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

Key Experimental Concepts: Simple titrations and variability of endpoints, titration curves
Analysis Goals: Continue to apply *F* and *t*-test statistics, work with large data sets.

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 sensor or an acid-base indicator, such as phenolphthalein. For phenolphthalein, the color change from colorless to pink marks the titration **end point**. The end point is the point in a titration where there is a sudden change in a physical property such as color or pH, and the end point can be used to measure the equivalence point. Phenolphthalein is an indicator that works well for marking 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, depending on how the pH at the equivalence point matches up with these color change pH ranges.

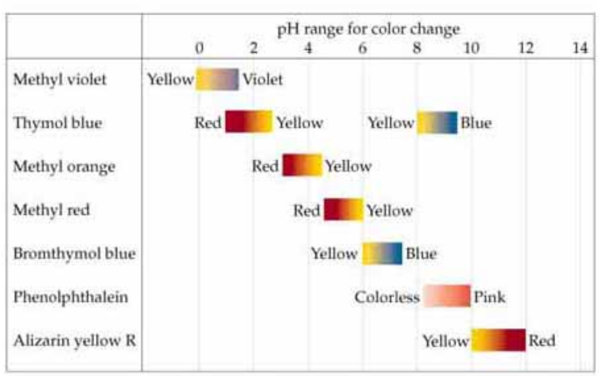


Figure 1: pH range for some common pH indicators

[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.

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.

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.

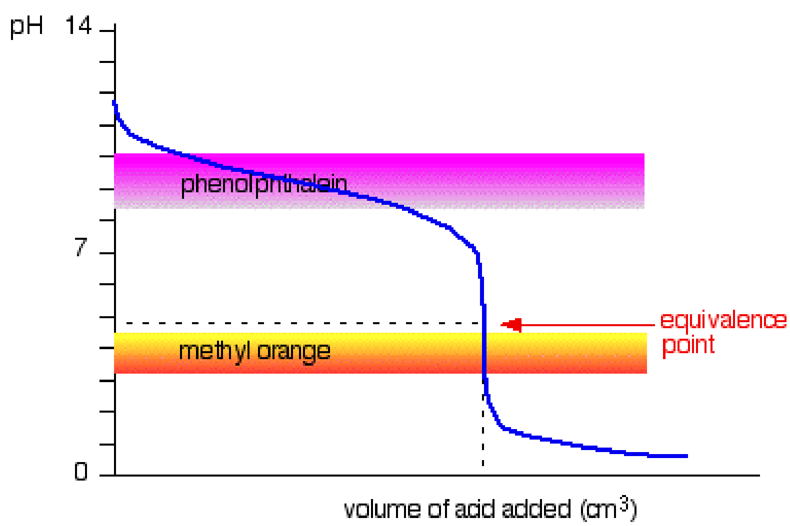


Figure 2: Generic Titration Curve of a weak base

Using appropriate statistical tools (mean, standard deviation, Grubbs test, *t*-test and *F*-test), in this experiment you'll 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:

- Accurately determine the HCl concentration, 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 reaction:

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

- 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

Prelab *to be completed in your ELN by 11:59 pm the night before the lab.*
(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) Calculate the pH at the equivalence point described above, assuming that the Tris was dissolved in water to make a 25 mL solution. (HINT: It's not 7.00.)

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 *F*- and *t*-tests to determine whether the trainee can work independently, based on the data below:

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

Remember that you can use your Python code for these calculations. If you choose to do this, show work by uploading a Jupyter notebook into the ELN pre-lab document.

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 tea or iced tea based on the current weather. My decision statement in "if-then" format would be something like: "If it is less than 75 F outside, then I will make hot tea". I might flip it the other way and say "If it is more than 75 F outside, then I will make iced tea". Note the outcome is the same, even if I phrased the decision differently, as long as there are only two choices!)

5) Polyprotic Titration Curves

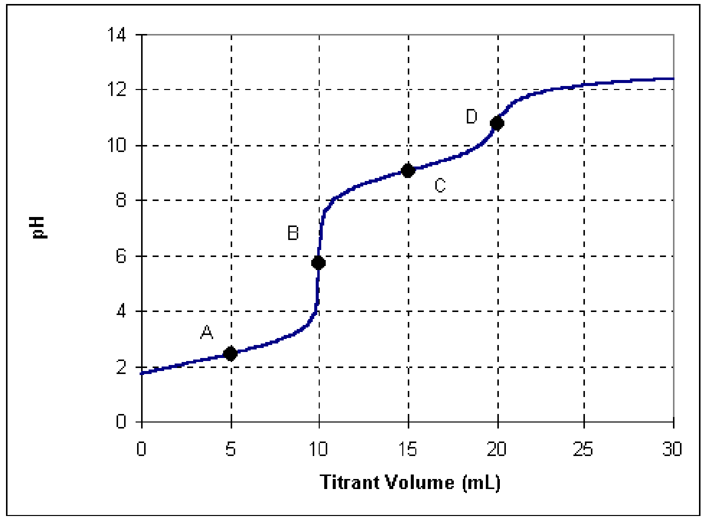
The amino acid, alanine ($C_3H_7NO_2$), is diprotic with a pK_{a1}=2.34 and pK_{a2}=9.87. In this problem, 89.1 mg of this amino acid is titrated with 0.1 M NaOH titrant. The titration curve is shown below. (Note: For parts b - d, the answer is NOT gained by eyeballing the number from the graph!)

a) Where is the first equivalence point?

b) Describe, in words, how you would calculate the theoretical pH at the first equivalence point:

c) What should the pH at point A be and why?

d) What should the pH at point C be and why?



6) Prepare your *Data & Obs* section in your ELN.

Procedure

Part 1: Using Indicators to find an End Point

7) Wash your Class A buret thoroughly with standardized 0.1 M HCl. (This is the approximate concentration – you want to find the exact concentration!) Discard the washings. Make sure that each wash "wets" the entire length of the buret. Fill the buret near (but not at) the 0 mL mark. Allow the buret to settle for a minute, and read the initial volume **to the nearest 0.01 mL**. The initial reading should NEVER be 0.00 mL.

8) Weigh out approximately the number of grams of Tris predicted in the prelab (but record weight to full precision) 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.

9) 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.

10) 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 as you approach the end point found in the rapid titration. When you are *very near* the end point, try "cutting" 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 0.01 mL.

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

12) Calculate the molarity of the HCl based on each titration. Include a sample calculation in your ELN Results & Analysis section. Looking at your calculated HCl values, if you have what appears to be an outlier, repeat the titration a 4^{th} time so you have enough data to do a Grubbs test. (If you have recorded an observation that shows you missed the endpoint, however, you may discard data without having to do a Grubbs test – but you'll still need that additional titration!)

13) Repeat steps 8 through 12 with a different indicator.

Reporting results: Use a Grubbs test (or previously recorded observation) to decide whether any of your individual results should be discarded. Show this work in the ELN. Report the retained values, their mean, their standard deviation, percent relative standard deviation and 95% confidence interval.
Report your results in a table in your ELN. The following table has already been added to the Results & Analysis section for you to modify:

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 =

14) Copy your calculated HCl concentrations for each *good* trial into the class GoogleSheet so that we can create a large dataset. Do not include any values you have eliminated via recorded observations or Grubbs tests.

Part 2: pH meter Autotitrations – with a lab partner

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

1. Weigh out approximately the grams of TRIS calculated in the prelab, record the precise mass (Data & Obs), 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). Bring this beaker, extra water, and your HCl solution to SCST 495 when it is your turn to use the autotitrator.
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. Add extra water if necessary.

c. Hit the START button. The instrument will begin dosing.
d. Press 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. We'll instead use data from the titration curve generated by the instrument.
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 (should be 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
   viii. Process data: In Python / Jupyter notebook, read in the datafile and use code copied from last week's PythonLab 1 to plot the titration curve pH vs volume of HCl. Use the derivative and Gran plot methods to determine the endpoint volume of the titration. Calculate the molarity of the HCl using the endpoints determined by each method.

Analysis and Results (in ELN): Be sure that each table and figure 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. You can organize the results of these calculations in your ELN using a table like the following:

Table 2 : Pooled Molarity Results

Indicator	# of measurements (n)	# of students (S)	Mean[a] 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) Present example calculations and a summary of your data for each indicator (Table 1).
2) Include the pooled class data and statistics (Table 2).
3) Do *F*-test and *t*-test calculations for the two indicators with the most similar HCl molarities in Table 2. Use the *F*-test first to determine if the data sets have different standard deviations. Then use the appropriate *t*-test to determine if the mean values are significantly different at the 95% confidence level. Be sure to include sample calculations. State all F-calc, F-table, t-calc, t-table, and DOF values used.
4) Repeat *F*-test and *t*-test calculations for two indicators the most different HCL molarities in Table 2.
5) Include properly labeled autotitrator titration curve and other plots used to determine end point with calculations to support the value of the molarity of HCl.
6) Remember that any tables/graphs must have proper formatting (titles and captions)

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

Address the following questions:

1) Based on the results in Table 2, is it valid to say that certain indicators gave the same results? Support your evaluation with *t*-test and *F*-test values.

2) Which indicators gave the least accurate results?

3) Discuss the strategies you used to determine the endpoint in the autotitrator data. Which do you think was most effective?

4) Compare the results of the two most similar indicators to the molarity of HCl determined from the autotitrator. Are the differences significant? Support your answers using the 95% CIs calculated for both indicators to see if they overlap with the autotitrator results.

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