Application of Statistical Concepts in Analysis Data Process & Introduction to Determination of Concentration of Acid & Base

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Distribution of Measurements & Probable Range in Analysis

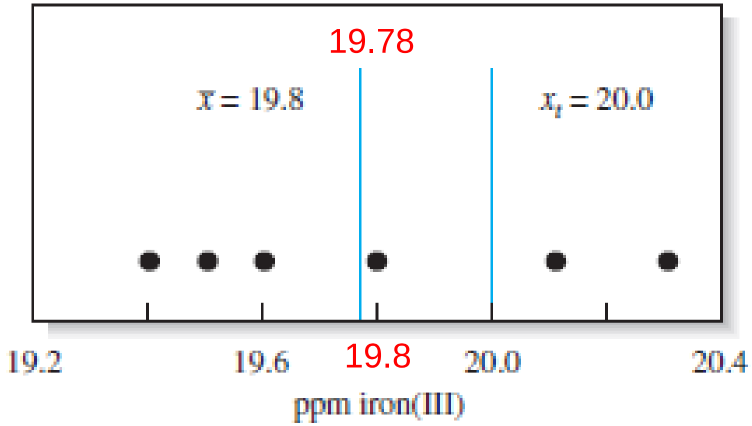


Figure 5-1 Results from six replicate determinations of iron in aqueous samples of a standard solution containing 20.0 ppm iron(III). The mean value of 19.78 has been rounded to 19.8 ppm (see Example 5-1).

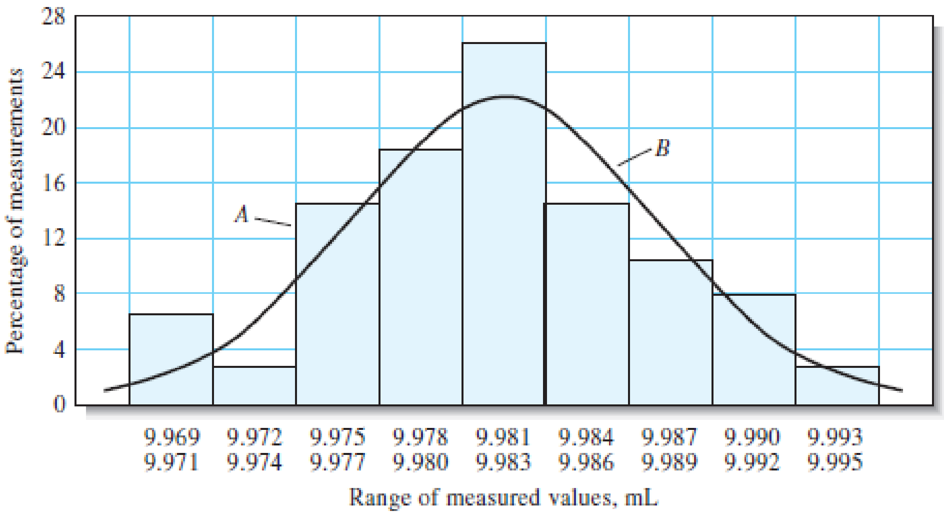


Figure 6-3 A histogram (*A*) showing distribution of the 50 results in Table 6-3 and a Gaussian curve (*B*) for data having the same mean and standard deviation as the data in the histogram.

Average: Arithmetic Mean

- Mean

$$\bar{x} = \frac{\sum_{i=1}^{N} x_i}{N} \qquad (5\text{-}1)$$

-

- Median: middle result

Statistical Concepts

- Replicate: number of replication
- Average: arithmetic mean
- Standard Deviation (SD)
- Precision
- Accuracy: absolute error; relative error
- Outlier data: decision rules to confirm or reject suspected data:
- Common decisions rules include:

✓ 2.5 D

✓ 4 D

✓ Q rejection test

Precision

- Closeness of the result of measurements
- Three terms describe precision:

✓ standard deviation

✓ variance

✓ Coefficient of Variation (CV)

Accuracy

- Closeness of measurement to true value

or

- Closeness of measurement to the accepted value

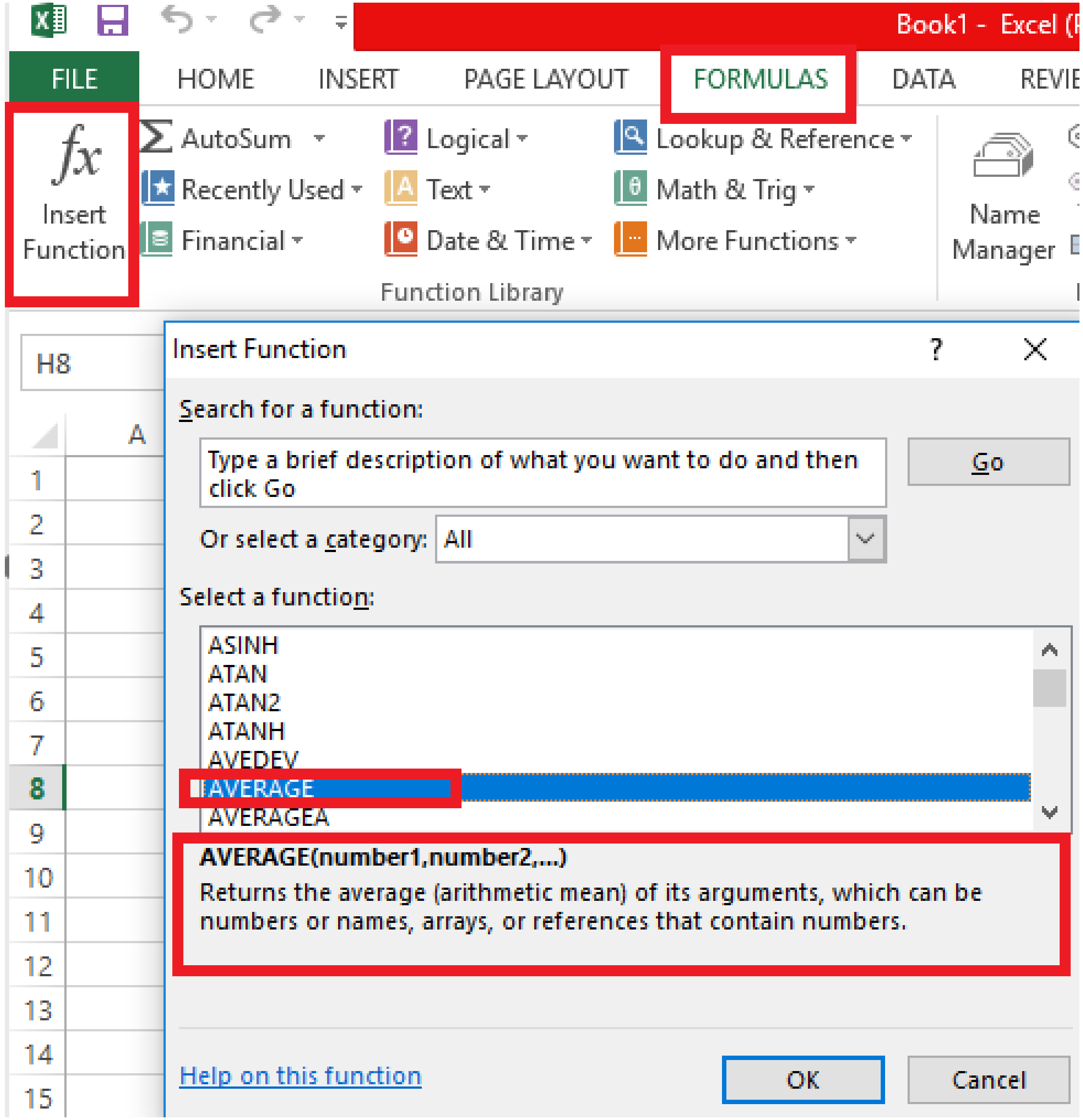
Standard Deviation (SD) & Variance

- SD: deviation from the mean

$$d_i = |x_i - \bar{x}| \qquad (5\text{-}2)$$

- Variance: σ^2

Function of Average by Excel in Office



Difference of Precision & Accuracy by Schematic Image

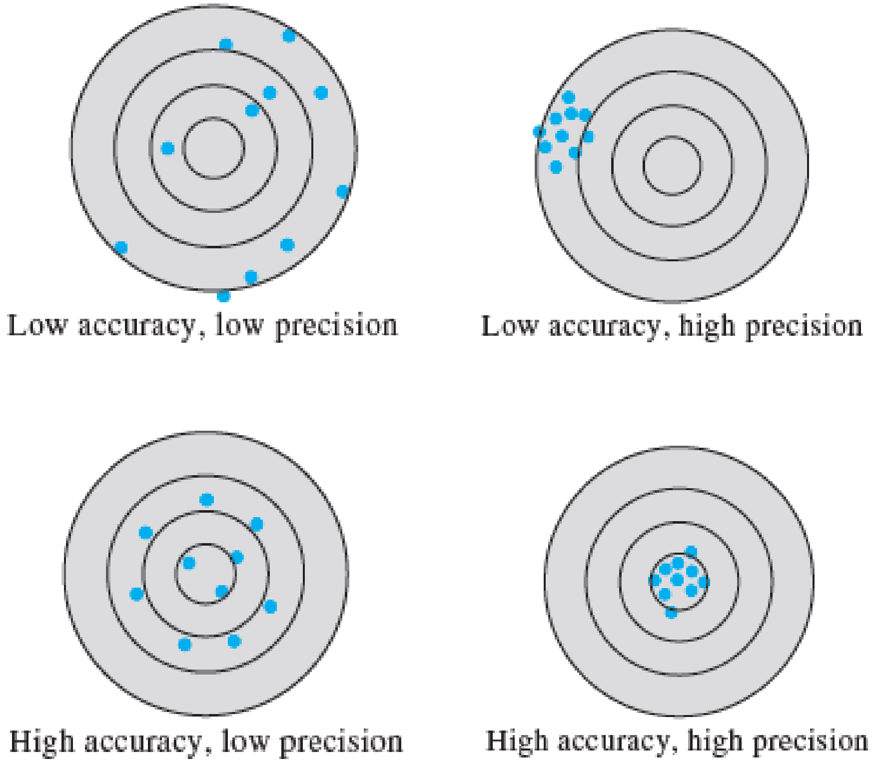


Figure 5-2 Illustration of accuracy and precision using the pattern of darts on a dartboard. Note that we can have very precise results (upper right) with a mean that is not accurate and an accurate mean (lower left) with data points that are imprecise.

Errors in Analysis

- Error: what is the meaning of error?
- Determinate error: systematic errors: affects accuracy
  - ✓ methodic error
  - ✓ instrumental error
  - ✓ operative (personal) error
  - ❖ Constant error
  - ❖ Proportional error: in proportion to the size of sample
- In-determinate or random error: affects precision
- Gross error: leads to outliers

Absolute Error & Relative Error

- Absolute error:

✓ the difference between measured value & true value

$$E = x_i - x_t \qquad (5\text{-}3)$$

- Relative error:

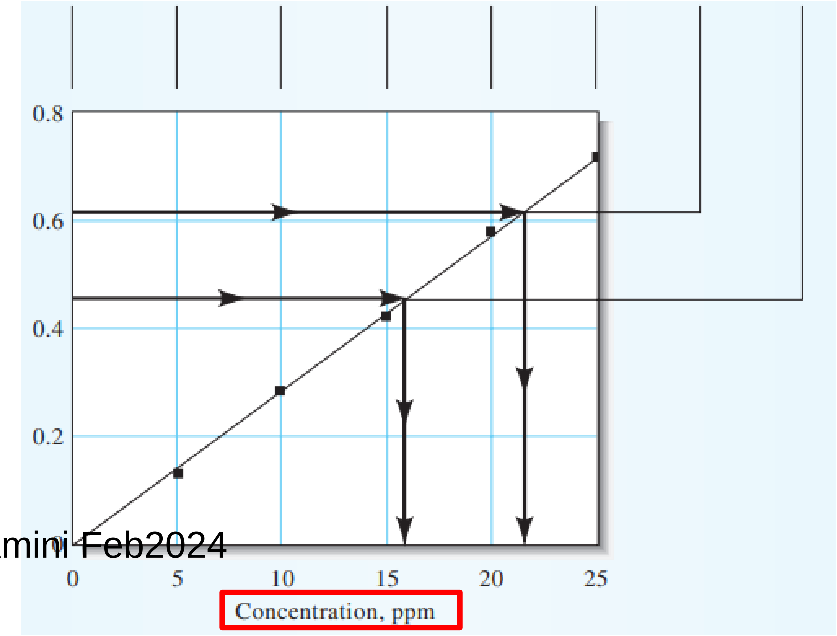
✓ the absolute error which is divided by true value

$$E_r = \frac{x_i - x_t}{x_t} \times 100\% \qquad (5\text{-}4)$$

✓ expressed as percent & part per thousand/million/billion (ppt, ppm, ppb)

Calibration in Analytical Methods

- To improve accuracy & precision of analysis
- To eliminate instrumental error
- Using standard samples in serial dilutions
- To determine the amount of unknown concentrations
- Analysis will be run following the selected method
- Plot calibration curve



Eliminate Instrumental Error by Calibration

- Follow calibration due to the type of instrument
- Draw calibration curve
- How to calibrate a pipet?
- How to calibrate a buret?

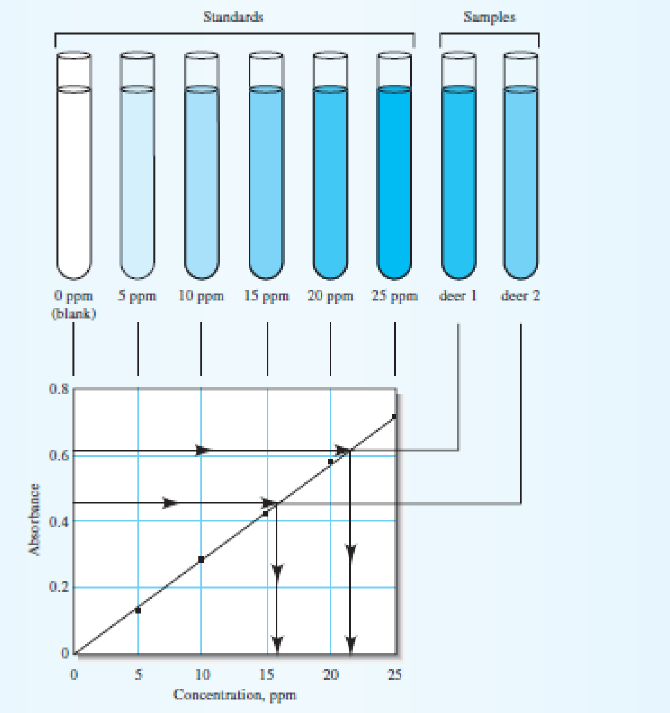


Figure 1F-2 Constructing and using a calibration curve to determine the concentration of arsenic. The absorbances of the solutions in the cuvettes are measured using a spectrophotometer. The absorbance values are then plotted against the concentrations of the solutions in the cuvettes, as illustrated in the graph. Finally, the concentrations of the unknown solutions are read from the plot, as shown by the dark arrows.

Decision Rules on Outlier Data

- Three rules to confirm or reject suspected data:

✓ 2.5 D: described in attached file.

✓ 4 D: described in attached file.

✓ Q rejection test: next slide.

Rejection Quotient (Q)

$$Q = \frac{|\text{suspect value} - \text{closest value}|}{\text{highest value} - \text{lowest value}}$$

TABLE 7-5

Critical Values for the Rejection Quotient, Q*

Number of Observations	Q_{crit} (Reject if $Q > Q_{crit}$)		
	90% Confidence	95% Confidence	99% Confidence
3	0.941	0.970	0.994
4	0.765	0.829	0.926
5	0.642	0.710	0.821
6	0.560	0.625	0.740
7	0.507	0.568	0.680
8	0.468	0.526	0.634
9	0.437	0.493	0.598
10	0.412	0.466	0.568

*Reprinted (adapted) with permission from D. B. Rorabacher, *Anal. Chem.*, **1991**, *63*, 139, **DOI**: 10.1021/ac00002a010. Copyright 1991 American Chemical Society.

Number of Analysis	3	4	5	6	7	8	9	10
$Q_{90\%}$	0.94	0.76	0.64	0.56	0.51	0.47	0.44	0.41

مثال برای تصمیم گیری درباره داده پرت

- چهار محاسبه نرماليته براي يك محلول به ترتيب ذيل بدست آمده است.

0.1014، 0.1102 ، 0.1001، 0.0985

با استفاده از روش D و نیز روش Q (Q Rejection Test) مشخص نمائید که داده ای برای حذف وجود دارد یا خیر؟

Concentration Calculations

Some Useful Formulas for Calculations in Analytical Chemistry

$n_A = \frac{m_A}{\mathcal{M}_A}$
where n_A is the amount of A, m_A is the mass of A, and $\mathcal{M}_A$ is the molar mass of A.

$c_A = \frac{n_A}{V}$ or $n_A = V \times c_A$

Any combination of grams, moles, and liters can be expressed in milligrams, millimoles, and milliliters. For example, a 0.1 M solution contains 0.1 mol of a species per liter or 0.1 mmol per milliliter. Similarly, the number of moles of a compound is equal to the mass in grams of that compound divided by its molar mass in grams or the mass in milligrams divided by its millimolar mass in milligrams.

13C-1 Some Useful Relationships

Most volumetric calculations are based on two pairs of simple equations that are derived from definitions of the mole, the millimole, and the molar concentration. For the chemical species A, we can write

$$\text{amount A (mol)} = \frac{\text{mass A (g)}}{\text{molar mass A (g/mol)}} \qquad (13\text{-}1)$$

$$\text{amount A (mmol)} = \frac{\text{mass A (g)}}{\text{millimolar mass A (g/mmol)}} \qquad (13\text{-}2)$$

The second pair of equations is derived from the definition of molar concentration, that is,

$$\text{amount A (mol)} = V\text{(L)} \times c_A\left(\frac{\text{mol A}}{\text{L}}\right) \qquad (13\text{-}3)$$

$$\text{amount A (mmol)} = V\text{(mL)} \times c_A\left(\frac{\text{mmol A}}{\text{L}}\right) \qquad (13\text{-}4)$$

where V is the volume of the solution.

Equations 13-1 and 13-3 are used when volumes are measured in liters, and Equations 13-2 and Equations 13-4 when the units are milliliters.

Some Useful Formulas for Calculations in Analytical Chemistry- Contd.

$$\text{no. meq analyte present} = \text{no. meq standard reagent added} \qquad \text{(A7-1)}$$

or

$$\text{no. eq analyte present} = \text{no. eq standard reagent added} \qquad \text{(A7-2)}$$

$$c_{N(A)} = \frac{\text{no. meq A}}{\text{no. mL solution}}$$

$$c_{N(A)} = \frac{\text{no. eq A}}{\text{no. L solution}}$$

$$\text{amount A} = \text{no. meq A} = \frac{\text{mass A (g)}}{\text{meqw A (g/meq)}} \qquad \text{(A7-6)}$$

$$\text{amount A} = \text{no. eq A} = \frac{\text{mass A (g)}}{\text{eqw A (g/eq)}} \qquad \text{(A7-7)}$$

$$\text{amount A} = \text{no. meq A} = V\text{(mL)} \times c_{N(A)}\text{(meq/mL)} \qquad \text{(A7-8)}$$

$$\text{amount A} = \text{no. eq A} = V\text{(L)} \times c_{N(A)}\text{(eq/L)} \qquad \text{(A7-9)}$$

Components & Keywords in Quantitative Titrimetric Analysis

- Analyte
- Titrant
- Titration; titrimetry: direct; in-direct(back) titration
- Complete reaction between analyte & titrant

Analyte(acid/base)+titrant(base/acid) $\longrightarrow$ products: salt + H_2O

- Equivalent point: major change in relative concentration
- End point: signaled by an observable physical change near eq. point

Equivalence point ≠ End point ?!

- Indicator
- Titration curve: plot of some function of the analyte or titrant concentration on y axis versus titrant volume on x axis.

Introduce Acid & Base

- According to Lewis:

✓ can donate (base) or accept (acid) electron

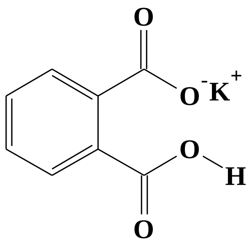
- According to Lowry-Bronsted:

can accept (base) or transfer (acid) hydronium (H^+)

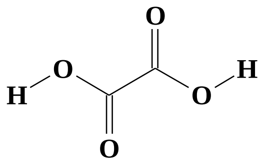
Primary Standards in Acid-Base Titration for Quantitative Analysis

- Acid as primary standard

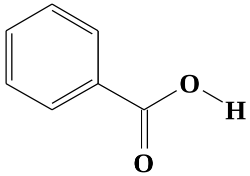
✓ KHP: potassium (K) Hydrogen Phthalate:



✓ oxalic acid:



✓ benzoic acid:



- Base as primary standard: ?

General Types of Acid Base Titration

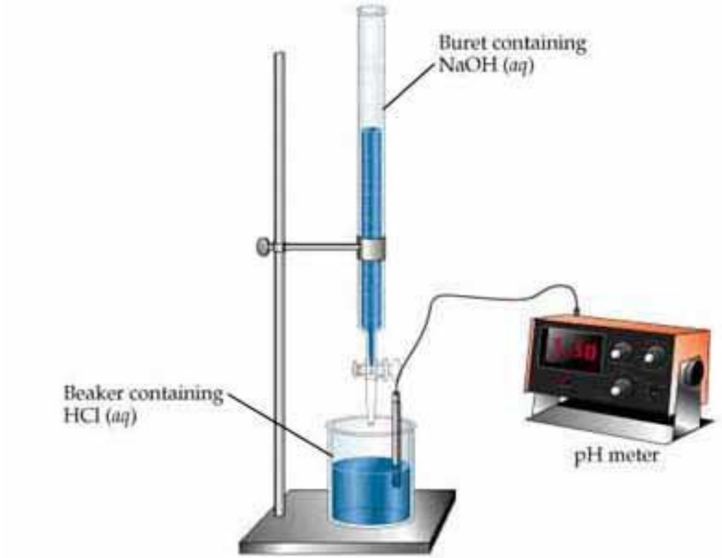
- Using pH- meter
- Using pH- indicator

Acid Base Titration Using pH-Meter

- A pH-meter is used to monitor the change in pH as the acid-base titration progresses.

- In the titration of an acid (analyte) by a base (titrant):

the pH-meter measures
the pH of the acid solution in the beaker
as a solution of a base with a known concentration
is added from the burette.



Acid Base Titration Using pH-Indicator

- A pH-indicator is used to monitor the change in pH as the acid-base titration progresses.
- In the titration of an acid (analyte) by a base (titrant):

the color of acid solution in the beaker

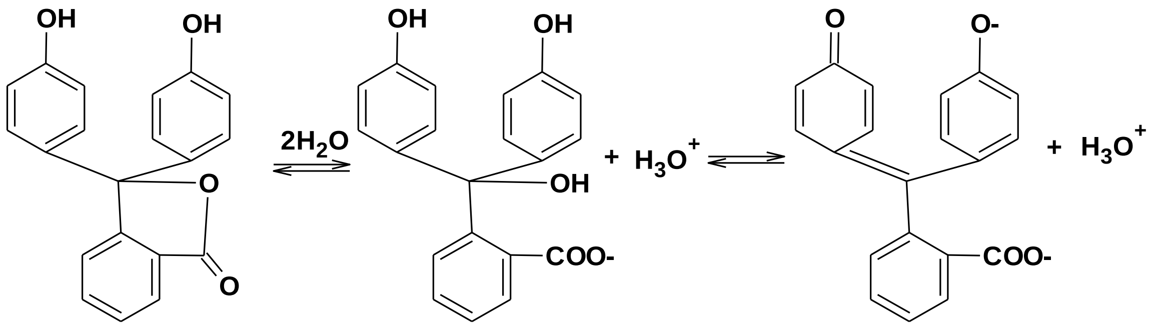
is changed by pH-indicator

as a solution of a base with a known concentration is added from the buret.

pH Indicators (HIn)

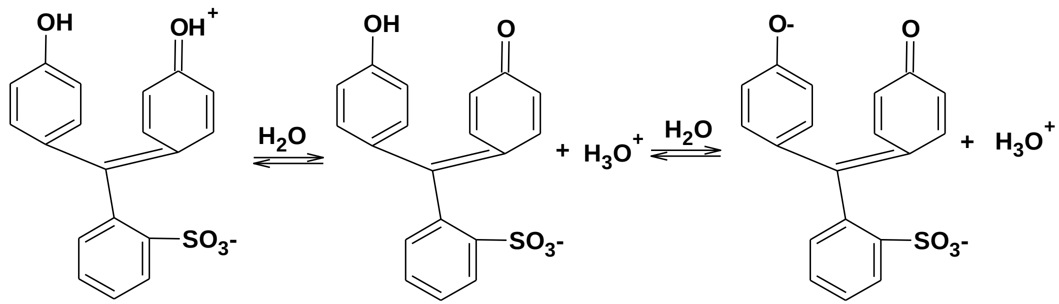
$$\frac{[HIn]}{[In^-]} \geq \frac{10}{1}$$

$$\frac{[HIn]}{[In^-]} \leq \frac{1}{10}$$



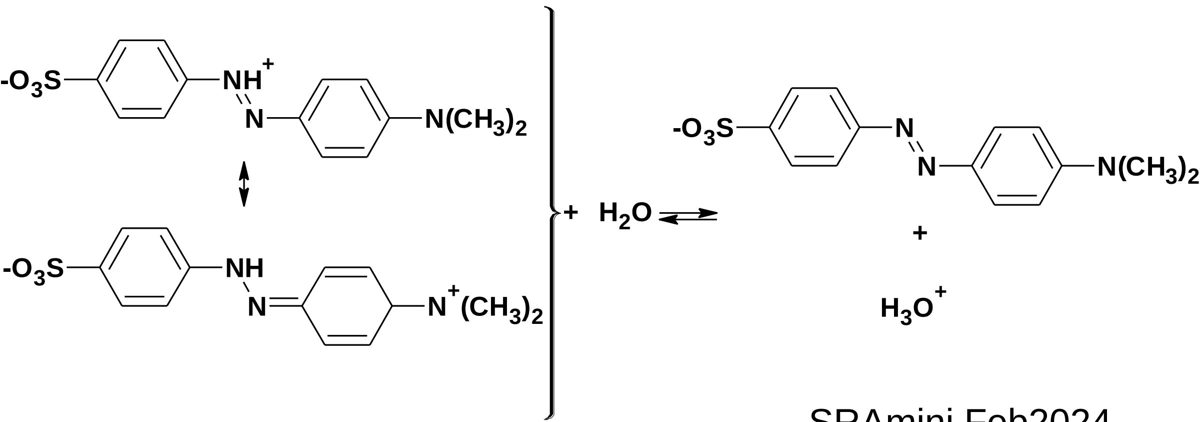
Phenolphthalein

$pK_a = 9.7$



Thymol blue

$pK_a = 1.65$



Methyl orange

$pK_a = 3.46$

Three Distinct Stages in Titration

- Pre-equivalence

- Equivalence

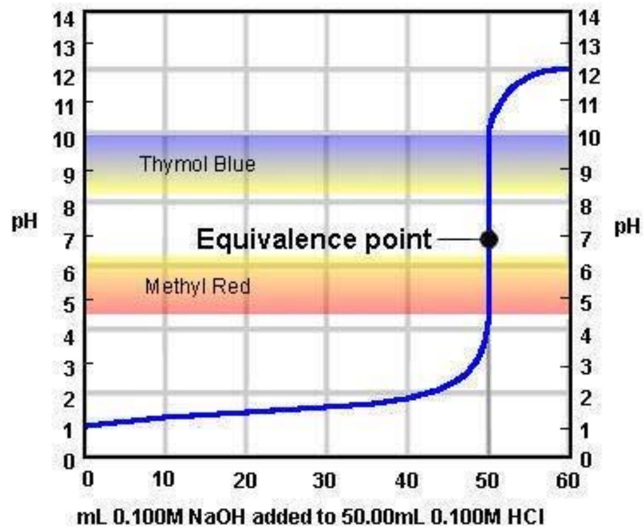
- Post-equivalence

- Acid base: neutralization:

Analyte(acid/base)+titrant(base/acid) $\longrightarrow$ products: salt + H_2O

pH Change (ΔpH) in Titration of Strong Acid (HCl:10 mL;0.1M) with Strong Base (NaOH;0.1M)

- Primary mmole of acid: M_aV_a
- $V_b<V_{eq}$
- $V_b=V_{eq}$
- $V_b>V_{eq}$
- pH $\frac{M_aV_a-M_bV_b}{V_a+V_b}$



Volume of NaOH (mL)	pH
0.00	1
5.0	-Log(0.333)= 1.47
10	7.00
15	pH=14-pOH= 12.31