestic, child-rearing activities, their biological function gives an undeniable advantage. This is the same idea as “comparative advantage” from an economic perspective: the term “refers to an economy’s ability to produce goods and services at a lower opportunity cost than trade partners” (“Comparative Advantage”); less effort is put into achieving certain tasks by one gender or the other purely by natural reasons. Men and women become specialized, and society becomes streamlined (this is one merit of delegation, of not sharing everything).

This most objective, economic view might make the impression that permanent gender is a useful construct of society (as it is for all mammals and intelligent creatures, including the rest of the Ekumen), and that the loss or lack of gender as an inherent part of one’s identity for the Gethenians is perhaps a harmful mutation of random natural selection, as an investigator initially notes (Le Guin, 89). Gethenian androgynes, normally sexually neutral but able to express female

or male sexuality during kemmer, are perhaps even more confusing than hermaphrodites such as snails, for there is an uncertainty every time one goes into kemmer (at least biologically, without the use of gender-forcing drugs). In the former and the latter, there is the certainty of being one of two sexes, or of being both at once. In the latter two, there is more of an equality between the two roles, and if a humanoid, intelligent species of hermaphrodites did exist, the society they would exist in would likely be similar to one of the Gethenians. In either case, lack of the basic societal specialization between man and woman would make a hermaphroditic society similarly as technologically slow-paced as Gethen.

But the people of Winter would still have their third, latent state that spans most of their lifetimes. A Gethenian is never certain which gender he will naturally assume during kemmer; he can only be certain that he *will* assume a gender, and that most of his life will be spent in some intermediate state between the two binary designations. A certainty of an uncertainty.

But this uncertainty of gender doesn't have a negative effect on the world—after all, they have no preconception of a world with binary genders. The Gethenians set up kemmerhouses to isolate the behavior from the rest of society. The confusion of sex resolves itself in kemmerhouses by shielding society's eyes from the kemmerers.

But while gender is often an active interaction (i.e., going into kemmer with someone else), it affects society in a more powerful way *passively*. At the beginning of the novel, Estraven is—or rather, is characterized by Genly as—a powerful man, “one of the most powerful men in the country … lord of a Domain and lord of the Kingdom, a mover of great events” (5). While Genly insists on using male pronouns for consistency, there is the strong sense of male-ness by the Terran connotation of lords with men, and men with power. But during Genly’s rescue

mission, Estraven becomes Genly's partner, resting between maternal and romantic figure. He grows into a relationship, responding to Genly's dominating male-ness. Genly, however, remains a man biologically (as dictated by nature) and in his mindset.

Usually, the call, the invocation of such a response, would be another Gethenian going into kemmer, but Genly's "pervertedness" is a constant signal. Terrans have only the arrogant signal of one gender or another, and never listen to or for a response. Undoubtedly this makes many Gethenians feel very uncomfortable around him; it is unnatural for them to be able to sustain high levels of one gender or the other and to ignore the sexual needs of others.

Nature's call is something natural and unavoidable. Unlike human males, who can avoid the pains of reproduction and can therefore safely assume long positions in office, all Gethenians are susceptible to the physical burden. King Argaven is no exception; his pregnancy, and the militarization of Karhide under the surrogate king, is a result of this natural responsibility.

There are, however, ways and reasons to meddle with sexual orientation. Drugs are used in Orgoreyn to force a specific gender, to effect kemmer, or to alleviate it; the latter two are much like sexual performance and birth control drugs in common use today. Gaum attempts to seduce Estraven in an attempt of political siding with the aid of such drugs (153). During a Handdarata foretelling ceremony, there is always a male pervert that keeps a kemmering Gethenian aroused throughout the ceremony. There is also a small proportion of the Gethenians who are perverts as a result of natural hormonal imbalances, so Genly's sexual situation is not totally alien (albeit looked down upon).

Gethenians are average in stature and strength in comparison to humans, and the typical Gethenian is weaker than a Terran male like Genly. In times of need, however, Gethenians

trained by the Handdarata can push past the boundaries of typical human strength using “dothe” strength. Imagine being able to sustain superhero-level strength for up to a day—only to be balanced afterwards by a much longer rest period, or thangen. Like kemmer, the male-ness is made up for in short, intense bursts, this time of strength rather than manliness.

What purpose does this adaptation serve for the Gethenians? As the investigator noted, “burden and privilege are shared out pretty equally; everybody has the same risk to run or choice to make” (93), citing the burden of childbearing and the privilege of free males. She also notes the absence of rape and the planet-wide lack of division and war. This is based on the earlier objective premise that women are physically disadvantaged by their reproductive function and men advantaged without such a need, emphasizing that this is the single most important difference between men and women; eliminating this difference, in the investigator’s eyes, eliminates the great natural inequality of sex.

But there is another factor—and this too is noted by the investigator, but with respect to war—more grave than any other of Winter: namely, winter weather itself. Winter is a cold and unforgiving barrier. Efficiency and technical dominance do not matter in a land where the elements guard prisons and dictate travelling routes; rather, the goal is survival. Gethenians cannot afford to have half of the race carry the burden of reproduction; kemmer allows every individual to carry children, and thus has a higher capacity for reproduction rate. And men, while stronger than women, use much more energy and have a smaller percentage body fat, so they are worse-equipped to endure cold weather; a mixture between the two genders provides a balance between physical longevity and performance. If Gethen’s situation is considered in such a way,

their physical adaptations (which would be inefficient on a planet with better living conditions) become well-justified— gender is a passive function of winter as well as relationships.

While Gethenians spend most of their time sexually latent and with average strength, kemmer and dothe are equally important. They are natural power-ups for use during rituals and emergencies. They are a way for Gethenians to semi-consciously control gender and strength, turning these aspects into functions of a person, a way for them to interact with each other using the construct of gender.

Differing physical circumstances define the role of gender in different societies. A person is born with a hardwired gender, and all of the benefits and deficiencies associated with the gender are invariable. The society on Winter is like that of a red dwarf, which can last ten trillion years. People there are wired differently: gender is something that happens to a person, and the extremes of both sexes disappear. In the first model, differences, extremes, and perhaps more interesting solutions are programmed as surely as data members of programmatic objects; in the other, a conservative egalitarianism.

Our Terran culture is like our sun, a red giant burning bright and fast, doomed to expand and wither in five billion years. The dwarf star is cooler and dimmer, but there's still a warm fire within.

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HSS1B

3 October 2018

The Language Addict

How does it feel to speak before one learns to read and write? How does it feel to think before one learns to speak? It's easy to take language for granted after learning it, and remember the process of learning to speak and write as trivial. In William Shakespeare's play *The Tempest*, the interactions between characters at different stages of language learning give a perspective into how language evolves with a person in stages: from understanding the concept of language, to understanding speech, to understanding written language, at every stage forgetting the difficulty of the previous understanding.

In the play, Prospero is the most knowledgeable of his language. Next are the well-educated royalty from Italy and the advisor Gonzalo. Still young are Ferdinand and Miranda, and least advanced is Caliban. While it may seem that the characters are very diverse, the education of the entire cast is comparable because they are all aristocrats, or raised by aristocrats (as Prospero teaches Miranda language, and Miranda teaches Caliban language), so each person represents a different stage of the same education.

Caliban is a special case because Italian¹ is not his first language. It is unclear whether or not Caliban knows a "language" before Miranda's arrival and her lessons. The only other intelligent life Caliban could communicate with prior to the humans' arrival was Sycorax, and it is unknown if Caliban had been old enough to learn language by the time she died. Because of

1. Because the language spoken by the Milanese and Neapolitans is not specified, it will be assumed to be Italian. While it is likely that the royalty is educated in Latin and some of the dialogue take place in Latin, the distinction is irrelevant to the claim.

the ambiguity of Caliban's background, it is only safe to assume that Caliban did not have any *spoken* language recognizable to Prospero and Miranda before the arrival of the two—Caliban remarks that Prospero “[taught] [Caliban] how \ To name the bigger light, and how the less, \ That burn by day and night” (Shakespeare, I.II.334-6), confirming only that he was taught *names* to objects. While Prospero and Miranda believe that Caliban is stupid before they taught him and that he should be grateful for the education, there is no indication that he is new to the concept of language. Miranda similarly declares that she “Took pains to make [Caliban] speak, taught [him] each hour … when [he] didst not, savage, \ Know [his] own meaning, but would gabble like \ A thing most brutish. I endowed thy purposes \ With words that made them known” (Shakespeare, I.II.354-8). Both of these declarations agree that Caliban is taught how to *speak*: *spoken* words are imputed to objects like the sun and the moon to allow Caliban “know [his] own meaning.”

But it is likely that Caliban's prior gabbling was some form of language, especially if he was able to teach Prospero and Miranda. He must have had some system of communication in order to show Prospero and Miranda around the island before he was taught speech; it may have been this gabble-talk or some system of gestures. The OED defines language primarily as “a system of spoken or written communication used by a particular country, people, community, etc., typically consisting of words used within a regular grammatical and syntactic structure,” but also as “an unsystematic or informal means of communicating other than by the use of words, as gesture, facial expression, etc.; non-verbal communication.” Caliban's language likely fits the latter description, “unsystematic or informal” means of “non-verbal communication,” a language simpler than Italian, and one that does not register as a language to Prospero and Miranda. He curses, “The red plague rid you \ For learning me your language!” (I.II.364-5). The wording hints that there is a distinction between *your language* (i.e., Italian) and his own—Caliban

doesn't regret being taught language in general (in fact, he confesses previously that "and then I loved thee" (I.II.336) when he was first taught speech), but rather is most likely hostile for one of two reasons: having the Italian language be imposed on him when he already has a language, or being forced to learn to speak.

So despite Prospero and Miranda's berating of Caliban as a monster and a savage, Caliban is already aware and capable of the concept of language; he is only new to speech.

All the other humans starkly contrast against Caliban in that they are all fluent in Italian as a first language.

Of these shipwreck victims, Ferdinand, Stephano, and Trinculo are the less mature (in age and attitude) of the group. They all act surprised, unsurprisingly, when learning that the islanders speak their speech. Stephano's first reaction when hearing Caliban speak his own language is to present him as an exotic gift to an emperor—he sees Caliban's ability to speak Italian as a keepsake-like trait. Ferdinand's reaction when he first recovers Miranda is different: "My language? Heavens! \ I am the best of them that speak this speech" (I.II.429-30). To be surprised that somebody else speaks the same language is interesting, but to immediately boast with respect to his language ("speech") is a strange reaction. Of course, meeting a monster and meeting a beautiful maiden warrant different reactions, but in both cases the idea of language is simply a worthy attribute of a person. Caliban is a monster *that can speak Italian*, and thus he is emperor-gift-worthy; Ferdinand is the best of the people *who can speak Italian*, which qualifies him as a civilized man. This perspective of language holds it as not any more a skill or weapon or study any more than a property. These characters are comfortable with speech, and they view the basic understanding of language (that Caliban has) as an elementary fact of life.

Also interesting is that in Ferdinand's speech, the word "speech" is used as opposed to "language," as if the ability to speak is a skill inherent to language. Because Italian involves speech, the skill is taken for granted.

The second group of Italians comprise the Neapolitan king Alonso, his brother Sebastian, his advisor Gonzalo, and the false Milanese duke Antonio. The dialogue between the members of this group are highly rhetorical. Gonzalo jokes about ruling the island and Antonio persuades Sebastian to overthrow Alonso by projecting his view of the future on him— both speak in terms of hypotheticals. This contrasts with the language of the younger people, whose dialogue focuses often on simple information transfer (e.g., Ferdinand declaring his love for Miranda, and Caliban describing the nature of the island's sounds to Stephano and Trinculo). This more advanced discourse, also in the form of dialogue, is common in modern literary education as well.

Prospero is arguably the most intellectual of the cast. What sets him apart is that he is the only character infatuated with the written language as well as the spoken one, evident by his books. His magical power is a manifestation of his books, a metaphor for the fact that the ability to store language in writing is much more potent than the ability to simply relay it.

And then it collapses.

Caliban understands the fundamental use of language. Ferdinand takes for granted speech as the standard means for communication. Gonzalo speaks with reason and humor. Prospero has gone through all these stages and more: for, as Caliban plots with Stephano and Trinculo: "Remember \ first to possess [Prospero's] books; for without them \ he's but a sot, as I am, nor hath not \ one spirit to command" (III.II.90-93). Without his books (and without his magic), Prospero is powerless ("but a sot"): no shipwreck would have occurred and Caliban could still be master of the island; having books is Prospero's only advantage over Caliban ("not one spirit to

command’’). These books were also the cause for Prospero’s overthrow (too captivated was he by the liberal arts to lead), the cause of mourning on Ferdinand and Alonso’s behalf, and the cause of great confusion on the part of Caliban, the shipwrecked crew, and the king’s consort returning to Italy. These books are both the cause of the problem that leads to the plot of *The Tempest* and the catalysts for Prospero’s return to the throne.

This idea of obsession can be explored in terms of other long-term skills or hobbies, and finds a pretty direct parallel in the study of mathematics. The first step is to establish the fundamentals: arithmetic by counting fingers. Like Caliban before Miranda’s arrival, the idea of arithmetic is understood, even without a formal system to describe it. When math is taught in class, a sort of mathematical fluency is developed, and expressing basic expressions as a system of sums and differences is trivial; a person forgets even that math (like language) is an artificial construct, and it becomes taken for granted. If the student chooses to pursue it further, then the study of written literature (and the creation of written research) in the field gives access to knowledge spanning history and distance. But invest a life’s worth of careless, fanatic toil, and a Frankenstein is created.

Prospero becomes such a Frankenstein, mindlessly applying his magic. He and Miranda are ignorant to the fact that Caliban has a difficult time understanding speech, and Prospero is so focused on his study of books that he becomes oblivious to the emotions of others. The answer is mindfulness— when Prospero takes a moment to think about the effect his magic has on Gonzalo, he immediately relinquishes his magic. If Caliban thinks about the larger picture and how speech will advance his speech, his suffering will be mitigated. Time spent reflecting on and being satisfied with the pains one has taken to master language (in speech or writing) will keep language under control.

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The Language Addict: Revisions from the Initial Draft

Cover Letter to the Second Draft

On the day we submitted the essay (unknowingly as the first of two submissions), I went to a writing center appointment and discussed my draft. The writing center associate first asked me if I could state the topic and claim of my paper. I couldn't. Worse, it was difficult to find direct textual evidence of the thesis in each major paragraph: many of the thoughts are not explicitly tied back to the main idea. The claim the paper followed was therefore too windy, too loosely-followed, and too non-applicable to draw meaning from the text.

The major revision process involved simplifying the claim (in the form of a thesis) and creating more explicit links from each major subtopic to some part of the central idea. This leads to a more cohesive paper that is easier to follow, while maintaining the complexity of the argument. If asked about the claim again, I can more easily state that humans go through a natural progression of stages in language learning, advancing through stages slowly and subtly (and dangerously so). (This claim is written, more clearly now, in my thesis statement.)

The previous version also had a missing conclusion: I didn't take the time to come up with a thoughtful culmination of the claim, so it was essentially omitted in the first draft. I tried my best to explain what exactly "mindfulness" means in this situation, and what happens when one is not mindful (in terms of Caliban, Miranda, and Prospero).

Minor grammatical changes were made, and small parts of paragraphs were moved around to improve the paper's logical flow.

Jonathan Lam

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HSS1B

17 October 2018

The Language Addict

How does it feel to speak before one learns to read and write? How does it feel to think before one learns to speak? It's easy to take language for granted after learning it, and to perceive the learning processes of speaking and writing as trivial in retrospect. In William Shakespeare's play *The Tempest*, the interactions between characters at different stages of language learning give a perspective into how language evolves with a person in stages: from the mastery of the concept of language itself, to speech, and finally to writing. And this process happens slowly and subtly enough that the importance of either evolutionary phase (i.e., from concept to speech, or from speech to writing) is lost upon the learner.

In the play, Prospero is the most knowledgeable of his language. Next are the well-educated royalty from Italy and the advisor Gonzalo. Still young are Ferdinand and Miranda, and least advanced is Caliban. While it may seem that the characters are very diverse, the education of the entire cast is comparable because they are all aristocrats, or raised by aristocrats (as Prospero teaches Miranda language, and Miranda teaches Caliban language), so each person represents a different stage of the same education.

Caliban is a special case because Italian¹ is not his first language. It is unclear whether or not Caliban knows a "language" before Miranda's arrival and her lessons. The only other intelligent life Caliban could communicate with prior to the humans' arrival was Sycorax, and it is unknown if Caliban had been old enough to learn language by the time she died. Because of

the ambiguity of Caliban's background, it is only safe to assume that Caliban did not have any *spoken* language recognizable to Prospero and Miranda before the arrival of the two—Caliban remarks that Prospero “[taught] [Caliban] how \ To name the bigger light, and how the less, \ That burn by day and night” (1.2.334-336), confirming only that he was taught *names* to objects. While Prospero and Miranda believe that Caliban is stupid before they taught him and that he should be grateful for the education, there is no indication that he is new to the concept of language. Miranda similarly declares that she “Took pains to make [Caliban] speak, taught [him] each hour … when [he] didst not, savage, \ Know [his] own meaning, but would gabble like \ A thing most brutish. I endowed thy purposes \ With words that made them known” (1.2.354-358). Both of these declarations agree that Caliban is taught how to *speak*: *spoken* words are imputed to objects like the sun and the moon to allow Caliban “know [his] own meaning.” He makes the first transition.

The transition implies that Caliban already has a grasp of language prior to the humans' arrival. He was able to teach Prospero and Miranda about the island; his language may have been this gabble-talk or some system of gestures. The OED defines language primarily as “a system of spoken or written communication used by a particular country, people, community, etc., typically consisting of words used within a regular grammatical and syntactic structure,” but also as “an unsystematic or informal means of communicating other than by the use of words, as gesture, facial expression, etc.; non-verbal communication.” Caliban’s language likely fits the latter description, “unsystematic or informal” means of “non-verbal communication,” a language simpler than Italian, and one that does not register as a language to Prospero and Miranda. He curses, “The red plague rid you \ For learning me your language!” (1.2.364-365). The wording hints that there is a distinction between *your language* (i.e., Italian) and his own—Caliban

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So despite Prospero and Miranda's berating of Caliban as a monster and a savage, Caliban is already aware and capable of the concept of language; he is new only to speech. But he downplays the significance of his new ability, debasing it to frivolous cursing, even while he uses that speech to argue against Prospero and plot with Stephano and Trinculo.

All the other humans stand in contrast with Caliban in that they are all fluent in Italian as a first language, but most view language likewise unappreciatively.

Of the shipwreck victims, Ferdinand, Stephano, and Trinculo are the less mature (in age and attitude) of the group. They all act surprised, unsurprisingly, when learning that the islanders speak their speech. Stephano's first reaction when hearing Caliban speak his own language is to present him as an exotic gift to an emperor—he sees Caliban's ability to speak Italian as a keepsake-like trait. Ferdinand's reaction when he first recovers Miranda is different: "My language? Heavens! \ I am the best of them that speak this speech" (1.2.429-430). To be surprised that somebody else speaks the same language is interesting, but to immediately boast with respect to his language ("speech") is a strange reaction. Of course, meeting a monster and meeting a beautiful maiden warrant different reactions, but in both cases the idea of language is simply a worthy attribute of a person. Caliban is a monster *that can speak Italian*, and thus he is emperor-gift-worthy; Ferdinand is the best of the people *who can speak Italian*, which qualifies him as a civilized man. This perspective of language holds it as not any more a skill or weapon

or study any more than a property. These characters are comfortable with speech, and they view the basic understanding of language (that Caliban has) as an elementary fact of life.

The second group of Italians comprises the Neapolitan king Alonso, his brother Sebastian, his advisor Gonzalo, and the false Milanese duke Antonio. The dialogue between the members of this group are highly rhetorical. Gonzalo jokes about ruling the island and Antonio persuades Sebastian to overthrow Alonso by projecting his view of the future on him— both speak in hypotheticals. This contrasts with the language of the younger people, whose dialogue focuses often on simple information transfer (e.g., Ferdinand declaring his love for Miranda, and Caliban describing the nature of the island's sounds to Stephano and Trinculo).

In Ferdinand's words to Miranda, the word "speech" is used as opposed to "language"— as Italian involves speech, language and speech are considered the same skill. This is not an uncommon perspective, as virtually all human languages are verbal. The senior aristocrats might find greater use in dialogue as a result of their rhetorical ability, but they too are stuck without a bigger picture of the significance of being able to speak, and speak so easily and eloquently.

Prospero is arguably the most intellectual of the cast. What sets him apart is that he is the only character infatuated with the written language as well as the spoken one, evident by his books. His magical power is a manifestation of his books, a metaphor for the fact that the ability to store language in writing is much more potent than the ability to simply relay it.

And then it collapses.

Caliban understands the fundamental use of language. Ferdinand takes for granted speech as the standard means of communication. Gonzalo speaks with reason and humor. Prospero has gone through all these stages and more: for, as Caliban plots with Stephano and Trinculo: "Remember \ first to possess [Prospero's] books; for without them \ he's but a sot, as I am, nor

hath not \ one spirit to command" (3.2.90-93). Without his books (and without his magic), Prospero is powerless ("but a sot"): no shipwreck would have occurred and Caliban could still be master of the island; having books is Prospero's only advantage over Caliban ("not one spirit to command"). These books were also the cause for Prospero's overthrow (too captivated was he by the liberal arts to lead), the cause of mourning on Ferdinand and Alonso's behalf, and the cause of great confusion on the part of Caliban, the shipwrecked crew, and the king's consort returning to Italy. These books are both the cause of the problem that leads to the plot of *The Tempest* and the catalysts for Prospero's return to the throne.

This idea of obsession can be explored in terms of other long-term skills or hobbies, and finds a pretty direct parallel in the study of mathematics. The first step is to establish the fundamentals: arithmetic by counting fingers. Like Caliban before Miranda's arrival, the idea of arithmetic is understood, even without a formal system to describe it. When math is taught in class, a sort of mathematical fluency is developed, and expressing basic expressions as a system of sums and differences is trivial; a person forgets even that math (like language) is an artificial construct, and it becomes taken for granted. If the student chooses to pursue it further, then the study of written literature (and the creation of written research) in the field gives access to knowledge spanning history and distance. But invest a life's worth of careless, fanatic toil, and a Frankenstein is created. Prospero becomes such a Frankenstein.

There is no inherent evil in language (like power), but the abuse of it.

Prospero and Miranda are ignorant of the fact that Caliban did not previously know language and has a difficulty with eloquent speech. But when Stephano and Trinculo meet Caliban, they treat him like a human because he can talk; they haven't the same preconception of him as speech-less and monstrous. Prospero becomes so engrossed with his books that he

becomes oblivious to the emotions of others. His books (i.e., his magic, the ability to control two souls as slaves and manipulate an island-full of people) are not natural in the slightest— yet his conscience does not flinch.

The resolution is a step back, a step away. Had Caliban taken the time to realize the immense accomplishment of transitioning from a wordless world, he may realize that rhetoric can defend himself against and influence Prospero and Miranda, much as it influences Trinculo and Stephano. Had Miranda and Prospero realized Caliban's progress towards speech and intelligence, perhaps their relationship would be much improved. Had Prospero realized what disasters his studious zealousness would wreak— which, as mentioned before, precipitate much of the drama in the plot— he may have held back on his studies, taken time to rule Milan and care for his family, leading to a happier life without the mess of usurpation and sorcery.

Language is no small feat, however natural it may feel. Without an outside view, what feels natural (or normal, or right) may be far from it. A more mindful life is often the more content one.

Notes

1. Because the language spoken by the Milanese and Neapolitans is not specified, it will be assumed to be Italian. While it is likely that the royalty is educated in Latin and some of the dialogue take place in Latin, the distinction is irrelevant to the claim.

Works Cited

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Tough Love and a Tougher Life

Cover Letter to the Second Draft

The bulk of the revisions was spent on two tasks: covering logical gaps and extracting more information from quotes.

The former involved a lot of work with transitions. For example, the list on pages 4/5 (that you marked unclear) had to be prefixed with a simple declaration of the list's contents, and a brief explanation of how it ties into the claim. I tried to make very clear the direct relationship between being in a loving family and having the confidence to fight your own fights (as was in Helene's case), and vice versa (as was in Hannah's case); there was a little clarification on the difference between the modern (materialistic) and ancient (unconditional) definitions of love and which one Eva represented; and what it means to live a "normal" life. In the first draft, these ideas were all mentioned but never explicitly addressed, and I think having a little more precision in these definitions is important for my claim (because if they were more ambiguous, the claim would be less interesting).

I also tried to clarify the counter-argument that is near the end (that "tough love" can be beneficial, but not in small family units or for extended periods of time). I'm not sure if it is very clear that it is a counter-argument, or why it is important; it could use a little more revision if I had more time.

Lastly, I edited some of the quote interpretations. I added one quote and kept all of the ones previously embedded, but I was trying to make the significance of each more clear (especially the one about Helene's strong will and Sula's lack of pride).

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HSS1B

10 December 2018

Tough Love and a Tougher Life

“Mamma, did you ever love us?” ...

“No. I don’t reckon I did. Not the way you thinkin’.”

(Morrison 67)

The answer should be simple. But for Eva Peace to her daughter Hannah, it’s not so.

Minutes later, Eva jumps out of the third-story window at Hannah to save her life. But Hannah dies, dancing, twitching in flames, and in the last conversation she ever has her mother tells her she was not loved.

The question is loaded. What does it mean to love? In poorer communities of developing nations, love is something to be expected from family, and the basic parental functions of feeding, clothing, and sheltering are accepted as loving actions. But in the modern world, or even in the early twentieth century United States, the connotation of family love has changed dramatically: the stereotypical image is of a large family huddled around a central Christmas tree opening gifts with big grins on their faces or a birthday celebration at a fancy restaurant. The simpler idea of love is not as easily accepted: people want some kind of acknowledgement of love. In the dialogue from Toni Morrison’s novel *Sula*, Hannah asks her mother with the newer sense of the term in mind: she wonders if Eva ever played with or pampered her children. Eva reprimands her, saying that having them survive was enough. Eva doesn’t feel that she has been

unfair to her children. The two connotations of familial love conflict in the Peace family as Eva tries to get by with a purely survival notion, but her children have an appetite for material love; the result is that her children feel unwanted and actually pass away sooner because of the lack of tender love, contradicting her original goal to have her family persist.

Consider the Wright family. While Helene was abandoned by her parents at a young age, a childhood with her loving grandmother led her to grow up strong and proud. Helene is described as a woman who “lost only one battle—the pronunciation of her name” (18)— being raised with care allows her to live with the goal of raising a family that would *not* abandon its children. Her grandmother’s example gives her the confidence to fight “battles” for her own sake, such as when she endured mens’ glares after smiling at a white conductor.

Harmonious relationships prosper in the Wright family: Helene lives with her grandmother for a long time, and she herself stays in a loyal marriage with Wiley, despite his often being away. While Nel feels uncomfortable following the strict rules of her parents, she understands that it is for the best—she understands that she has to be as strong as her mother. Then Nel leads a comfortable relationship with Jude for a decade with three children. The example and image of stability begets another generation of stability.

The Peace family, on the other hand, lives pragmatically. Eva heads the household: everything else is a result of her doing. The three Deweys, for instance, are referred to by her collectively because of the similarity of their attitudes, and they indeed become a single practical entity. There was plenty of space in the house for Eva to live on the third floor on her managerial wheelchair, for newlyweds and drug addicts to rent rooms, and for Hannah to have

affairs in the pantry. The tangled house with additions built over the years exemplifies the behavior of the home: changes are made as necessary to accommodate the types of visitors the house might serve, much as the family absorbs different kinds of troubles. There's a lot of physical material there, a lot that Eva has shaped for her family to grow up around. But this is not the same as a parent consciously, deliberately buying an apartment and presenting it as a gift for their child. Rather, it's part of Eva's spontaneous personality to provide for her children's survival, without asking if her children wanted it or desiring for anything in return.

Unfortunately, to her children, these acts simply doesn't seem like love, and in the mess nor does it seem responsible.

After asking if Eva loves her, Hannah asks why Eva kills Plum— the answer is that Plum's life was wasting away, and that death was the quicker and more merciful end. It is possible that Hannah's subsequent fiery death was a coincidence, but it is more likely that grief or shock at Eva's apathy was the culprit.

To Eva, these two statements— not loving her children in the traditional way, and killing Plum— are attempts to save her children from worse deaths. She was willing to amputate her leg for money; she puts her body in mortal risk again to try to save Hannah from her untimely death. It is more difficult to justify burning Plum directly. He sees Eva as “the great wing of an eagle” (47) to release him from his misery, and perhaps the validity of her claim can be seen; but to the more empathic, such as Hannah, death is no rescue, and Eva pitilessly misguidedly murders based on the unimportant, material fact that Plum is a heroin addict who steals money.

The problem is that Eva attempts to save her children from a past reality. She was left to raise three children with no money and no supporting husband, so her life was focused on plain survival and monetary success. At her nadir, all she had was “\$1.65, five eggs, three beets, and no idea of what or how to feel. The children needed her; she needed money, and needed to get on with her life” (32). If Eva’s greatest ambitions could be summarized, it was to get as far as possible from encountering that lowly situation again. So she ran her leg over with a train for insurance money. She used the last of the lard to save Plum. She built a house and rented out rooms to make money. She became extremely efficient in order to survive and to make money. Just like Helene Wright wanted to let her children live in a loving household because of her abandonment, Eva Peace set her life on creating an environment where her children did not have to worry about basic survival nor about lacking money to live stably. But even after the children grow up, Eva directs the household mechanically, not displaying any affection for her children.

What does this mean for her family? How does it feel to be fed by a robot? Eva may have kept all of her children alive until adulthood, but then what? They don’t know how to take care of children, because they haven’t been loved (in the traditional way) for their whole life. And when they become adults and move on with their lives after being brought up by Eva, life is not what they were taught to expect. Hannah and Plum continue to live with Eva, and their lives parallel that of their mother. Sula, the only mentioned grandchild of Eva, also begins to inherit some of these traits from her mother. The characteristics of Eva’s narrow-minded will to survive become intergenerational:

1. Eva never held a long relationship; in fact, she had a child with only one person. Hannah only held a child with Rekus, and only flitting relationships with other men, as does Sula. Plum never had a relationship due to his drug addiction.
2. It can be inferred Hannah doesn't spend much of her time with Sula (as she spends much of her time with men), much the same way Eva didn't spend much taking care of her children. Sula and Plum do not spend time with children because they do not have any.
3. Eva had her leg run over by a train and collects rent in order to make money. There is no mention of how Hannah makes money in the novel. Plum is also known to steal money with which to buy heroin, and does not have a source of income.

The simple diagnosis is bad parenting passed down from mother to child. The only success was to keep their children alive to adulthood, the initial cause Eva's pragmatic-ness, but it was inherited. Plum, Pearl, and Hannah all have Eva's discipline but none of her plights: they are hardy enough to survive famine or lack of shelter, but incapable of what may be considered "ordinary living": properly caring for children, having a respectable paying job, and taking care of their own bodies. With the lack of confidence in ordinary activities, Plum, Hannah, and Sula all have a low self respect. For the faults that stem from Eva's single-minded focus to survive, there is only a contradictory weaker will to live.

By the end of the novel, Sula comes to the realization that "I like my own dirt ... I'm not proud" (142). With a steady job and children to take care of, Nel is a proud and independent woman, but Sula feels that her life is as important as dirt, and she falls ill as she gets sick and disillusioned with her unstable lifestyle.

It's not to say that tough love and practicality are completely unnecessary in harsh conditions. After all, in times of extended hardship in a community, the suffering is communal and society works to help each other out. It doesn't matter if it is "floods, white people, tuberculosis, famine, [or] ignorance" (90) or later, Sula's promiscuity, as the people of Medallion are known to endure; everyone works together and strong friendships are forged. In the small family unit, however, the stress may be too great. Eva survived a period of crisis when she was left with nothing, but the way she continued to live in crisis-mode wore down on the family. Just like physical overexertion or a mental breakdown, living constantly practically, without the niceties and gestures of "material love," can become disastrous.

In the end, Eva is the only Peace left in the peace-less family after the death of her children and Sula. She survived, and trained her children to survive—but at what cost?

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Working with Words

Word: “Perdition.” Context: “The dire spectacle of the wrack, which touched \ The very virtue of compassion in thee, \ I have with such provision in mine art \ So safely ordered that there is no soul -- \ No, not so much perdition as an hair \ Betid to any creature in the vessel \ Which thou heard’st cry, which thou saw’st sink.” (Shakespeare, 1.2.27-32)

- Merriam Webster dictionary definition:
 1. a) (archaic) : utter destruction; b) (obsolete) : loss
 2. a) : eternal damnation; b) : hell
- OED etymology: < Anglo-Norman perdiciun, perdicioun, perdission, Anglo-Norman and Middle French perdition loss, ruin, (in religion) damnation (c1100 in Old French as perdiciun ; French perdition) and its etymon post-classical Latin perdition-, perditio, ruin, loss, moral corruption, hell (Vetus Latina, Vulgate) < classical Latin perdit- , past participle stem of perdere to make away with, destroy, lose (< per- per- prefix + dare to give, put: see datum n.) + -iō -ion suffix1. Compare Old Occitan perdicio (a1150; Occitan perdicion), Catalan perdició (c1200), Spanish perdición (first half of the 13th cent.), Italian perdizione ruin (a1294–6), damnation (1305).
- OED definitions:
 1. a. The fact or condition of being destroyed or ruined; utter destruction, complete ruin.; b. Chiefly rhetorical. Loss; diminution; degradation. Obsolete.; c. A thing which causes destruction; the ruin of something. Obsolete. rare.
 2. Theology. The state of final spiritual ruin or damnation; the consignment of the unredeemed or wicked and impenitent soul to hell; the fate of those in hell; eternal death.; b. The place of destruction or damnation; hell.; c. son of perdition n. an

