Chapter 10

ACID-BASE TITRATIONS

Strong Acid-Strong Base Titrations

Abbreviations

V_a = volume of strong acid, S.A.

V_b = volume of strong base, S.B.

V_e = vol. titrant acid or base needed to reach the ***equivalence point***

Example: A 50.00 mL solution of 0.0100 M NaOH is titrated with 0.100 M HCl. Calculate the pH of solution at the following volumes of HCl added: 0, 1.00, V_e, and 5.50 mL.

Net ionic equation:

$$H^+ + OH^- \longrightarrow H_2O$$

What is K for this reaction at 25 ^{0}C?

$$K = 1/K_w$$

- Very large K;
  reaction goes to completion

S.A. – S.B. Titrations (Cont.)

WORK: First you must determine V_e

Since the reaction stoichiometry is 1:1,

mol H^+ = mol OH^- ***At the equiv. pt.***

Thus, $M_a \times V_a = M_b \times V_b$

Since HCl is the titrant we substitute V_e for V_a:

$M_a \times \mathbf{V_e} = M_b \times V_b$ ***At the equiv. pt.***

or

$$\boxed{\mathbf{V_e} = \frac{M_b \times V_b}{M_a}}$$

$\mathbf{V_e}$ = {(50.00 mL)(0.0100 M)}/0.100 M

Substituting the given quantities we get: $\mathbf{V_e}$ = 5.00 mL

S.A. – S.B. Titrations (Cont.)

Calculate the solution pH at different V_a's

Region 1: Before the equivalence point (When $\mathbf{V_a < V_e}$)

What species is in solution?

- There is unreacted NaOH in solution, so the pH is still basic
- Amount of excess NaOH determines pH

(a) pH when $V_a = 0$

- Only 0.0100 M NaOH is solution,

  pOH = - log (0.0100 M) = 2.00

pH = 12.00 **when $V_a = 0$**

S.A. – S.B. Titrations (Cont.)

Region 1: Before the equiv. pt. (Cont.)

(b) pH when V_a = 1.00 mL

- Since V_e = 5.00 mL, we know that V_a = 1.00 mL is only 20 % of V_e
- Thus, 80 % of NaOH remains unreacted
- But wait, the total volume of has been changed by addition of titrant!

S.A. – S.B. Titrations (Cont.)

WORK – Cont.

(b) pH when V_a = 1.00 mL

- Use changes in # moles OH^- during titration with H^+ to calc. pH

$$[OH^-] = \left(\frac{\text{Initial mol } OH^- - \overset{= \text{ mol } H^+ \text{ added}}{\text{mol } OH^- \text{ reacted}}}{V_{tot}} \right)$$

$$[OH^-] = \left(\frac{[(0.0100\text{ M})(50.00\text{ mL})] - \overset{= \text{ mol } H^+ \text{ added}}{(0.100\text{ M})(1.00\text{ mL})}}{51.00\text{ mL}} \right)$$

$[OH^-] = 7.84 \times 10^{-3}$ M

$\boxed{\text{pH} = 11.89}$ **when V_a = 1.00 mL**

S.A. – S.B. Titrations (Cont.)

Calculate the solution pH at different V_a's

Region 2: At the equivalence point (When $V_a = V_e$)

What species is in solution?

- Equimolar amounts of HCl and NaOH have reacted to form NaCl and H_2O
- NaCl is made of spectator ions, S.I. => gives neutral pH in solution

Thus, $\boxed{pH = 7.00}$ **At the equivalence point**

S.A. – S.B. Titrations (Cont.)

Region 3: Beyond the equivalence point (When $V_a > V_e$)

What species is in solution?

- Excess titrant, H^+, determines solution pH

pH when $V_a = 5.50$ mL

- 0.50 mL of H^+ is in excess of V_e
- Do not ignore dilution

vol. in x's of V_e

$$[H^+]_{x's} = M_a \times \left(\frac{V_a - V_e}{V_{tot}}\right) = (0.100\ M)\left(\frac{0.50\ mL}{(5.50 + 50.00)\ mL}\right)$$

$[H^+]_{x's} = 9.01 \times 10^{-4}$ M; $\boxed{pH = 3.05}$ **when $V_a > V_e$**

S.A. – S.B. Titrations (Cont.)

Alternative work: Construct an **I-C-F table** (F = final). Remember that titration reactions go to completion so there is no equilibrium (E).

Example: A 50.00 mL solution of 0.0100 M NaOH is titrated with 0.100 M HCl. Calculate the pH of solution at the following volumes of HCl added: (a) 1.00, (b) V_e, and (c) 5.50 mL.

WORK: **(a) when V_a = 1.00 mL** Note: V_{total} sol'n = 51.00 mL

- mol added H^+ = M_a x V_a = 1.00×10^{-4}
- initial mol OH^- = M_b x V_b = 5.00×10^{-4}

	H^+	**+**	**OH^-**	$\longrightarrow$	**H_2O**
I (mol):	1.00×10^{-4}		5.00×10^{-4}		liquid
C (mol):	$- 1.00 \times 10^{-4}$		$- 1.00 \times 10^{-4}$		liquid
F (mol):	0		4.00×10^{-4}		liquid

$$[OH^-] = \frac{mol\ OH^-}{V_{total}} = \frac{4x10^{-4}\,mol}{0.05100\,L} = 7.84x10^{-3}\,M$$

pOH = 2.11; **pH = 11.89**

S.A. – S.B. Titrations (Cont.)

Alternative work (Cont)

WORK: **(c) when V_a = 5.50 mL** Note: V_{total} sol'n = 55.50 mL

	H^+	**+**	**OH^-**	$\longrightarrow$	**H_2O**
I (mol):	5.50×10^{-4}		5.00×10^{-4}		liquid
C (mol):	$- 5.00 \times 10^{-4}$		$- 5.00 \times 10^{-4}$		liquid
F (mol):	0.50×10^{-4}		0		liquid

$$[H^+]_{x's} = \frac{mol\ H^+}{V_{total}} = \frac{0.5x10^{-4}\,mol}{0.05550\,L} = 9.01x10^{-3}\,M$$

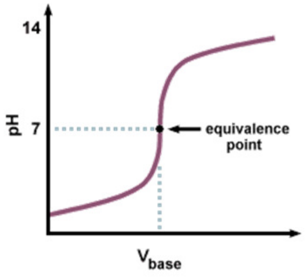
pH = 3.05

S.A. – S.B. Titrations (Cont.)

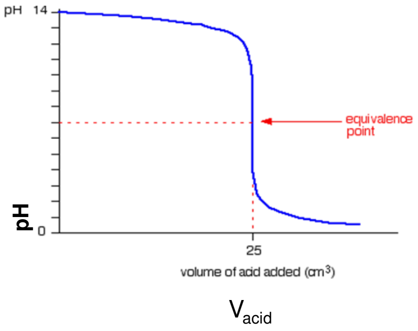
Homework: Consider the titration of 25.00 mL of 0.100 M HBr with 0.200 M KOH. Calculate the pH at the following volumes of KOH added: 0, 8.00, 12.50 and 15.00 mL.

Titration Curves: *Strong acid-strong base titration*

Strong acid titrated with a strong base



Strong base titrated with a strong acid



- **pH is acidic before the equiv. pt. (H^+ in sol'n)**
- **pH = 7 at the equiv. pt.**
- **pH is basic (due to x's OH^- beyond the equiv. pt.**

- **pH is basic before the equiv. pt. (OH^- in sol'n)**
- **pH = 7 at the equiv. pt.**
- **pH is acidic (x's H^+ beyond equiv. pt.**

Weak Acid-Strong Base Titrations

HA **Titrant** (always)

Titration reaction: $\underbrace{HA}_{\text{Weak acid}} + \underbrace{OH^-}_{\text{Titrant}} \longrightarrow \underbrace{A^-}_{\text{Conj. base}} + H_2O$

- $K = 1/K_{b\,(A-)}$ = very large; Reaction goes to completion

Calculate the solution pH at different V_a's

Example: Consider the titration of 25.00 mL of 0.0500 M formic acid with 0.0500 M NaOH. Calculate the pH of solution at the following volumes of NaOH added: 0, 10.00, V_e, and 26.00 mL.

Region 1: Before the equivalence point (When $V_b < V_e$)

What species is in solution?

- Only HA in solution, so the pH is acidic
- Calculate pH from amount of HA that dissociated

W.A. – S.B. Titrations (Cont.)

Region 1: Before the equivalence point (Cont.)

(a) pH when V_b = 0 mL (Only HA in solution)

Solution equilibria: $HA \overset{K_a}{\rightleftarrows} H^+ + A^-$

- Use K_a and F_{HA} to calculate pH ($K_a = 1.80 \times 10^{-4}$ for formic acid)

$$K_a = \frac{x^2}{F_{HA} - x} \qquad 1.80 \times 10^{-4} = \frac{x^2}{(0.0500 - x)}$$

Solving for x quadratically we get:

$x = [H^+] = 2.91 \times 10^{-3}$ M

$\boxed{pH = 2.54}$ **when $V_b = 0$**

W.A. – S.B. Titrations (Cont.)

Region 1: Before the equivalence point (Cont.)

(b) pH when V_b = 10.00 mL

- Some HA have reacted to form A^-
- Mixture of unreacted HA and A^- = ***a buffer!***

Work: ***Use moles*** and ***I-C-F table***

- Keep track of total vol. solution, V_{total}

We have to know V_e first:

$$V_e = \frac{M_a \times V_a}{M_b} = [(0.0500\ M)(25.00\ mL)]/(0.0500\ M) \qquad V_e = 25.00\ mL$$

- Thus, $V_b < V_e$, so the equiv. pt. has not been reached

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initial mol HA = $M_{HA} \times V_{HA}$

= (0.0500 mol/L)(0.02500 L)

= 1.25×10^{-3} mol

mol OH^- reacted = $M_b \times V_b$

= (0.0500 mol/L)(0.01000 L)

= 5.00×10^{-3} mol

Titration reaction:	HA +	OH^- $\longrightarrow$	A^- +	H_2O
Initial mol (I):	1.25×10^{-3}	5.00×10^{-4}	0	---
Change (C):	$- 5.00 \times 10^{-4}$	$- 5.00 \times 10^{-4}$	$+ 5.00 \times 10^{-4}$	---
Final mol (F):	7.50×10^{-4}	0	5.00×10^{-4}	---

$$pH = 3.745 + \log\left(\frac{5.00 \times 10^{-4}}{7.50 \times 10^{-4}}\right)$$

pH = 3.569

- Alternative work: Use of volume fractions

We have to know V_e first:

$$V_e = \frac{M_a \times V_a}{M_b} = [(0.0500\ M)(25.00\ mL)]/(0.0500\ M) \qquad V_e = 25.00\ mL$$

Titration reaction: $HA + OH^- \longrightarrow A^- + H_2O$

	HA	OH^-	A^-	H_2O
Relative initial amounts:	**25/25**	**10/25**	**0**	**---**
Change:	**- 10/25**	**- 10/25**	**+ 10/25**	**---**
Relative final amounts:	**15/25**	**0**	**10/25**	**---**

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) \qquad pH = 3.745 + \log\left(\frac{10/25}{15/25}\right)$$

$$\boxed{pH = 3.569} \qquad \text{when } V_b < V_e$$

W.A. – S.B. Titrations (Cont.)

Region 2: At the equivalence point

pH when $V_b = V_e$

What species is in solution?

- All the HA has been converted to ***A^-, a weak base***
- Hydrolysis of A^- will determine solution pH

Solution equilibria: $A^- + H_2O \overset{K_b}{\rightleftharpoons} HA + OH^-$

- First, calculate F_{A-}, then use K_b and F_{A-} to calculate the pH of solution

$$F_{A-} = \frac{\text{mol } A^-}{V_{tot}} = \frac{\text{initial mol HA}}{V_{tot}} = \frac{(0.0500\ M)(25.00\ mL)}{(25.00 + 25.00)\ mL}$$

$$F_{A-} = 0.0250\ M$$

W.A. – S.B. Titrations (Cont.)

Region 2: At the equivalence point

pH when $V_b = V_e$ (Cont.)

$F_{A^-} = 0.0250$ M $\quad K_b = K_w/(1.80 \times 10^{-4}) = 5.56 \times 10^{-11}$

$$K_b = \frac{y^2}{F_{A^-} - y}$$

Substituting and solving for y gives:

$y = [OH^-] = 1.18 \times 10^{-6}$ M

pOH = 5.93

$\boxed{pH = 8.07}$ **At the equiv. pt.**

- ***pH*** at the equiv. pt. ***> 7*** because ***A^- is a weak base***

W.A. – S.B. Titrations (Cont.)

Region 3: Beyond the equivalence point (When $V_b > V_e$)

What species is in solution?

- Excess titrant, NaOH; 1.00 mL is in excess of V_e
- $[OH^-]_{x's}$ determines solution pH

$$[OH^-]_{x's} = M_b \times \left(\frac{V_b - V_e}{V_{tot}}\right) = (0.0500\text{ M}) \times (1.00\text{ mL}/51.00\text{ mL})$$

$[OH^-]_{x's} = 9.80 \times 10^{-4}$ M; $\quad$ pOH = 3.01

$\boxed{pH = 10.99}$ **Beyond the equiv. pt.**

W.A. – S.B. Titrations (Cont.)

Summary

(1) Before titration

- ➢ Only HA in solution; Use K_a equil. to calculate pH

(2) Before the equiv. pt. ($V_b < V_e$)

- ➢ Mixture of unreacted HA and A^- = buffer

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) \qquad pH = pK_a \text{ when } V_b = \tfrac{1}{2} V_e$$

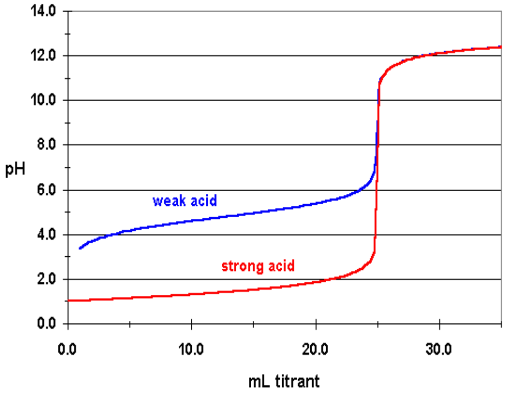
(3) At the equiv. pt. ($V_b = V_e$)

- ➢ Only A^- in solution; Use K_b equil. to calculate pH

(4) Beyond the equiv. pt. ($V_b > V_e$)

- ➢ Only excess OH^- titrant in solution, which determines pH

Titration Curve: *Weak acid-strong base titration*
(versus ***strong acid-strong base titration***)



Three major differences:

1. The weak-acid solution, HA, has a higher initial pH. (Less H^+ per mol HA for a weak acid)
2. For HA, the pH rises more rapidly at the start, but less rapidly near the equiv. point => *formation of buffer!*
3. For HA, the pH at the equiv. point does not equal 7.00 => *formation of A^-, a weak base!*

http://www.chemicool.com/img1/graphics/titration-strong-weak.gif

Weak Base-Strong Acid Titrations

B **Titrant** (always)

Net ionic equation: **$B + H^+ \longrightarrow BH^+$**

What is K for this reaction at 25 ^{0}C? ***$K = 1/K_a$***

- Very large K; reaction goes to completion

Region 1: Before the equivalence point

(a) Before titration

- Only the weak base, B, is in solution
- Use $K_{b\,(B)}$ equilibrium to calc. pH

(b) When $V_a < V_e$

- Mixture of unreacted B and BH^+ = *a buffer!*
- Use the H-H equation to calc. pH; Use $pK_{a\,(BH+)}$

W.B. – S.A. Titrations (Cont.)

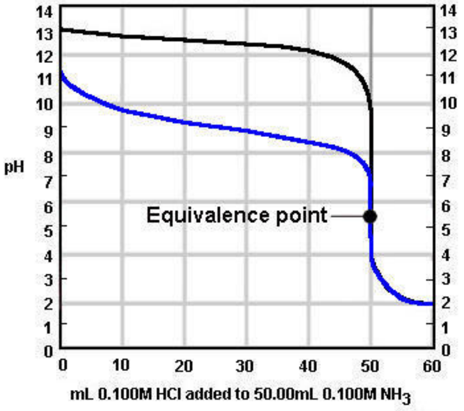
Region 2: At the equivalence point

- All of B has reacted; Only BH^+, a weak acid, in solution
- Use $K_{a\,(BH+)}$ equil. to calculate pH

Region 3: Beyond the equivalence point

- Only excess titrant, H^+, in solution
- $[H^+]_{x's}$ determines pH of solution

Titration Curve: *Weak base-strong acid titration*



NOTES:

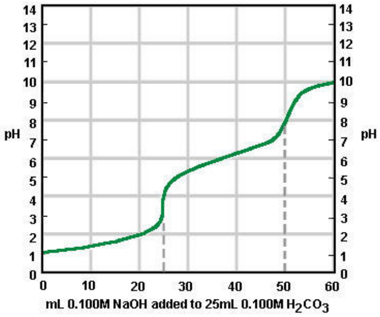
1. The weak base solution has a lower initial pH.
2. The pH drops more rapidly at the start, but less rapidly near the equivalence point.
3. The pH at the equivalence point does not equal 7.00.

POINT OF EMPHASIS : The equivalence point for a weak base-strong acid titration has a pH < 7.00.

http://www.chem.ubc.ca/courseware/pH/section14/content.html

Titrations of Polyprotic Systems

Titration Curve: *Weak diprotic acid–strong base titration*



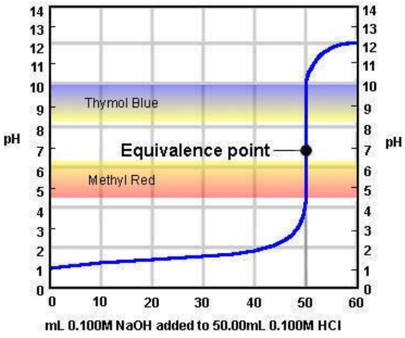
NOTES:

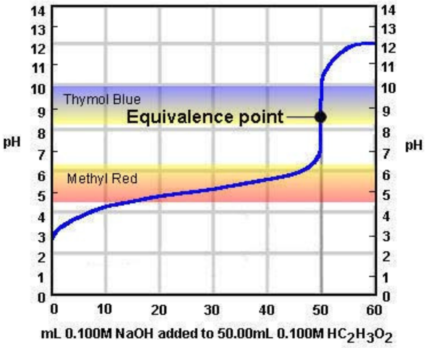
1. There are 2 breaks in the titration curve corresponding to successive deprotonation of the 2 acidic H's.
2. The volume of titrant at the 2nd equivalence point V_{e2}, is 2 x V_{e1}. (Discussed in class in details)

http://www.chem.ubc.ca/courseware/pH/section14/content.html

Acid-Base Indicators

Here are the titrations of both a strong acid and a weak acid with a strong base, using methyl red and thymol blue as possible indicators.



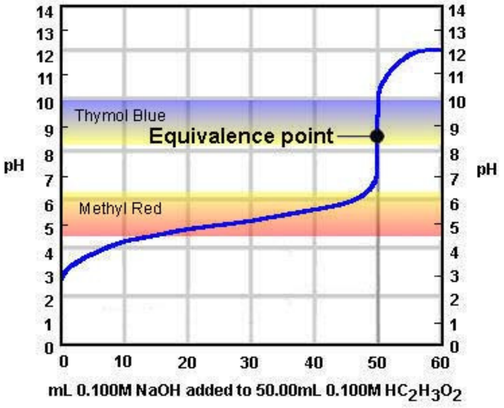


- In the strong acid titration (left), both indicators begin to change color at the equivalence point (50 mL of base) so both work equally well.
- In the weak acid titration, thymol blue changes color at the equivalence point, but methyl red begins to change color after only 15mL of base are added, which is far from the equivalence point, illustrating the importance of choosing an appropriate indicator.

http://www.chem.ubc.ca/courseware/pH/section15/index.html

Choosing an Acid-Base Indicator

- Select an indicator whose transition pH overlaps with the steepest part of the titration curve
- *Example*: Thymol blue works for the titration of acetic acid with NaOH, but methyl red does not.



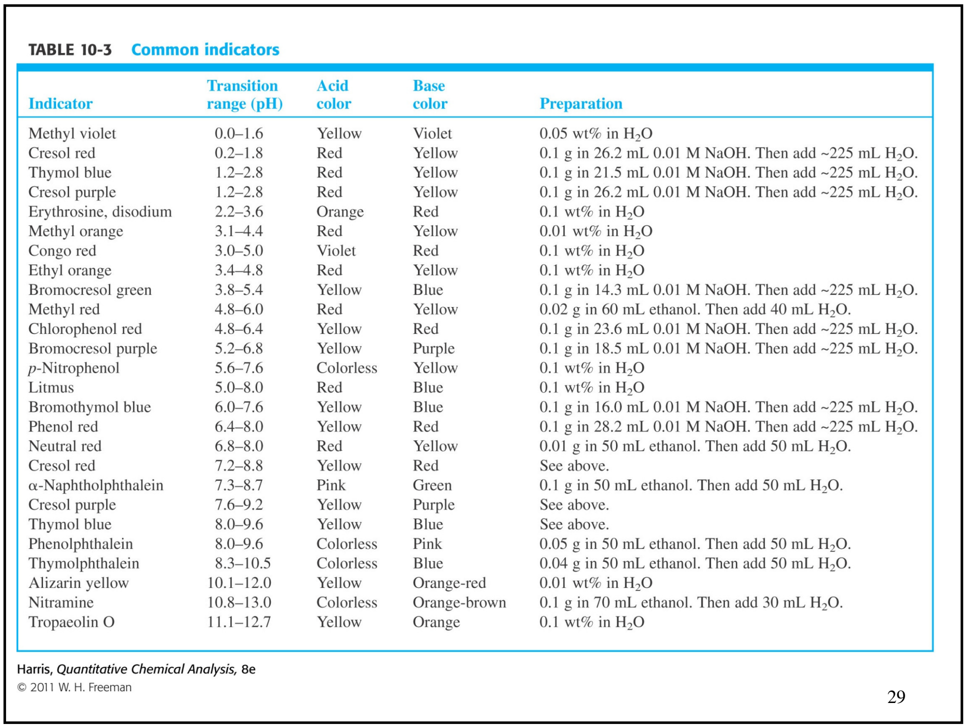


TABLE 10-3 Common indicators

Indicator	Transition range (pH)	Acid color	Base color	Preparation
Methyl violet	0.0–1.6	Yellow	Violet	0.05 wt% in H_2O
Cresol red	0.2–1.8	Red	Yellow	0.1 g in 26.2 mL 0.01 M NaOH. Then add ~225 mL H_2O.
Thymol blue	1.2–2.8	Red	Yellow	0.1 g in 21.5 mL 0.01 M NaOH. Then add ~225 mL H_2O.
Cresol purple	1.2–2.8	Red	Yellow	0.1 g in 26.2 mL 0.01 M NaOH. Then add ~225 mL H_2O.
Erythrosine, disodium	2.2–3.6	Orange	Red	0.1 wt% in H_2O
Methyl orange	3.1–4.4	Red	Yellow	0.01 wt% in H_2O
Congo red	3.0–5.0	Violet	Red	0.1 wt% in H_2O
Ethyl orange	3.4–4.8	Red	Yellow	0.1 wt% in H_2O
Bromocresol green	3.8–5.4	Yellow	Blue	0.1 g in 14.3 mL 0.01 M NaOH. Then add ~225 mL H_2O.
Methyl red	4.8–6.0	Red	Yellow	0.02 g in 60 mL ethanol. Then add 40 mL H_2O.
Chlorophenol red	4.8–6.4	Yellow	Red	0.1 g in 23.6 mL 0.01 M NaOH. Then add ~225 mL H_2O.
Bromocresol purple	5.2–6.8	Yellow	Purple	0.1 g in 18.5 mL 0.01 M NaOH. Then add ~225 mL H_2O.
p-Nitrophenol	5.6–7.6	Colorless	Yellow	0.1 wt% in H_2O
Litmus	5.0–8.0	Red	Blue	0.1 wt% in H_2O
Bromothymol blue	6.0–7.6	Yellow	Blue	0.1 g in 16.0 mL 0.01 M NaOH. Then add ~225 mL H_2O.
Phenol red	6.4–8.0	Yellow	Red	0.1 g in 28.2 mL 0.01 M NaOH. Then add ~225 mL H_2O.
Neutral red	6.8–8.0	Red	Yellow	0.01 g in 50 mL ethanol. Then add 50 mL H_2O.
Cresol red	7.2–8.8	Yellow	Red	See above.
α-Naphtholphthalein	7.3–8.7	Pink	Green	0.1 g in 50 mL ethanol. Then add 50 mL H_2O.
Cresol purple	7.6–9.2	Yellow	Purple	See above.
Thymol blue	8.0–9.6	Yellow	Blue	See above.
Phenolphthalein	8.0–9.6	Colorless	Pink	0.05 g in 50 mL ethanol. Then add 50 mL H_2O.
Thymolphthalein	8.3–10.5	Colorless	Blue	0.04 g in 50 mL ethanol. Then add 50 mL H_2O.
Alizarin yellow	10.1–12.0	Yellow	Orange-red	0.01 wt% in H_2O
Nitramine	10.8–13.0	Colorless	Orange-brown	0.1 g in 70 mL ethanol. Then add 30 mL H_2O.
Tropaeolin O	11.1–12.7	Yellow	Orange	0.1 wt% in H_2O

Harris, *Quantitative Chemical Analysis,* 8e