

# **Chapter 7            Titrations**

## **Homework**

Due Friday, February 17

Chapt. 7: 7-2, 7-7, 7-18

# **Chapter 8            Activity**

## **Homework**

Due Friday, February 17

Chapt. 8: 8-1, 8-3, 8-4, 8-5, 8-7, 8-12

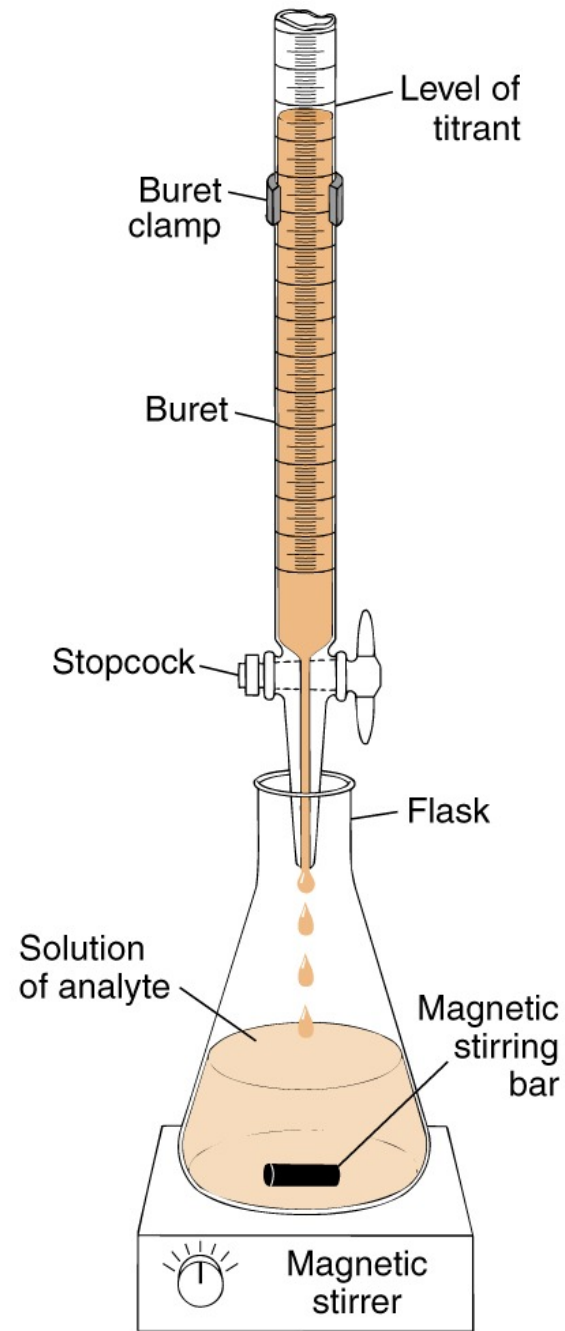
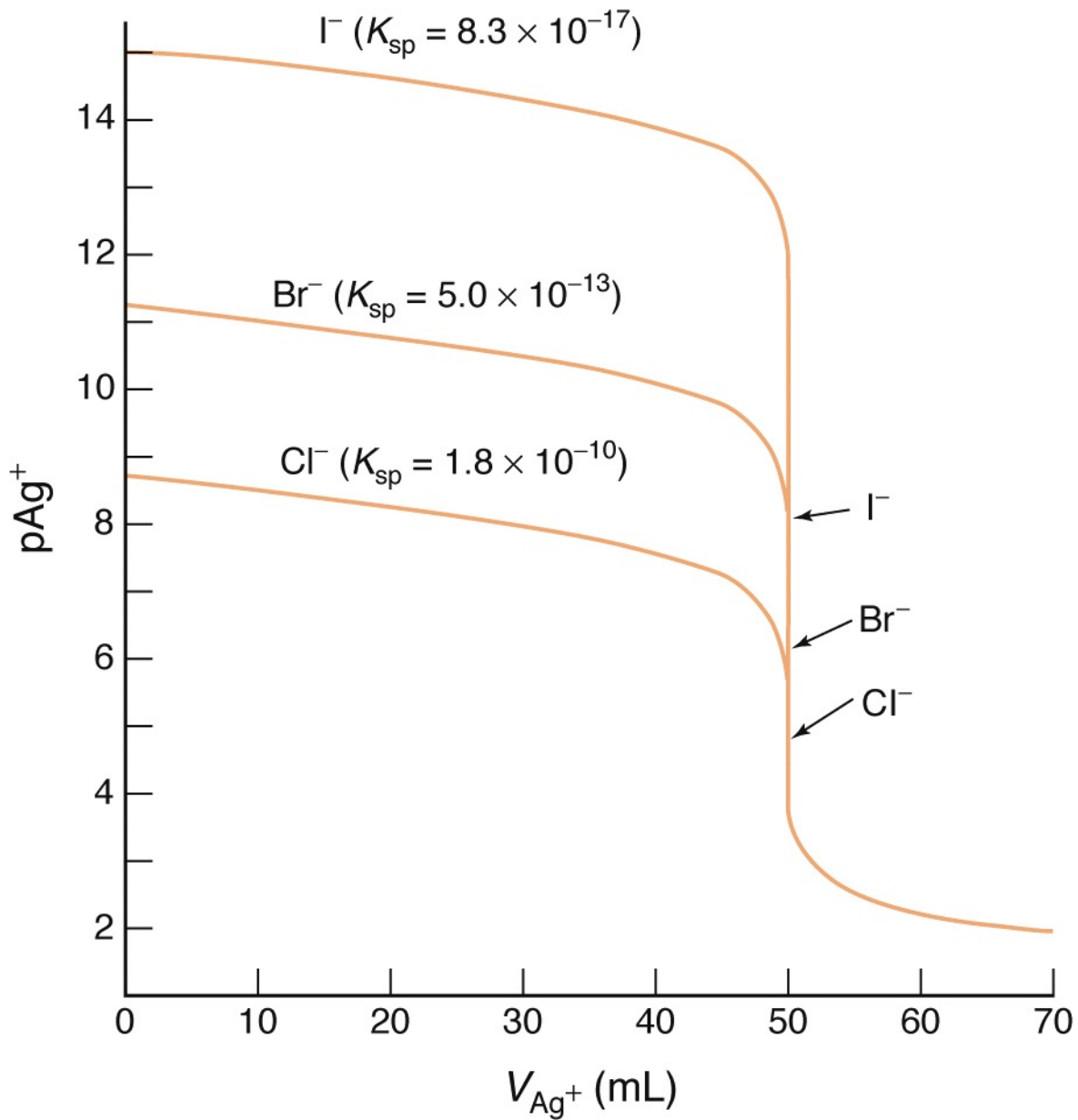
# Chapter 7: Titrations

**Titration** - Incremental addition of a reagent solution (**titrant**) to react with the analyte. From the amount of reagent added, the quantity of analyte can be determined.

**Equivalence point** – when the quantity of added titrant is the exact amount need to stoichiometrically react with the quantity of analyte.

**End point** – the point that is marked by a change in a physical property that signifies that the reaction of the titrant and the analyte is complete. (this is measured experimentally)

**Indicator** – the substance added to the analyte solution that provides the physical change needed to be observed for the end point.



# Requirements for titrant

- Known concentration
- Stable
- Quantitatively added to analyte
- Distinct reaction with analyte

Often titrants must be standardized to get an accurate value for their concentration. A primary standard is used to standardize the titrant. A primary standard should be: *High purity, Stable in air, Absence of hydrate water, Available at moderate cost, Soluble, Large M.W.*

# Precipitation Titration Curve

p-function       $pX = -\log_{10}[X]$

Precipitation titration curve:

four types of calculations

- initial point
- before equivalence point
- equivalence point
- after equivalence point

# 1<sup>st</sup> step in deriving a calibration curve:

*Determine the volume of titrant need to react (titrate) the analyte*

# moles titrant = # moles analyte

$$\text{\#moles}_{\text{analyte}} = (V * M)_{\text{analyte}}$$

$$V_{\text{titrant}} = \text{\# moles}_{\text{analyte}} / M_{\text{titrant}}$$

**EXAMPLE:** Derive a curve for the titration of 50.00 mL of 0.00500 M NaBr with 0.0100 M AgNO<sub>3</sub>.



titration curve => pAg (free Ag) vs. vol. AgNO<sub>3</sub> (titrant) added

**What volume of AgNO<sub>3</sub> is needed to titrate Br<sup>-</sup> ?**

$$\begin{aligned} V_{\text{Br}^-} M_{\text{Br}^-} &= (0.050 \text{ L})(0.00500 \text{ mole/L NaBr}) \\ &= 2.5 \times 10^{-4} \text{ moles Br}^- \end{aligned}$$

$$\begin{aligned} V_{\text{Ag}} (\text{equi pt}) &= (2.5 \times 10^{-4} \text{ moles})(1\text{L}/0.01 \text{ moles}) \\ &= .025 \text{ L (or 25 ml AgNO}_3) \end{aligned}$$

**EXAMPLE:** Derive a curve for the titration of 50.00 mL of 0.00500 M NaBr with 0.0100 M AgNO<sub>3</sub>.

**before equivalence point**

after 5.0 mL of AgNO<sub>3</sub> added

$$M_{\text{NaBr unreacted}} = \frac{V_{\text{NaBr}} * M_{\text{NaBr}} - V_{\text{AgNO}_3} * M_{\text{AgNO}_3}}{V_{\text{NaBr}} + V_{\text{AgNO}_3}}$$

$$M_{\text{NaBr unreacted}} = \frac{(50.00\text{mL} * 0.00500\text{M}) - (5.00\text{mL} * 0.01000\text{M})}{(50.00 + 5.00)\text{mL}}$$

$$M_{\text{NaBr unreacted}} = 3.64 \times 10^{-3}\text{M}$$

**EXAMPLE:** Derive a curve for the titration of 50.00 mL of 0.00500 M NaBr with 0.0100 M AgNO<sub>3</sub>.

**before equivalence point**

after 5.0 mL of AgNO<sub>3</sub> added

$$M_{\text{NaBr unreacted}} = 3.64 \times 10^{-3} \text{M}$$

$$[\text{Br}^-]_{\text{total}} = [\text{Br}^-]_{\text{NaBr unreacted}} + [\text{Br}^-]_{\text{dissolved AgBr}}$$

$$[\text{Br}^-]_{\text{total}} = 3.64 \times 10^{-3} \text{M} + [\text{Ag}^+]_{\text{dissolved AgBr}}$$

where  $[\text{Br}^-]_{\text{dissolved AgBr}} = [\text{Ag}^+]_{\text{dissolved AgBr}}$

**EXAMPLE:** Derive a curve for the titration of 50.00 mL of 0.00500 M NaBr with 0.0100 M AgNO<sub>3</sub>.

**before equivalence point**

after 5.0 mL of AgNO<sub>3</sub> added

$$[\text{Br}^-]_{\text{total}} = 3.64 \times 10^{-3} \text{M} + [\text{Ag}^+]_{\text{dissolved AgBr}}$$

where  $[\text{Br}^-]_{\text{dissolved AgBr}} = [\text{Ag}^+]_{\text{dissolved AgBr}}$

except very near the equivalence point,

$$3.64 \times 10^{-3} \text{M} \gg [\text{Ag}^+]_{\text{dissolved AgBr}}$$

Thus  $[\text{Br}^-]_{\text{total}} \sim 3.64 \times 10^{-3} \text{M}$

**EXAMPLE:** Derive a curve for the titration of 50.00 mL of 0.00500 M NaBr with 0.0100 M AgNO<sub>3</sub>.

**before equivalence point**

after 5.0 mL of AgNO<sub>3</sub> added

$$K_{sp} = [\text{Ag}^+][\text{Br}^-] = 5.2 \times 10^{-13}$$

$$[\text{Ag}^+] = 5.2 \times 10^{-13} / [\text{Br}^-]$$

$$= 5.2 \times 10^{-13} / 3.64 \times 10^{-3}$$

$$= 1.43 \times 10^{-10}$$

$$\text{pAg} = -\log (1.43 \times 10^{-10})$$

$$= 9.84$$

**EXAMPLE:** Derive a curve for the titration of 50.00 mL of 0.00500 M NaBr with 0.0100 M AgNO<sub>3</sub>.  
**equivalence point**

at 25.00 mL of AgNO<sub>3</sub> added

$$K_{sp} = [Ag^+][Br^-] = 5.2 \times 10^{-13}$$

becomes when  $[Ag^+] = [Br^-]$

$$[Ag^+]^2 = 5.2 \times 10^{-13} M^2$$

$$[Ag^+] = 7.21 \times 10^{-7} M$$

$$pAg = -\log [Ag^+] = -\log[7.2 \times 10^{-7}]$$

$$pAg = 6.14$$

**EXAMPLE:** Derive a curve for the titration of 50.00 mL of 0.00500 M NaBr with 0.0100 M AgNO<sub>3</sub>.

### **after equivalence point**

After the equivalence point there is very little change in the amount of precipitate present (except very close to the equivalence point).

Thus, at 25.10 mL of AgNO<sub>3</sub> added

$$M_{\text{AgNO}_3 \text{ unreacted}} = \frac{V_{\text{AgNO}_3} * M_{\text{AgNO}_3} - V_{\text{NaBr}} * M_{\text{NaBr}}}{V_{\text{AgNO}_3} + V_{\text{NaBr}}}$$

**EXAMPLE:** Derive a curve for the titration of 50.00 mL of 0.00500 M NaBr with 0.0100 M AgNO<sub>3</sub>.

**after equivalence point**

$$M_{\text{AgNO}_3 \text{ unreacted}} = \frac{V_{\text{AgNO}_3} * M_{\text{AgNO}_3} - V_{\text{NaBr}} * M_{\text{NaBr}}}{V_{\text{AgNO}_3} + V_{\text{NaBr}}}$$

$$M_{\text{AgNO}_3 \text{ unreacted}} = \frac{(25.10 \text{ mL} * 0.01000 \text{ M}) - (50.00 \text{ mL} * 0.00500 \text{ M})}{(25.10 + 50.00)\text{mL}}$$

$$M_{\text{AgNO}_3 \text{ unreacted}} = 1.33 \times 10^{-5} \text{ M}$$

**EXAMPLE:** Derive a curve for the titration of 50.00 mL of 0.00500 M NaBr with 0.0100 M AgNO<sub>3</sub>.

**after equivalence point**

thus, at 25.10 mL of AgNO<sub>3</sub> added

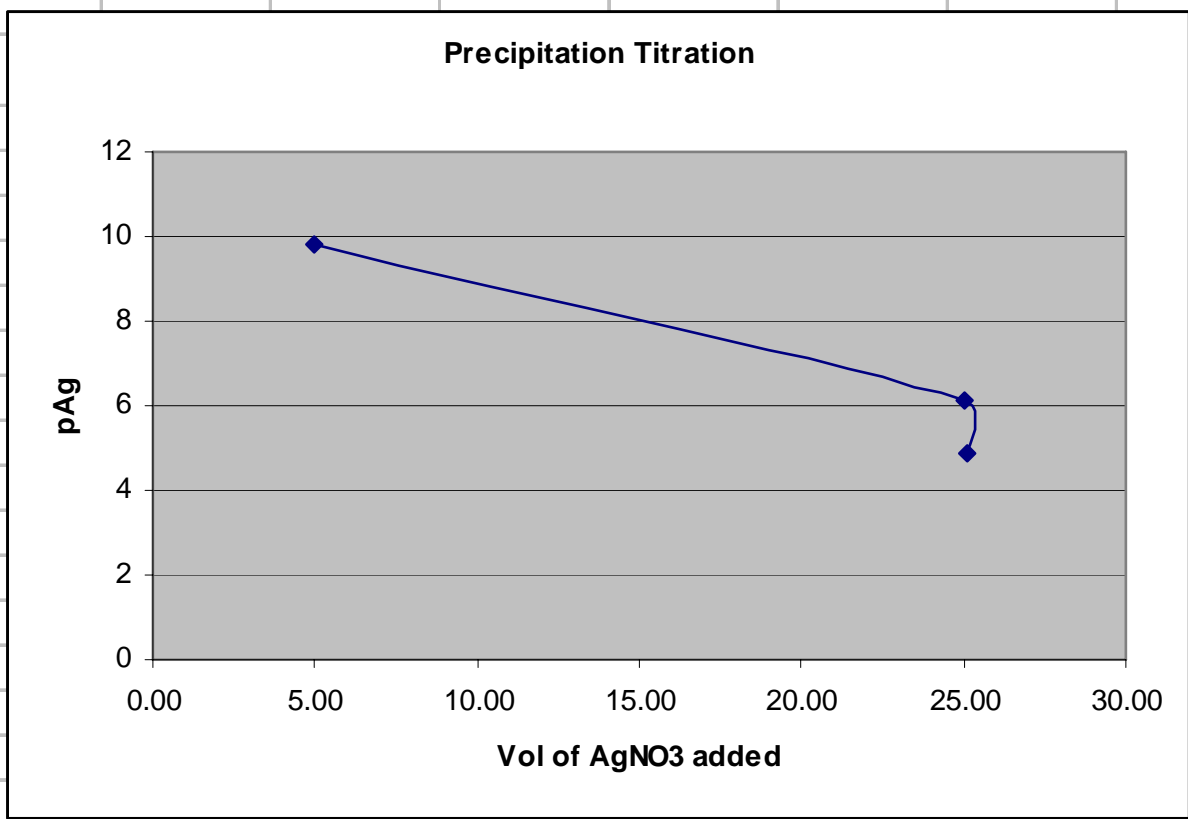
$$[\text{Ag}^+]_{\text{total}} = [\text{Ag}^+]_{\text{AgNO}_3 \text{ unreacted}} + [\text{Ag}^+]_{\text{dissolved}}$$

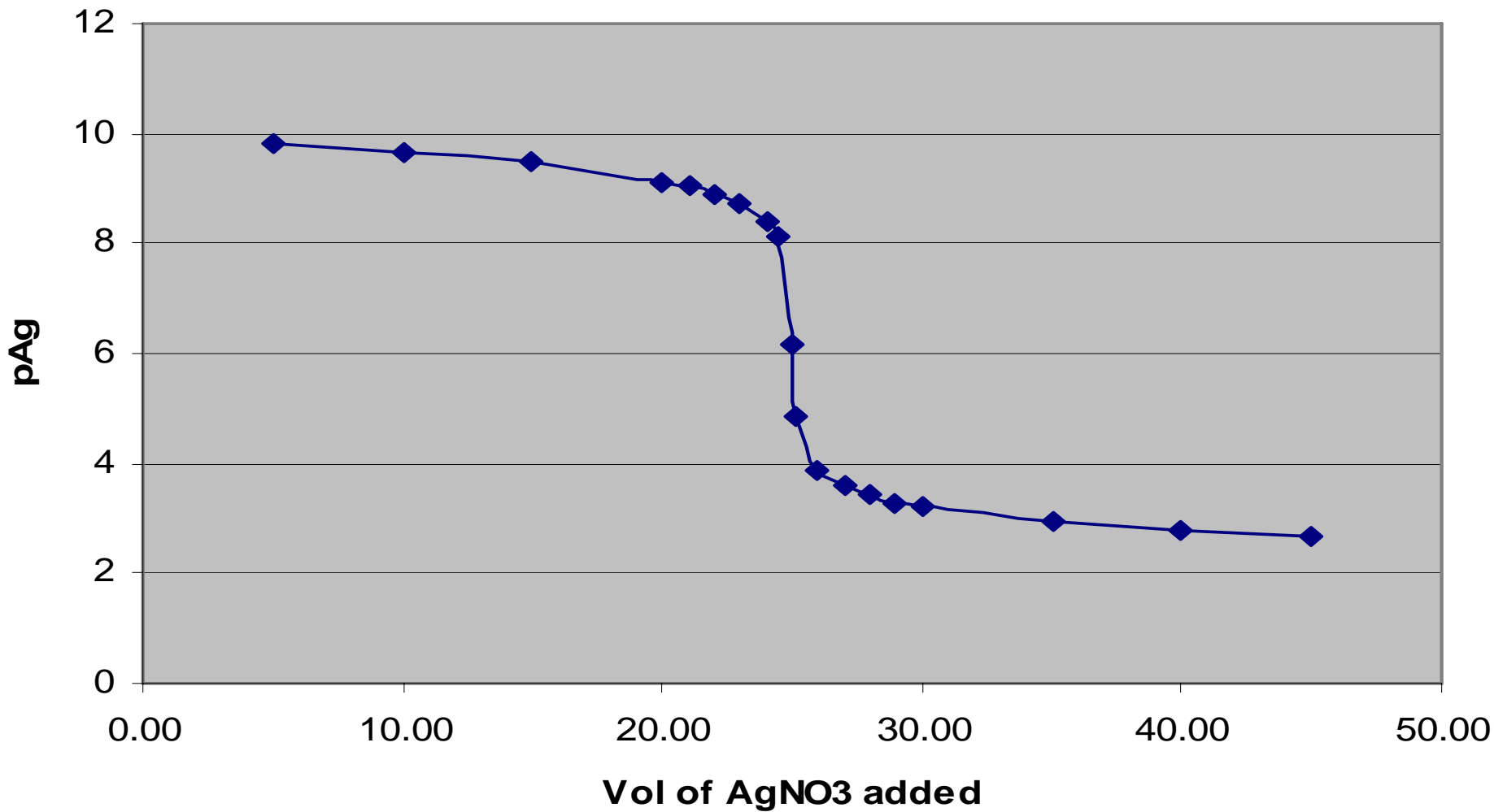
$$[\text{Ag}^+]_{\text{total}} = 1.33 \times 10^{-5} \text{M} + \overset{0 \text{ AgBr}}{\cancel{[\text{Ag}^+]_{\text{dissolved AgBr}}}}$$

$$[\text{Ag}^+]_{\text{total}} \sim 1.33 \times 10^{-5} \text{M}$$

$$\text{pAg} = -\log [\text{Ag}^+] = -\log (1.33 \times 10^{-5}) = 4.88$$

| Vol of | pAg  |
|--------|------|
| 5.00   | 9.84 |
| 25.00  | 6.14 |
| 25.10  | 4.88 |





# Real World Uses of Titrations

- Complexometric Titration — Determination of water hardness
- Gravimetric Methods — Determination of Chloride
- Precipitation Titration — Determination of Chloride by Fajans Methods
- Acid/Base Titration – Alkalinity (Bicarbonate in natural waters)