

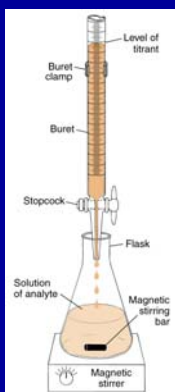
Chapter 13

Titrimetric Methods; Precipitation Titrimetry

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Titration

- Titration
 - A procedure in which one substance (titrant) is carefully added to another (analyte) until complete reaction has occurred.
 - The quantity of titrant required for complete reaction tells how much analyte is present.
- Volumetric Analysis
 - A technique in which the volume of material needed to react with the analyte is measured



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Titration Vocabulary

- Titrant
 - The substance added to the analyte in a titration (reagent solution)
- Analyte
 - The substance being analyzed
- Equivalence point
 - The point in a titration at which the quantity of titrant is exactly sufficient for stoichiometric reaction with the analyte.

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Features of Titrations

- Simple, inexpensive, very accurate and precise if done correctly.
- An analytical tool involving fundamental chemistry.
- Complete reaction between the analyte and a known concentration of titrant.
- Calculation of the amount of the analyte is straight forward using consumed standard titrant solution.

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Volumetric Procedures and Calculations

relate the moles of titrant to the moles of analyte

For 1:1 ratio reaction: $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$

moles titrant = # moles analyte

$$\# \text{moles}_{\text{titrant}} = (\text{C} \cdot \text{V})_{\text{titrant}}$$

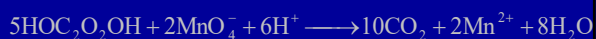
$$\# \text{moles}_{\text{analyte}} = (\text{C} \cdot \text{V})_{\text{analyte}}$$

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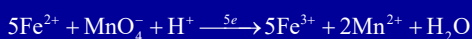
Volumetric Procedures and Calculations

relate the moles of titrant to the moles of analyte

For non 1:1 ratio reaction:



5 moles 2 moles

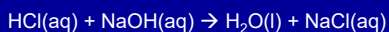


5 moles : 1 mole

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Example - Unknown concentration of a strong acid titrated by a strong base.

- The reaction:



- Let's say that [HCl] is the unknown and the sample volume is 50.00 mL
- Titrant: [NaOH] = 0.5000 M

We find that it takes 25.00 mL of NaOH to completely react with all of the HCl (i.e. neutralize), what is the concentration of [HCl] in the sample?



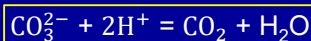
$$[C_{\text{HCl}} \times 50.00] = [0.5000 \times 25.00]$$

$$C_{\text{HCl}} = [25.00 \text{ mL} \times (0.5000 \text{ mol/L})_{\text{NaOH}}] / (50.00 \text{ mL})_{\text{HCl}} = 0.2500 \text{ M}$$

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The Equivalence Point vs End Point

- Finding the equivalence point is the goal of the titration.
- If our unknown contains 0.250 moles of CO_3^{2-} , and we are titrating with H^+ , then the equivalence point is reached when 0.500 moles of H^+ is added.



1 mole : 2 mole

0.250 mole : x x = 0.500 mole

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- End point

- The point in a titration at which there is a sudden change in a physical property (e.g., indicator color, pH, conductivity, or absorbance).
- Used as a measure of the equivalence point.

--Usually occurs after a small excess of titrant had been added.

--In most cases, the difference in the *End Point* and the *Equivalence Point* is insignificant and can be ignored.

- Indicator

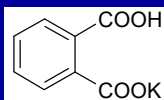
- A compound having a physical property (usually color) that changes **abruptly** near the equivalence point of a chemical reaction.

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Primary standards for bases.

- Potassium Hydrogen Phthalate (KHP)

- -Nonhygroscopic
- -High MW
- -Stable to drying
- -Inexpensive
- $\text{HP}^- + \text{OH}^- \rightarrow \text{P}^{2-} + \text{H}_2\text{O}$



- Other possibilities:

- Benzoic Acid
- Potassium Hydrogen Iodate $\text{KH}(\text{IO}_3)_2$

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Primary Standards for acids

- NaHCO_3 – major disadvantage low MW
84.00 g/mol

- Others available such as Na_2CO_3 .

- $\text{KHP} \rightarrow \text{NaOH} \rightarrow \text{HCl}$

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- Standardization

- The process whereby the concentration of a reagent is determined by reaction with a known quantity of a second reagent.

- Standard Solution

- A solution whose composition is known by virtue of the way it was made from a reagent of known purity or by virtue of its reaction with a known quantity of a standard reagent.

- Direct Titration

- One in which the analyte is treated with titrant, and the volume of titrant required for complete reaction is measured.

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Back Titrations

- Back titrations are used when the reaction between an analyte and titrant are slow, or if a suitable indicator is not available.
 - Add excess titrant so that all analyte is reacted and a small amount of excess titrant is present.
 - Titrate the excess titrant with a second titrant back to the equivalence point.

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Back Titration: Example

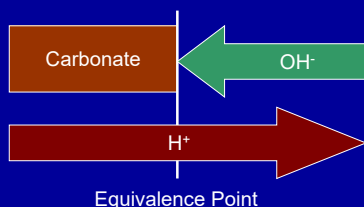
- Determine the carbonate content of limestone:



- Add excess H^+ and heat to drive off the CO_2 from solution.
 - We end up with a solution containing H^+ and Ca^{2+} .
- Titrate the excess H^+ with NaOH back to the equivalence point.
 - fast reaction, available indicator.

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Back Titration: Example



Amount of H^+ needed to reach the equivalence point =
moles of H^+ added – moles of OH^- added

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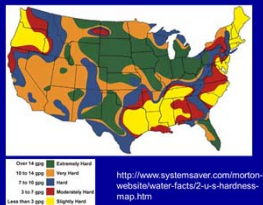
Titration Requirements

- Equilibrium constant must be large
 - reaction goes to completion.
- Must be a way to determine when the reaction has reached completion
 - through the use of an indicator.
 - by monitoring the concentration of one component.

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Types of Titrations

- Acid-base
 - most common (Soda ash lab)
- Complex formation
 - (Water hardness lab)
- Precipitation
- Oxidation/reduction



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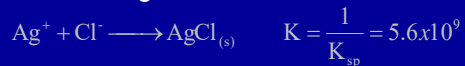
Precipitation Titration



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Precipitation Titration

- Titrate 50.00mL of 0.0750M Cl⁻ with 0.0500M Ag⁺.



- How many mL of Ag⁺ solution must be added to reach the equivalence point?

$$\frac{50.00\text{mL Cl}^- \text{ soln}}{1\text{mL}} \left| \frac{0.0750\text{ mmol Cl}^-}{1\text{mmol Cl}^-} \right| \left| \frac{1\text{mmol Ag}^+}{1\text{mmol Cl}^-} \right| \left| \frac{1\text{mL Ag}^+ \text{ soln}}{0.0500\text{mmol Ag}^+} \right| = 75.00\text{mL titrant}$$

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- What are the concentrations of Ag⁺ and Cl⁻ in solution *before* reaching the equivalence point?
- Suppose 40.00 mL of titrant have been added.
 - Moles of Ag⁺ added:

$$\frac{40.00\text{mL titrant}}{1\text{mL titrant}} \left| \frac{0.0500\text{ mmol Ag}^+}{1\text{mL titrant}} \right| = 2.000\text{mmol Ag}^+$$

- Moles Cl⁻ originally:

$$\frac{50.00\text{mL Cl}^- \text{ soln}}{1\text{mL soln}} \left| \frac{0.0750\text{ mmol Cl}^-}{1\text{mL soln}} \right| = 3.750\text{mmol Cl}^-$$

- Moles of Cl⁻ remaining in solution:

$$3.750 - 2.000 = 1.750\text{mmol Cl}^-; \frac{1.750\text{mmol Cl}^-}{90.00\text{mL}} = 0.01944\text{M Cl}^-$$

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- Moles of Ag⁺ in solution:
 - Use the equilibrium expression

$$[\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10}$$

	Ag ⁺	Cl ⁻
Initial	0	0.01944
Change	+x	+x
At Equilibrium	x	0.01944 + x

$$[x][0.01944+x] = 1.8 \times 10^{-10}$$

ignore +x

$$[x] = \frac{1.8 \times 10^{-10}}{0.01944} = 9.3 \times 10^{-9} \text{M Ag}^+$$

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- What are the concentrations of Ag^+ and Cl^- at the equivalence point?
 - At the equivalence point there is no excess Cl^- or excess Ag^+ .
 - The concentrations of Cl^- and Ag^+ are determined by the equilibrium.

	Ag^+	Cl^-
I	0	0
C	+x	+x
E	x	x

$$[\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10}$$

$$x^2 = 1.8 \times 10^{-10}$$

$$x = 1.3 \times 10^{-5} \text{ M } \text{Cl}^- \text{ and } \text{Ag}^+$$

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- What are the concentrations of Ag^+ and Cl^- in solution *after* reaching the equivalence point?
- Suppose 85.00 mL of titrant have been added.
 - Excess moles of Ag^+ added:

$$\frac{10.00 \text{ mL titrant}}{1 \text{ mL titrant}} \left| \frac{0.0500 \text{ mmol } \text{Ag}^+}{1 \text{ mL titrant}} \right| \rightarrow \frac{0.5000 \text{ mmol}}{135.00 \text{ mL}} = 3.704 \times 10^{-3} \text{ M } \text{Ag}^+$$

– Cl^- in solution:

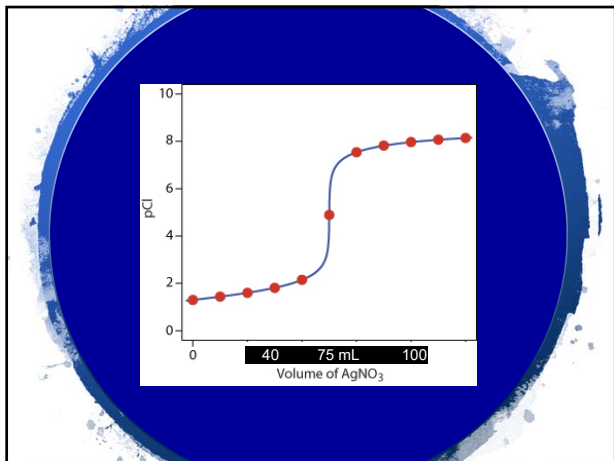
	Ag^+	Cl^-
I	3.704×10^{-3}	0
C	+x	+x
E	$3.704 \times 10^{-3} + x$	x

$$[3.704 \times 10^{-3} + x][x] = 1.8 \times 10^{-10}$$

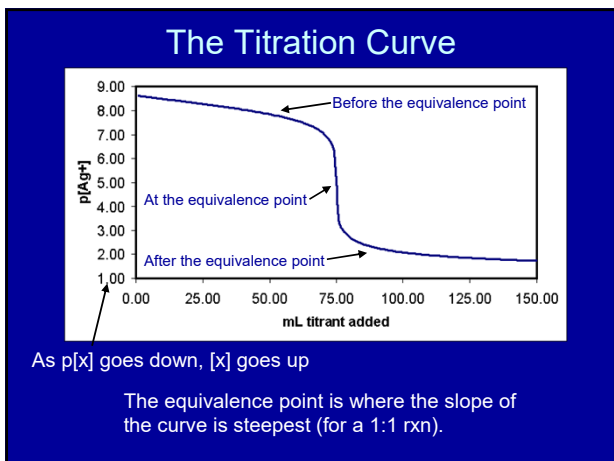
ignore + x

$$[x] = \frac{1.8 \times 10^{-10}}{3.704 \times 10^{-3}} = 4.9 \times 10^{-8} \text{ M } \text{Cl}^-$$

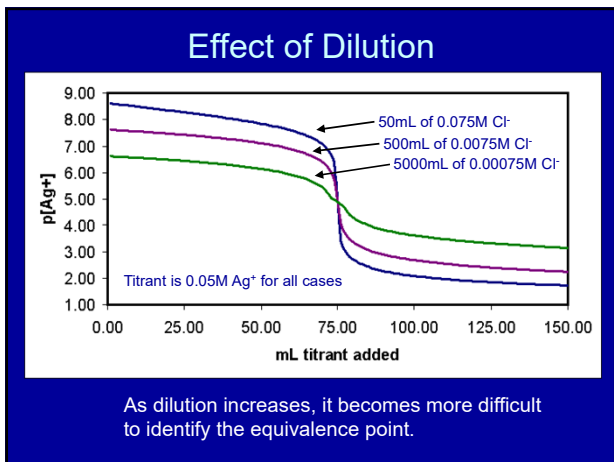
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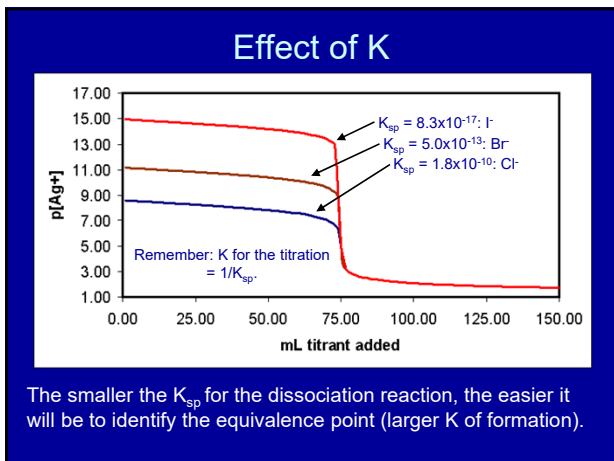
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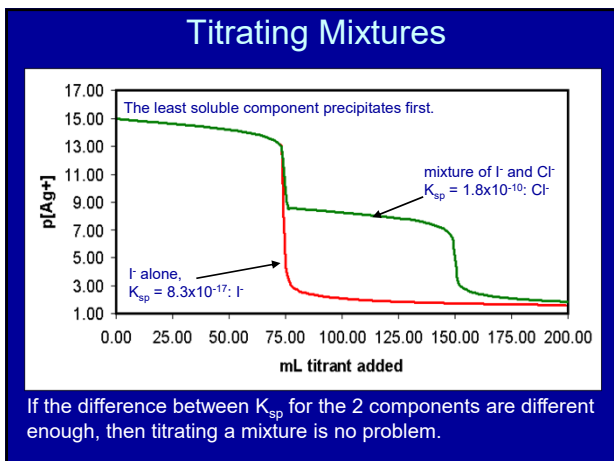
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Indicators for Argentometric Titrations (Involving Ag^+ ions)

(Ag^+ used as titrant or analyte)

- Chemical
 - Chromate Ion as indicating species → Mohr's method
 - Adsorption Indicators (fluorescein) → Fajan's ("Fay'yahns") method
 - Fe(III) Ion → Volhard method
- Sensors –Potentiometric or amperometric
 - We will look at potentiometric sensors later.

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Chromate Ion: The Mohr Method

(Ag^+ used as titrant for Cl^- analysis)


Precipitation Type
 Ag_2CrO_4 precipitation in neutral pH solution (why?) is formed at the end point
 Product is coloured

Titration reaction:
 $Ag^+ + Cl^- \rightleftharpoons AgCl(s)$ [white]

Indication reaction:
 $2Ag^+ + CrO_4^{2-} \rightleftharpoons Ag_2CrO_4(s)$ [red]

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Why neutral pH is required?




K_2CrO_4 Potassium Chromate

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

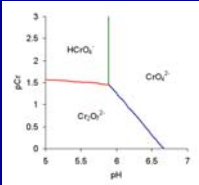
yellow Orange

$HCrO_4^-$

Red-Orange



$K_2Cr_2O_7$ Potassium Dichromate



Partial predominance diagram

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Adsorption indicators: Fajans Method

(Ag^+ used as titrant for Cl^- analysis)

A red dye attaches to the silver salt, on the surface of the analyte precipitate particle.

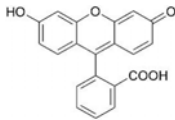
This happens only when the silver ion Ag^+ is in excess, i.e., just after the equivalence point.


Fluorescein (yellow-green in soln)

↓ $AgCl(s)/Ag^+$ (white)


$AgCl(s)/(Ag^+-Fluorescein)_{adsorption}$ (red)

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UV lamp

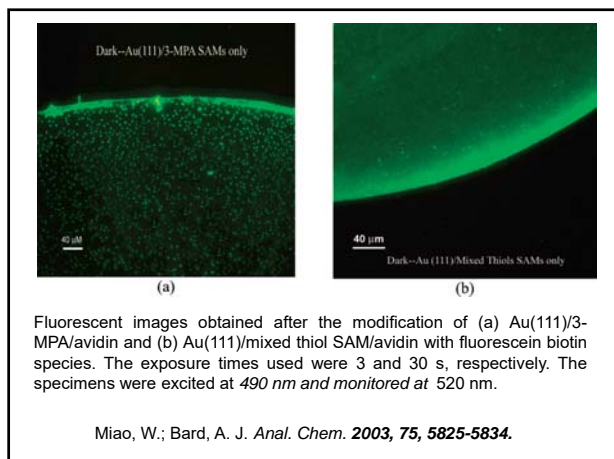


Eye Examination by an eye doctor (optometrist)



Fluorescein imaging of contact lens fit

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Fe(III) Ion: Volhard Method

(Ag⁺ as analyte and SCN⁻ as titrant)

- Chemical method for silver analyses with standard thiocyanate, CNS⁻, as titrant, and Fe (III) is the indicator as it forms a red complex ion with CNS⁻, FeCNS²⁺ (red) [in acidic condition, why?]

Titration reaction:
 $\text{Ag}^+ + \text{SCN}^- \rightleftharpoons \text{AgSCN(s)} \text{ [white]}$

Indication reaction:
 $\text{SCN}^- + \text{Fe}^{3+} \rightleftharpoons \text{FeSCN}^{2+} \text{ (red)}$

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Fe(III) Ion: Volhard Method

The method can be adapted to chloride analyses—back titrations.

$\text{Ag}^+ \text{ (St'd, Excess)} + \text{Cl}^- \text{ (Analyte)} \rightarrow \text{AgCl(s)} \text{ [white]}$

$\text{SCN}^- \text{ (titrant)} + \text{Ag}^+ \text{ (left)} \rightleftharpoons \text{AgSCN(s)} \text{ [white]}$

$\text{Fe}^{3+} + \text{SCN}^- \rightleftharpoons \text{FeSCN}^{2+} \text{ (red)}$

Youtube: Chemical Cut
<https://melscience.com/US-en/articles/chemical-cut-experiment/>

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Applications of Standard AgNO₃ Solutions

TABLE 13-3

Typical Argentometric Precipitation Methods

Substance Being Determined	End Point	Remarks
AsO ₄ ³⁻ , Br ⁻ , I ⁻ , ClO ₃ ⁻ , SCN ⁻	Volhard	Removal of silver salt not required
CO ₃ ²⁻ , CrO ₄ ²⁻ , CN ⁻ , Cl ⁻ , C ₂ O ₄ ²⁻ , PO ₄ ³⁻ , S ²⁻ , NCS ⁻	Volhard	Removal of silver salt required before back-titration of excess Ag ⁺
BH ₄ ⁻	Modified Volhard	Titration of excess Ag ⁺ following BH ₄ ⁻ + 8Ag ⁺ + 8OH ⁻ → 8Ag(s) + H ₂ BO ₃ + 5H ₂ O
Epoxide	Volhard	Titration of excess Cl ⁻ following hydrohalogenation
K ⁺	Modified Volhard	Precipitation of K ⁺ with known excess of H(C ₆ H ₅) ₄ , addition of excess Ag ⁺ giving AgH(C ₆ H ₅) ₄ (s), and back-titration of the excess
Br ⁻ , Cl ⁻	2Ag ⁺ + CrO ₄ ²⁻ → Ag ₂ CrO ₄ (s) red	In neutral solution
Br ⁻ , Cl ⁻ , I ⁻ , SeO ₄ ²⁻	Absorption indicator	Direct titration with Ag ⁺
Vi(OH) ₄ , fatty acids, mercaptans	Electroanalytical	Precipitation as ZnHg(SCN) ₂ , filtration, dissolution in acid
Zn ²⁺	Modified Volhard	addition of excess Ag ⁺ , back-titration of excess Ag ⁺
F ⁻	Modified Volhard	Precipitation as PbClF, filtration, dissolution in acid, addition of excess Ag ⁺ , back-titration of excess Ag ⁺

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Chapter 13 Summary

- Determine analyte by volumetric titrations
- Advantages and disadvantages of volumetric titrations
- Primary and secondary standards, standard solution and standardization
- Back-titrations
- Titration errors
- Endpoint vs equivalence point
- Calculations of titrations
- Precipitation titrations (Argentometry with various indicators)

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