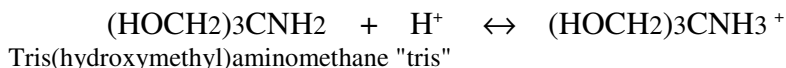


CHEM 241L Expt. 5: Statistical Evaluation of Acid-Base Indicators

(Adapted from D.C. Harris, *Quantitative Chemical Analysis*. 8th ed.
Freeman and Co. New York, 2011 based on I. D. T. Harvey, *J. Chem. Ed.* **1991**, 68, 329)

This experiment introduces you to the use of indicators and to the statistical concepts of mean, standard deviation, Grubbs test, and t test. You will compare the accuracy of different indicators in locating the end point in the titration of the base "tris" with hydrochloric acid:



REAGENTS

~0.1 M HCl: Each student needs ~500 mL of unstandardized solution, all from a single batch that will be analyzed by the whole class.

Tris: Solid, primary standard powder should be available (~4 g/student).

Indicators: Bromothymol blue (BB), methyl red (MR), bromocresol green (BG), and methyl orange (MO) should be available in dropper bottles. See Table 12-4 in the textbook for their preparation.

Color changes to use for the titration of *tris* with HCl are

BB: blue (pH 7.6) to yellow (pH 6.0) (end point is disappearance of green)

MR: yellow (pH 6.0) to red (pH 4.8) (end point is disappearance of orange)

BG: blue (pH 5.4) to yellow (pH 3.8) (end point is green)

MO: yellow (pH 4.4) to red (pH 3.1) (end point is first appearance of orange)

PROCEDURE

Each student should carry out the following procedure with *one* of the indicators. Different students should be assigned different indicators so that at least four students evaluate each of the indicators.

1. Calculate the molecular mass of *tris* and the mass required to react with 35 mL of 0.10 M HCl. Weigh this much *tris* into a 125-mL flask.
2. It is good practice to rinse a buret with a new solution to wash away traces of previous reagents. Wash your 50-mL buret with three 10-mL portions of 0.1 M HCl and discard the washings. Tilt and rotate the buret so that the liquid washes the walls, and drain the liquid through the stopcock. Then fill the buret with 0.1 M HCl to near the 0-mL mark, allow a minute for the liquid to settle, and record the reading to the nearest 0.01 mL.
3. The first titration will be rapid, to allow you to find the approximate end point of the titration. Add ~20 mL of HCl from the buret to the flask and swirl to dissolve the tris. Add 2–4 drops of indicator and titrate with ~1-mL aliquots of HCl to find the end point.

From the first titration, calculate how much *tris* is required to cause each succeeding titration to require 35–40 mL of HCl. Weigh this much *tris* into a clean flask.

4. Refill your buret to near 0 mL and record the reading. Repeat the titration in Step 3, but use 1 drop at a time near the end point. When you are very near the end point, use less than a drop at a time. *To do this, carefully suspend a fraction of a drop from the buret tip and touch it to the inside wall of the flask. Carefully tilt the flask so that the bulk solution overtakes the droplet and then swirl the flask to mix the solution.*
5. Record the total volume of HCl required to reach the end point to the nearest 0.01 mL. Calculate the molality of HCl.
6. Repeat the titration to obtain at least six accurate measurements of the HCl molarity.
7. Use the Grubbs test (see lecture notes) to decide whether any results should be discarded. Report your retained values, their mean, their standard deviation, and the % RSD.

DATA ANALYSIS – Expt. 5 Statistical Analysis of ...Acid-Base Indicators

(1) Pool the data from your class to fill in Table 1, which shows two possible results.

The quantity s_x is the standard deviation of all results reported by many students.

The pooled standard deviation, s_p , is derived from the standard deviations reported by each student. NOTE: If two students see the end point differently, each result might be very reproducible, but their reported molarities will be different. Together, they will generate a large value of s_x (because their results are so different), but a small value of s_p (because each one was reproducible).

(2) *F-test for equal variances.* To figure out which equation to use for your t-test (in the next step), you have to determine first if the variances (squared standard deviation, S^2) of the two sets of data you are comparing are “equal” or not significantly different using the F-test.

- From Table 1 data, select the pair of indicators giving average HCl molarities that are farthest apart.
- Calculate the variance, s^2 , for each set of selected indicator. Use s_x for s . Assign s_1^2 for the set of data with a higher standard deviation.
- Determine $F_{\text{calculated}}$ using the equation 4-12 from your text:

$$F_{\text{calculated}} = \frac{s_1^2}{s_2^2} \quad (4-12) \quad \text{where } s_1 > s_2$$

- Determine the degrees of freedom, n_1-1 and n_2-1 , for each set of selected data. Note that n_1 is the number of measurements for the set of data with the larger standard deviation, s_1 .
- Use the F table (attached) to determine F_{table} for n_1-1 and n_2-1 degrees of freedom.
- If $F_{\text{calculated}} < F_{\text{table}}$, the two variances are equal. Use Equations 4-8 and 4-9 for your t-test. See step 3 of Data Analysis.
- If $F_{\text{calculated}} > F_{\text{table}}$, the two variances are different. Use Equation 4-8a for your t-test.

(3) *t-test.* Using the data for the selected pair of indicators above, you will use the t-test to determine if the mean HCl molarities from these two sets of data are significantly different from each other at the 95% confidence level.

To be used if $F_{\text{calculated}} < F_{\text{table}}$:

For two sets of data consisting of n_1 and n_2 measurements (with averages \bar{x}_1 and \bar{x}_2), we calculate a value of t with the formula

$$t_{\text{calculated}} = \frac{|\bar{x}_1 - \bar{x}_2|}{s_{\text{pooled}}} \sqrt{\frac{n_1 n_2}{n_1 + n_2}} \quad (4-8)$$

where $|\bar{x}_1 - \bar{x}_2|$ is the absolute value of the difference (a positive number) and s_{pooled} is a *pooled* standard deviation making use of both sets of data:

$$s_{\text{pooled}} = \sqrt{\frac{\sum_{\text{set 1}} (x_i - \bar{x}_1)^2 + \sum_{\text{set 2}} (x_j - \bar{x}_2)^2}{n_1 + n_2 - 2}} = \sqrt{\frac{s_1^2(n_1 - 1) + s_2^2(n_2 - 1)}{n_1 + n_2 - 2}} \quad (4-9)$$

$t_{\text{calculated}}$ from Equation 4-8 is compared with t in Table 4-2 for $n_1 + n_2 - 2$ degrees of freedom. If $t_{\text{calculated}}$ is greater than t_{table} at the 95% confidence level, the two results are considered to be different. There is less than a 5% chance that the two sets of data were drawn from populations with the same population mean.

To be used if $F_{\text{calculated}} > F_{\text{table}}$:

$$t_{\text{calculated}} = \frac{|\bar{x}_1 - \bar{x}_2|}{\sqrt{s_1^2/n_1 + s_2^2/n_2}} \quad (4-8a)$$

Compare your $t_{\text{calculated}}$ with t_{table} using Table 4-2 (attached) for $n_1 + n_2 - 2$ degrees of freedom.

(4) Form your conclusion based on t-test

If $t_{\text{calculated}} > t_{\text{table}}$ the two means (molarity of HCl) are significantly different at the 95 % confidence level. If $t_{\text{calculated}} < t_{\text{table}}$, then the two means are the same.

(5) Select the pair of indicators giving the second most different molarities and use the F test and the t test again to see whether or not this second pair of results is significantly different. State your conclusion.

Table 1. Pooled data

Indicator	Number of measurements	Number of students	Mean HCl molarity (M) ^a		Relative standard deviation (%)	
	(<i>n</i>)	(<i>S</i>)	(\bar{x})	s_x (M) ^b	$100 s_x / \bar{x}$	s_p (M) ^c
BB	28	5	0.095 65	0.002 25	2.35	0.001 09
MR						
BG	29	4	0.086 41	0.001 13	1.31	0.000 99
MO						

Grubbs test.

- Computed from all values that were not discarded with the t -test.
- s_x = standard deviation of all n measurements (degrees of freedom = $n - 1$)
- s_p = pooled standard deviation for S students (degrees of freedom = $n - S$). Computed with the equation

$$s_p = \sqrt{\frac{s_1^2(n_1-1) + s_2^2(n_2-1) + s_3^2(n_3-1) + \dots}{n-S}}$$

where there is one term in the numerator for each student using that indicator.

Note: If your calculated degrees of freedom does not have a specified value in Table 4-2 (e.g. $n_1 + n_2 - 2 = 22$ does not have an entry), you have to extrapolate to get an estimate of t_{table} .

Degrees of freedom	Confidence level (%)					
	50	90	95	98	99	99.5
1	1.000	6.314	12.706	31.821	63.657	127.32
2	0.816	2.920	4.303	6.965	9.925	14.089
3	0.765	2.353	3.182	4.541	5.841	7.453
4	0.741	2.132	2.776	3.747	4.604	5.598
5	0.727	2.015	2.571	3.365	4.032	4.773
6	0.718	1.943	2.447	3.143	3.707	4.317
7	0.711	1.895	2.365	2.998	3.500	4.029
8	0.706	1.860	2.306	2.896	3.355	3.832
9	0.703	1.833	2.262	2.821	3.250	3.690
10	0.700	1.812	2.228	2.764	3.169	3.581
15	0.691	1.753	2.131	2.602	2.947	3.252
20	0.687	1.725	2.086	2.528	2.845	3.153
25	0.684	1.708	2.060	2.485	2.787	3.078
30	0.683	1.697	2.042	2.457	2.750	3.030
40	0.681	1.684	2.021	2.423	2.704	2.971

For your Lab Report: REPORTING YOUR RESULTS

1. Generate your own table of results (see Table 2 below) with your 5 or 6 good titrations, depending on the result of Grubbs test. For the G_{calc} value and G_{test} result, you can do it manually or use the conditional "IF" function in Excel.
2. Show an example calculation of each of the statistical tests:
 - Grubbs test
 - F test for equal variances
 - t-test for

Table 2. Individual data for the statistical evaluation of acid-base indicators

Trial #	Mass of TRIS base (g)	Moles of TRIS	Volume of HCl used (mL)	Moles of HCl	Calculated Molarity of HCl (mol/L)	G_{calc}	G_{test}	Mean M_{HCl}	s	s^2	%RSD
1											
2											
3											
4											
5											
6											

3. Form your conclusion based on the two t-tests (one for the pair of indicators giving average HCl molarities that are farthest apart, and another from pair of indicators giving the second most different molarities).
 - If $t_{calculated} > t_{table}$ the two means (molarity of HCl) are significantly different at the 95 % confidence level. If $t_{calculated} < t_{table}$, then the two means are the same.