Experiment 3
Statistical Evaluation of Acid-Base Indicators[1]

Key Experimental Concepts: Simple titrations and variability of endpoints
Analysis Goals: More advanced statistics, working with large data sets.
Report Goals: Write a good **results/discussion** for the results obtained.

Introduction

In any type of titration (acid-base, oxidation-reduction, etc.), the **equivalence point** is the point at which the quantity of the titrant is exactly sufficient for a stoichiometric reaction with the analyte. In other words, if you titrate 1.000 mol of HCl with NaOH, the equivalence point occurs at exactly 1.000 mol of NaOH added. In an ideal world, we would perform a titration to the equivalence point and know the exact quantity of the analyte.

In the case of our HCl-NaOH titration, how do we know when we have reached the equivalence point? Will the solution change color? Will there be any physically observable phenomenon that will indicate the equivalence point of this titration? Our HCl-NaOH solution will remain colorless, but the concentration of H_3O^+ will change throughout the titration. We can monitor this change in pH by a pH meter or an acid-base indicator, such as phenolphthalein. The color change from colorless to pink marks the **end point** of the titration. The end point is the point in a titration where there is a sudden change in a physical property such as color, and the end point can be used to measure the equivalence point. Phenolphthalein is an indicator that marks the end point of a titration with a strong acid and strong base.

However, each indicator undergoes a color change over its own particular pH region as seen in **Figure 1**. Therefore each indicator can yield a different result for each titration.

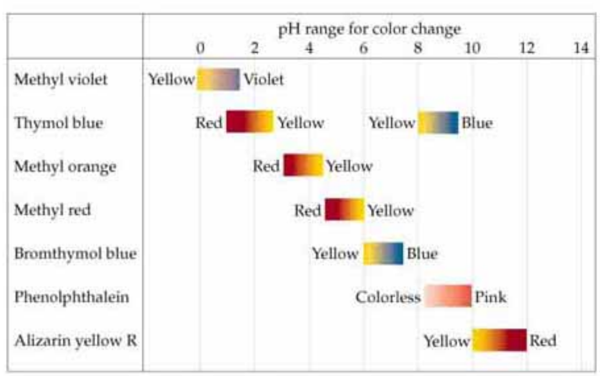

Figure 1: pH range for some common pH indicators

Primary Standards
In order to be as accurate as possible during a titration, chemists usually first determine the concentration of the titrant (the hydrochloric acid, in this case) by calibrating it with a primary standard. For a substance to be a primary standard, the following criteria should be met.

[1] D.T. Harvey, *J. Chem.Ed*. **1991**, *68*, 329; D.C. Harris, "Exploring Chemical Analysis", 1996, W.H. Freeman and Company, New York, pg. 386.

A primary standard substance should be:

•Available in very pure form
•Reasonably soluble
•Stable in the pure form and in solution
•Nonhygroscopic (doesn't pick up water from the air) and easily dried
•A compound with a reasonably high formula weigh

In the this experiment Tris(hydroxymethyl)aminomethane ("tris"), a weak base, will be used as the primary standard to determine the precise concentration of the HCl (aq) solution. Since Tris is a weak base it will alter the shape of the pH curve as seen in Figure 2 and will demonstrate the importance of picking the correct pH indicator for the titration.

Using the concepts of mean, standard deviation, grubs test, t-test and f-test, this experiment will explore the proper indicators for a titration of a known amount of the base Tris(hydroxymethyl)aminomethane ("tris") with an unknown concentration of HCl. The goals of this experiment are to:

- determine the concentration of the HCl, and
- gain confidence in the use of the analytical balance and buret
- use statistical methods to compare indicators
- apply automation to a titration
- compare the accuracy of the results of the various indicators for locating the end point of the following titration:

$$(HOCH_2)_3CNH_2\ (aq) + H_3O^+\ (aq) \rightarrow (HOCH_2)_3CNH_3^+\ (aq) + H_2O\ (l)$$

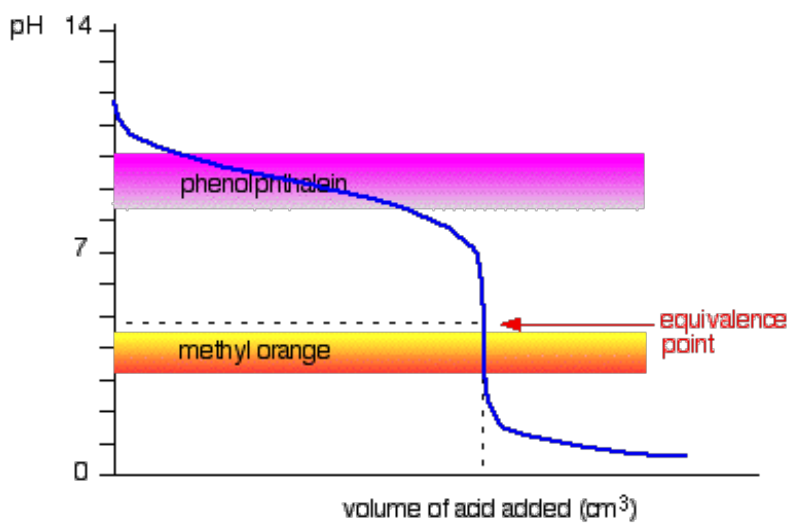

Figure 2: Generic Titration Curve of a weak base

- Apply what you learn to choosing the correct indicator for any acid/base

Reagents

Approximately 0.1 M HCl (approx. 500 mL)
Tris (approx. 4 g per student)
Indicators

Bromothymol Blue	Phenolphthalein
Methyl Red	Methyl Orange
Bromocresol Green	Thymolphthalein

Procedure

Prelab in your notebook before you arrive. These questions are posted in your ELN.

1) Calculate the mass of Tris required to react with 7.5 mL of 0.10 M HCl.

2) Insert the equations from your textbook that you will use for the comparing replicate measurements in two different sets of data. (Hint: Make sure you've read the sections in Chapter 4 about f-test and t-tests)

3) A trainee in a medical lab will be released to work on her own if her results agree with the results obtained by an experienced worker (at the 95% confidence interval). Use the F and T test equations to determine whether the trainee can work alone, based on the data below:

	Trainee	Experienced Worker
average	14.6 mg/dL	13.95 mg/dL
standard deviation	0.05 mg/dL	0.4 mg/dL
number of samples	6	5

4) Write out the series of decisions you needed to make in question 3, in the format "if ________ , then __________". (For example, I decide whether to drink hot coffee or iced coffee based on the current weather. My decision statement in "if-then" format would be something like: "If it is less than 88 F outside, then I will make hot coffee". I might flip it the other way and say "If it is more than 88 F outside, then I will make iced coffee". Note the outcome is the same, even if I phrased the decision differently, as long as there are only two choices!)

When lab begins:
Part 1: Using Indicators to find an End Point

5) Wash your Class A buret thoroughly with standardized 0.1 M HCl. Discard the washings. Make sure that each wash "wets" the entire length of the buret. Fill the buret near the 0 mL mark. Allow the buret to settle for a minute, and read the initial volume to the nearest 0.002 mL.

6) Weigh out the number of grams of Tris (but record weight to full precision) predicted in the prelab and place in a 125 mL flask. Add ~25 mL of water and be sure that all the Tris dissolves. If it doesn't add more water to make sure it dissolves.

7) Add 2-4 drops of indicator to the solution. Carry out a rapid titration to find the approximate end point of the titration. (This step is optional, you may go straight to performing three careful titrations.) **Be sure to record the indicator used and color before and after each change**! Refer

to Table 11.3 on page 249 in *Harris* for color changes of each indicator. Record the final volume of HCl, and calculate the titration volume.

8) If necessary to continue with the next titration, refill the buret near the 0 mL mark and make a reading of the initial volume of HCl. Repeat the titration, but use one drop at a time *near* the end point found in the rapid titration. When you are *very near* the end point, "cut" fractional drops. To do this, carefully suspend a fraction of a drop from the buret tip and touch it to the inside wall of the flask. Tilt the flask so that the bulk of the solution overtakes the droplet and mix the solution. Record the final volume of HCl added to the nearest 0.02 mL.

9) Repeat the titration to obtain at least three precise measurements of the concentration of HCl.

10) Calculate the average molarity of the HCl for each titration.

11) Repeat steps three through six with a different indicator.

Reporting results: Use the Grubbs-test (p.80 in text book) to decide whether any of your individual results should be discarded. Show the work in the lab notebook. Report the retained values, their mean, their standard deviation, percent relative standard deviation and 95% confidence interval.

Report your results in a table similar to the following:

Table 1: Individual Titration Summary

Trial	Mass of Tris from balance (g)	Volume of HCl (mL)	Initial Color	Final Color	Calculated molarity of HCl (M)
1					
2					
3					
4, etc.					
					Average =
					Standard deviation =
					Relative standard deviation =
					95% CI =

12) Record your raw data in the class excel document at the front of the room. Do not include any values you may have Grubbs tested out.

Part 2: pH meter and End Point – with a lab partner

Instructions for using Hanna auto-titrator for acid-base titrations:

1. Weigh out the calculated number of grams of TRIS of your (or your partner's) from the prelab, record mass, and transfer to a 250 mL beaker. Add enough water to dissolve the solid and to be able to read pH (to cover the tip of the pH sensor)
2. Collect data:
   a. Place tubing into your HCl solution
   b. Carefully immerse glass electrode, stir bar and temperature probe in your sample solution all the way to the electrode junction
   c. Hit the START button. The instrument will begin dosing.
   d. Hit bottom tab labeled "view curve"
   e. BEEP indicates dosage is complete when the curve reaches a preset pH (check with instructor).
   f. Ignore "endpoint volume" announced by the instrument. Only use data from the curve generated.
   g. After a titrations ends (how will you know?), export your data:
      i. Make sure your USB drive is plugged in to the instrument.
      ii. From the main screen, press GENERAL OPTIONS
      iii. Use the arrow keys to highlight Save Files to USB Storage Device
      iv. Press SELECT, and the list of files will appear.
      v. Use the left and right arrow keys to select the file type: "report files"
      vi. Highlight the name of the report file to be transferred (probably the most recent report file) and press COPY FILE
      vii. Transferring a report will automatically transfer the corresponding log file and titration graph. Press ESCAPE twice to return to the main screen
      i. Process data: In excel, plot the titration curve pH vs volume of HCl. In calculations (results and analysis), determine the equivalence point of the volume of the titration and calculate the molarity of the HC

Analysis and Results (lab notebook): Be sure that each table and figure/table has narrative introducing it and narrative tying it back to the goal of the experiment.

Pooled results and Analysis:

The class data for all of the indicators will be made available on Blackboard. Analyze this data for the mean concentration of HCl for each indicator, the standard deviation, the relative standard deviation and 95% CI.

Table 2 : Pooled Molarity Results

Indicator	# of measurements (n)	# of students (S)	Mean HCl molarity $\bar{x}$ (M)	s_x (M)$_b$	RSD (%) $s_x/\bar{x}$	95% CI
BB						
MR						
BG						
MO						
P						
Th						

a. Computed from all values that were not discarded by the Grubbs test
b. s_x= standard deviation of all n measurements (degrees of freedom = n-1)

1) Calculations and presentation of your data for each indicator (Table 1).
2) The pooled class data and statistics (Table 2).
3) T-test and F-test calculations for most similar molarities in Table 2. Use the F-test first to determine if the data set is a "variant" or "Non-variant" set of data. Then use the t-test to determine if these values are significantly different to 95% confidence levels. Be sure to use the appropriate t-test (you could use 4-8a and 4-9a if non-variant and 4-9b and 4-10b if the data set is variant) based on your F-test results. Be sure to include sample calculations. State all F-table, t-table, and DOF values used.
4) T-test and F-test calculations for most different molarities in Table 2, same as above.
5) Properly labeled titration curve and other plots used to determine end point with calculations to support the value of the molarity of HCl from the *equivalence point* curve.
6) Remember that any tables/graphs must have proper formatting (titles and captions)

Posrt-lab Discussion questions – To be addressed in the ELN

1) Address the following questions: Based on the results in Table 2, discuss the validity of pooling similar indicator results. State your conclusions regarding the indicators that give the most and least accurate results. Support your evaluation with T-test and F-test values. Refer back to Summary Tables in the results section. (Comparing means case #2 chapter 4))

2) Compare the results for the two most similar indicators to the molarity of HCl determined from the equivalence point on the pH curve from auto-titration. State and support your conclusions with the indicators 95% CI to see if it overlaps with the

equivalence point of the titration curve as the "true" molarity of HCl. (Comparing means case #1 chapter 4)

3) Discuss the significance of determining the molarity of an acid using the end point versus the equivalence point. Use results to support your position.

4) Discuss the importance of choosing the **appropriate** indicator in an acid-base titration. Use results to support your position.