5. Statistical Evaluation of Acid-Base Indicators[1]

Green Profile
See Section 0

This experiment introduces you to the use of indicators and to the statistical concepts of mean, standard deviation, Grubbs test, *F* 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:

$$(HOCH_2)_3CNH_2 + H^+ \rightarrow (HOCH_2)_3CNH_3^+$$

Tris(hydroxymethyl)aminomethane
"tris"

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 section.

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

Indicators should be available in dropper bottles:

Bromothymol blue (BB): Dissolve 0.100 g in 16.0 mL 0.0100 M NaOH and add 225 mL H_2O

Methyl red (MR): Dissolve 20 mg in 60 mL of ethanol and add 40 mL H_2O

Bromocresol green (BG): Dissolve 0.100 g in 14.3 mL 0.0100 M NaOH and add 225 mL H_2O

Methyl orange (MO): Dissolve 10 mg in 100 mL H_2O

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

BB:	blue	(pH 7.6) →	yellow	(pH 6.0)	(end point is disappearance of green)
MR:	yellow	(pH 6.0) →	red	(pH 4.8)	(end point is disappearance of orange)
BG:	blue	(pH 5.4) →	yellow	(pH 3.8)	(end point is green)
MO:	yellow	(pH 4.4) →	red	(pH 3.1)	(end point is first appearance of orange)

Procedure

Each student should perform the following procedure with *two* indicators. Different students should be assigned different indicators so that at least 10-12 students evaluate each indicator.

1. D. T. Harvey, *J. Chem. Ed.* **1991**, *68*, 329.

1. Calculate the molecular mass of tris and the mass required to react with 35-40 mL of 0.10 M HCl. Weigh this much tris into a 125-mL flask. Weigh no more than three samples of tris at a time as the number of 125-mL flasks is limited.
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.
4. 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. 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. Record the total volume of HCl required to reach the end point to the nearest 0.01 mL. Calculate the molarity of HCl.
5. Repeat the titration to obtain at least six accurate measurements of the HCl molarity.
6. Repeat steps 1-5 for the other indicator.
7. Report your molarities, their mean, their standard deviation, and the relative standard deviation ($s/\bar{x}$). Use the Grubbs test in Section 4-6 in the textbook to decide whether any results should be discarded. In your laboratory notebook and on the cover sheet circle any outliers before you enter your data into the section spreadsheet.

Data Analysis

Pool the data from your lab section (not the entire class) to fill in the tables on the coversheet. Table 1 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. If two students see the end point differently, each result might be very reproducible, but the reported molarities will be different. Together, they will

Table 1. Pooled data

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

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

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

where there is one term in the numerator for each student using that indicator, giving S terms.

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). In the bottom table on the coversheet you will pool your data with the rest of the lab section.

Use the t test (Equation 4-9a in the textbook) to decide whether the average molarities are significantly different from each other at the 95% confidence level. When you calculate the pooled standard deviation for Equation 4-9a, the values of s_1 and s_2 in Equation 4-10a in the textbook are the values of s_x (not s_p) in Table 1.

A condition for using Equations 4-9a and 4-10a is that the standard deviations for the two sets of measurements should not be "significantly different" from each other. The F test tells us whether two standard deviations are "significantly" different from each other. F is the quotient of the squares of the standard deviations:

$$F_{\text{calculated}} = \frac{s_1^2}{s_2^2} \qquad (1)$$

We always put the larger standard deviation in the numerator so that $F \geq 1$. If $F_{\text{calculated}} > F_{\text{table}}$ in Table 2 (FINV or F.INV.RT function in Excel), then the difference is significant.

Use the F test in Equation 1 to decide whether or not the standard deviations for the two indicators giving the largest difference in mean HCl molarity are significantly different. If they are significantly different, use Equations 4-9b and 4-10b of the textbook for the t test.

Table 2. Critical values of $F = s_1^2 / s_2^2$ at 95% confidence level

Degrees of freedom for s_2	Degrees of freedom for s_1													
	2	3	4	5	6	7	8	9	10	12	15	20	30	∞
2	19.0	19.2	19.2	19.3	19.3	19.4	19.4	19.4	19.4	19.4	19.4	19.4	19.5	19.5
3	9.55	9.28	9.12	9.01	8.94	8.89	8.84	8.81	8.79	8.74	8.70	8.66	8.62	8.53
4	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.91	5.86	5.80	5.75	5.63
5	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77	4.74	4.68	4.62	4.56	4.50	4.36
6	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06	4.00	3.94	3.87	3.81	3.67
7	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64	3.58	3.51	3.44	3.38	3.23
8	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35	3.28	3.22	3.15	3.08	2.93
9	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14	3.07	3.01	2.94	2.86	2.71
10	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98	2.91	2.84	2.77	2.70	2.54
11	3.98	3.59	3.36	3.20	3.10	3.01	2.95	2.90	2.85	2.79	2.72	2.65	2.57	2.40
12	3.88	3.49	3.26	3.11	3.00	2.91	2.85	2.80	2.75	2.69	2.62	2.54	2.47	2.30
13	3.81	3.41	3.18	3.02	2.92	2.83	2.77	2.71	2.67	2.60	2.53	2.46	2.38	2.21
14	3.74	3.34	3.11	2.96	2.85	2.76	2.70	2.65	2.60	2.53	2.46	2.39	2.31	2.13
15	3.68	3.29	3.06	2.90	2.79	2.71	2.64	2.59	2.54	2.48	2.40	2.33	2.25	2.07
16	3.63	3.24	3.01	2.85	2.74	2.66	2.59	2.54	2.49	2.42	2.35	2.28	2.19	2.01
17	3.59	3.20	2.96	2.81	2.70	2.61	2.55	2.49	2.45	2.38	2.31	2.23	2.15	1.96
18	3.56	3.16	2.93	2.77	2.66	2.58	2.51	2.46	2.41	2.34	2.27	2.19	2.11	1.92
19	3.52	3.13	2.90	2.74	2.63	2.54	2.48	2.42	2.38	2.31	2.23	2.16	2.07	1.88
20	3.49	3.10	2.87	2.71	2.60	2.51	2.45	2.39	2.35	2.28	2.20	2.12	2.04	1.84
30	3.32	2.92	2.69	2.53	2.42	2.33	2.27	2.21	2.16	2.09	2.01	1.93	1.84	1.62
∞	3.00	2.60	2.37	2.21	2.10	2.01	1.94	1.88	1.83	1.75	1.67	1.57	1.46	1.00