Titrimetry based on complexation

Questions

What is the main principle of titrimetry?

What is the analytical signal in titrimetry?

Formation of complexes

$$Ag^+ + 2CN^- \leftrightarrow [Ag(CN)_2]^-$$

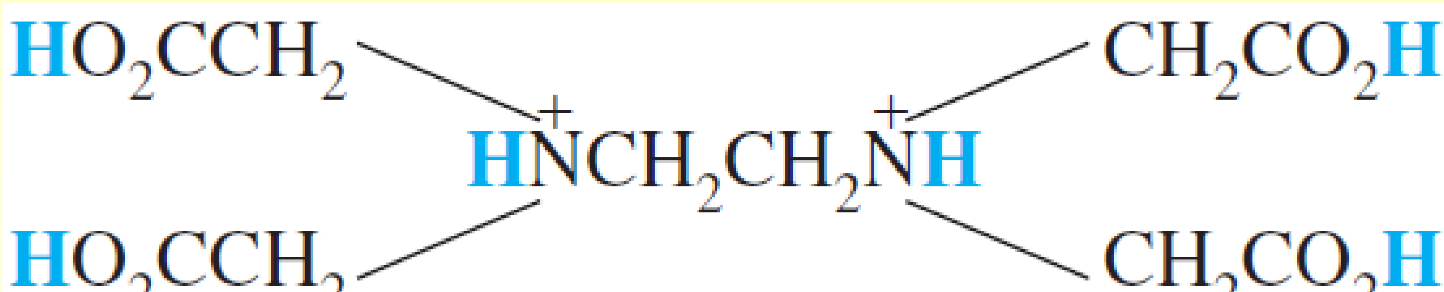
Formation constants

$$Ag^+ + CN^- \leftrightarrow [AgCN] \qquad \beta_1 = \frac{[AgCN^-]}{[Ag^+][CN^-]}$$

$$Ag(CN) + CN^- \leftrightarrow [Ag(CN)_2]^- \qquad \beta_2 = \frac{[Ag(CN)_2^-]}{[Ag^+][CN^-]}$$

$$\beta = \beta_1 \cdot \beta_2 \qquad \beta = \frac{[Ag(CN)_2^-]}{[Ag^+][CN^-]}$$

EDTA

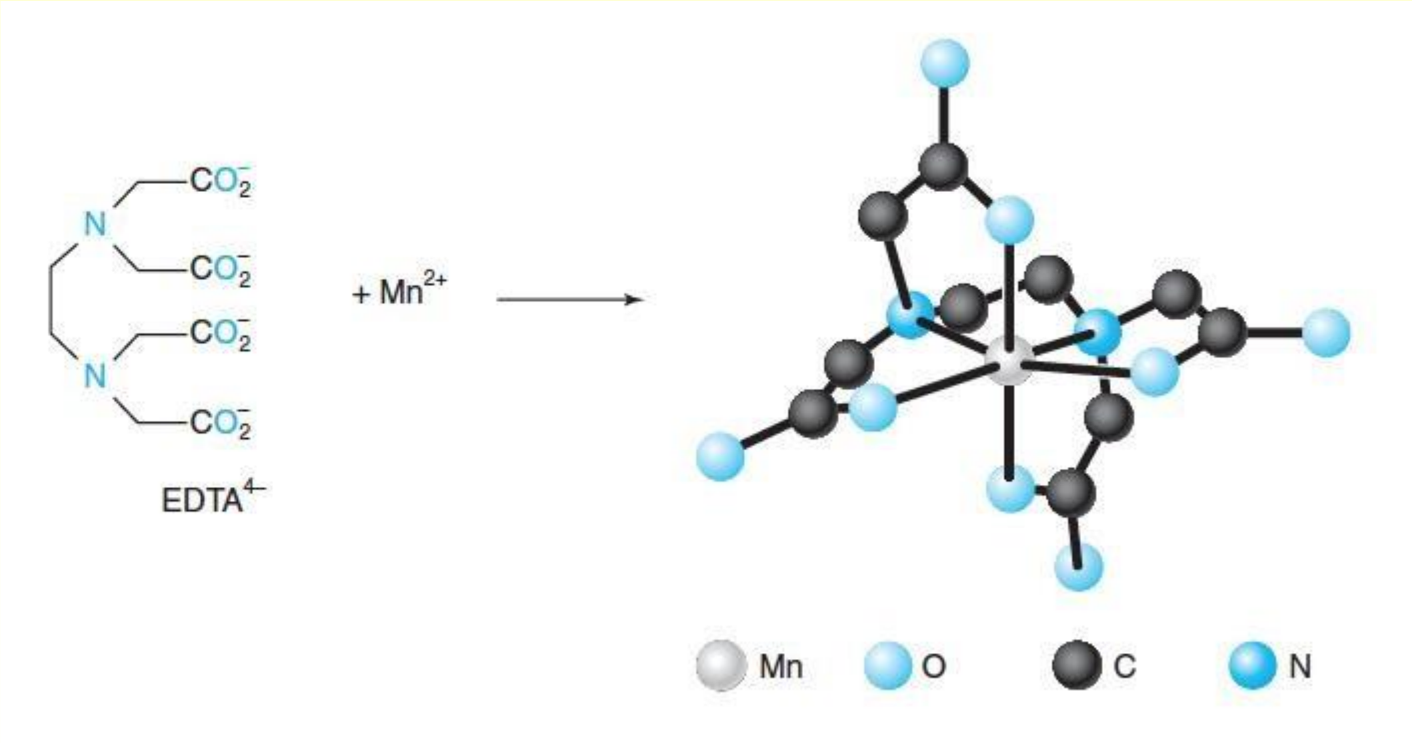


H_6Y^{2+}

Ethylenediaminetetraacetic acid

EDTA forms 1:1 complexes with most metals

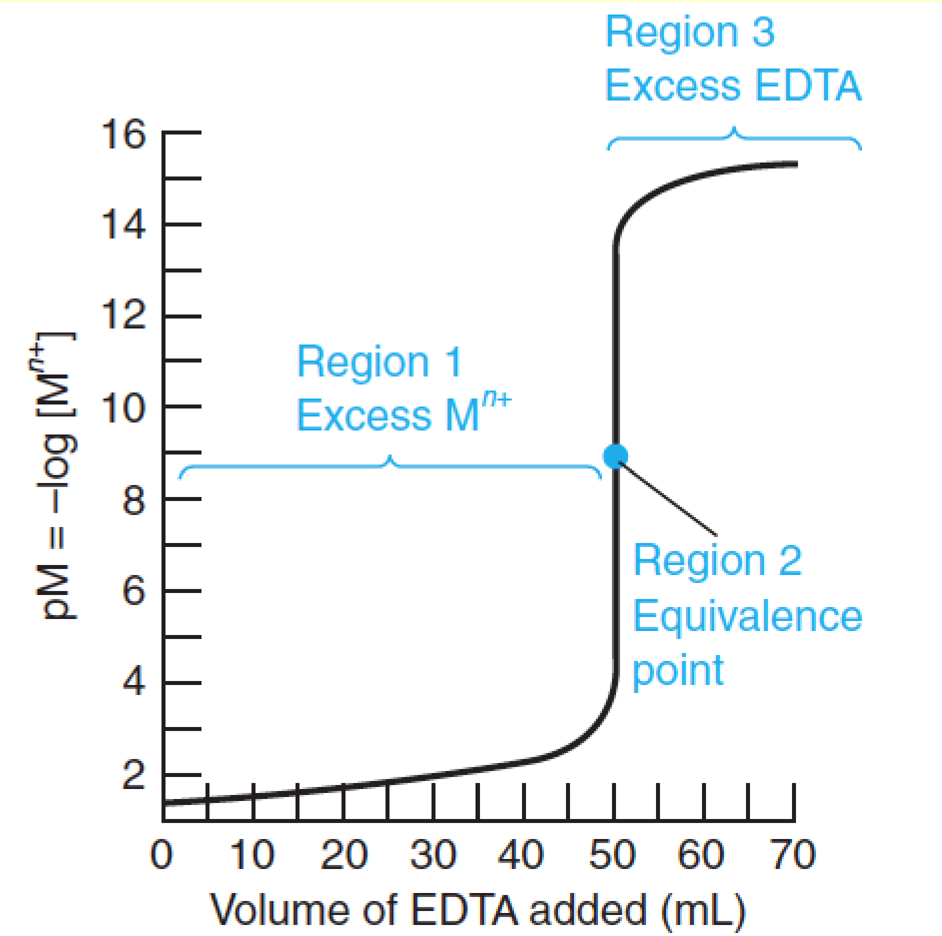
EDTA + Mn^{2+}



Formation constants

Ion	log K_f	Ion	log K_f	Ion	log K_f
Li^+	2.95	V^{3+}	25.9[a]	Tl^{3+}	35.3
Na^+	1.86	Cr^{3+}	23.4[a]	Bi^{3+}	27.8[a]
K^+	0.8	Mn^{3+}	25.2	Ce^{3+}	15.93
Be^{2+}	9.7	Fe^{3+}	25.1	Pr^{3+}	16.30
Mg^{2+}	8.79	Co^{3+}	41.4	Nd^{3+}	16.51
Ca^{2+}	10.65	Zr^{4+}	29.3	Pm^{3+}	16.9
Sr^{2+}	8.72	Hf^{4+}	29.5	Sm^{3+}	17.06
Ba^{2+}	7.88	VO^{2+}	18.7	Eu^{3+}	17.25
Ra^{2+}	7.4	VO_2^+	15.5	Gd^{3+}	17.35
Sc^{3+}	23.1[a]	Ag^+	7.20	Tb^{3+}	17.87
Y^{3+}	18.08	Tl^+	6.41	Dy^{3+}	18.30
La^{3+}	15.36	Pd^{2+}	25.6[a]	Ho^{3+}	18.56
V^{2+}	12.7[a]	Zn^{2+}	16.5	Er^{3+}	18.89
Cr^{2+}	13.6[a]	Cd^{2+}	16.5	Tm^{3+}	19.32
Mn^{2+}	13.89	Hg^{2+}	21.5	Yb^{3+}	19.49
Fe^{2+}	14.30	Sn^{2+}	18.3[b]	Lu^{3+}	19.74
Co^{2+}	16.45	Pb^{2+}	18.0	Th^{4+}	23.2
Ni^{2+}	18.4	Al^{3+}	16.4	U^{4+}	25.7
Cu^{2+}	18.78	Ga^{3+}	21.7		
Ti^{3+}	21.3	In^{3+}	24.9		

Titration curve



Before titration

$$[M] = C_0$$

$$pM = -\lg C_0$$

Before the equivalence point

Excess of metal ion is present

$$[\mathrm{M}] = \frac{moles\ of\ untitrated\ \mathrm{M}}{total\ volume} = \frac{C_0 \times V_0 - C_\mathrm{T} \times V_\mathrm{T}}{V_0 + V_\mathrm{T}}$$

At the equivalence point

$$K' = \frac{[\mathrm{MY}]}{[\mathrm{M}]\,[EDTA]} = \frac{[MY]}{[\mathrm{M}]^2}$$

$$[MY] = \frac{C_0 \times V_0}{V_0 + V_t}$$

$$[\mathrm{M}] = \sqrt{\frac{[MY]}{K'}}$$

After equivalence point

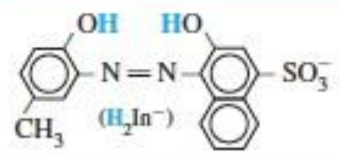
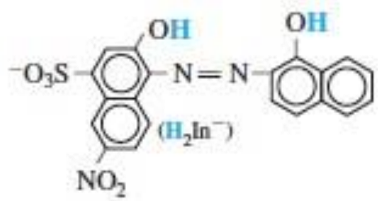
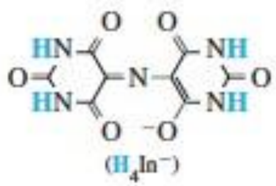
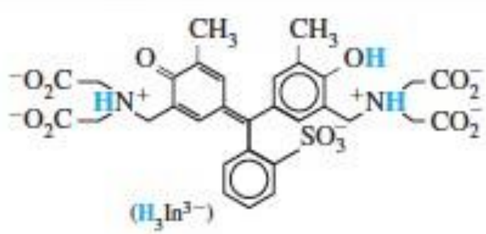
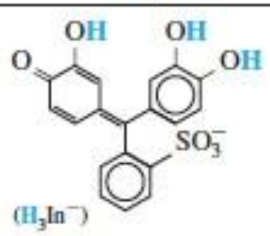
Excess of EDTA in the solution

$$[M] = \frac{[MY]}{K' \times [EDTA]}$$

$$[MY] = \frac{C_0 \times V_0}{V_0 + V_t}$$

$$[EDTA] = \frac{n\ moles\ of\ excess\ EDTA}{total\ volume} = \frac{C_t \times V_t - C_0 \times V_0}{V_0 + V_t}$$

Indicators

Name	Structure	pK_a	Color of free indicator	Color of metal ion complex
Calmagite		$pK_2 = 8.1$ $pK_3 = 12.4$	H_2In^- red HIn^{2-} blue In^{3-} orange	Wine red
Eriochrome black T		$pK_2 = 6.3$ $pK_3 = 11.6$	H_2In^- red HIn^{2-} blue In^{3-} orange	Wine red
Murexide		$pK_2 = 9.2$ $pK_3 = 10.9$	H_4In^- red-violet H_3In^{2-} violet H_2In^{3-} blue	Yellow (with Co^{2+}, Ni^{2+}, Cu^{2+}); red with Ca^{2+}
Xylenol orange		$pK_2 = 2.32$ $pK_3 = 2.85$ $pK_4 = 6.70$ $pK_5 = 10.47$ $pK_6 = 12.23$	H_5In^- yellow H_4In^{2-} yellow H_3In^{3-} yellow H_2In^{4-} violet HIn^{5-} violet In^{6-} violet	Red
Pyrocatechol violet		$pK_1 = 0.2$ $pK_2 = 7.8$ $pK_3 = 9.8$ $pK_4 = 11.7$	H_4In red H_3In^- yellow H_2In^{2-} violet HIn^{3-} red-purple	Blue

Precipitation titrimetry

$$nA^+ + mB^- \leftrightarrow A_nB_m\downarrow$$

$$K_{sp}(A_nB_m) = [A^+]^n \cdot [B^-]^m = const$$

Precipitate should have low K_{sp}

Types

Argentometric (by $AgNO_3$):

$$Ag^+ + An^- \leftrightarrow AgAn\downarrow$$

Thiocyanite (by NH_4CNS):

$$Ag^+ + CNS^- \rightarrow AgCNS\downarrow$$

Mercurometric (by $Hg2(NO_3)_2$):

$$2Cl^- + Hg_{2_{2+}} \rightarrow Hg_2Cl_2\downarrow$$

Before titration

$$[A] = C_0$$

$$pA = -\lg C_0$$

Before equivalence point

$$[\mathrm{A}] = \frac{mole\ of\ untitrated\ \mathrm{A}}{total\ volume} = \frac{C_0 \times V_0 - C_\mathrm{T} \times V_\mathrm{T}}{V_0 + V_t}$$

if $C_0 = C_\mathrm{T}$:

$$[\mathrm{A}] = \frac{C_0(V_0 - V_\mathrm{T})}{V_0 + V_t}$$

At the equivalence point

$$[\mathrm{A}] = [\mathrm{B}] = \sqrt{K^{\circ}_{s(\mathrm{AB})}}$$

After equivalence point

Excess of titrant

$$[\mathrm{A}] = \frac{K^{\circ}_{s(\mathrm{AB})}}{[\mathrm{B}]} \quad и \quad \mathrm{pA} = \mathrm{p}K^{\circ}_{s(\mathrm{AB})} - \mathrm{pB}$$

$$[\mathrm{B}] = \frac{moles\ of\ excess\ \mathrm{B}}{total\ volume} = \frac{C_0 \times V_0 - C_{\mathrm{T}} \times V_t}{V_0 + V_t}$$

if $C_0 = C_t$:

$$[\mathrm{B}] = \frac{C_0(V_0 - V_t)}{V_0 + V_t}$$