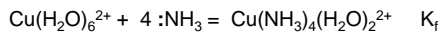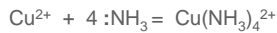## Complexometric Titrations

Most <u>metal ions</u> form very stable <u>complexes</u> ($K_f >> 1$) readily with reagents having <u>electron donor groups</u> (ligands). The number of coordinate bonds formed with ligands equals the coordination number of metal ion in that complex.

Uni-dentate:

$$Cu^{2+} + 4 :NH_3 = Cu(NH_3)_4^{2+}$$

$$Cu(H_2O)_6^{2+} + 4 :NH_3 = Cu(NH_3)_4(H_2O)_2^{2+} \quad K_f$$

A multi-step process, as many molecules are bonded sequentially. Formation constant values differ and decreases with the increasing number 'steps' of formation.

The complexes form when;

1. The central atom (metal) accepts an electron pair(s) from one or more ligands.
2. The ligand possesses at least one electron pair to donate.
3. Bonding (coordinate covalent bonding) occurs between the metal ion and the ligand.

A number of common anionic and molecular ligands that can form complexes are:

<u>Anionic ligands</u> include halides, SCN^{1-}, CN^{1-}, OH^{1-}, $RCOO^{1-}$, S^{2-}, $C_2O_4^{2-}$ (oxalate), etc.

<u>Molecular ligands</u> include water, ammonia, RNH_2 (amines) C_5H_5N (pyridine) $H_2NCH_2CH_2NH_2$ (ethylenediamine), etc.

Complexes where M^{+n} forms *more than one bond* per ligand (*multidentate*) are termed *<u>chelates</u>*, e.g. bidentate ligand (glycine) forms a "<u>chelate ring</u>."
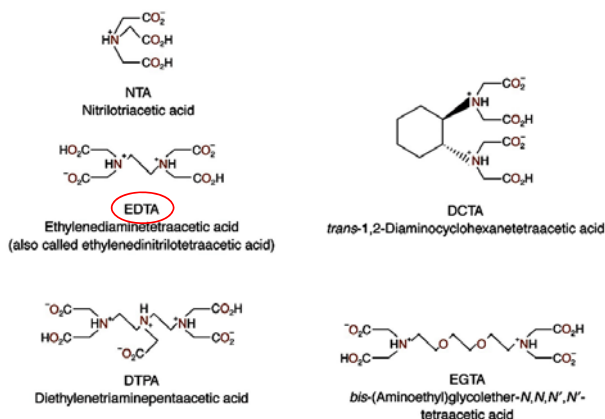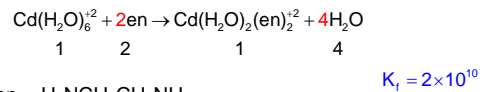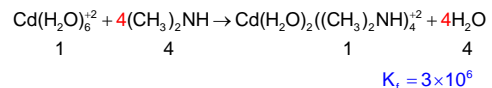
As titrants for measuring metal ions, multidentate ligands are preferred (less number of 'steps' to form the complex), larger K_f values, giving sharper end/equivalence points.


glycine   partial structure
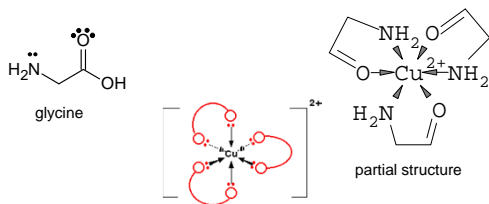
Chelate Effect:

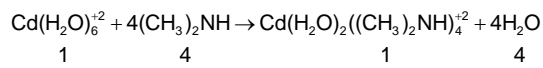$K_{f, chelate} >> K_{f, monodentate}$

Driving force of chelation: Entropy effect - entropy gain (more disordered product side) is higher for reactions involving multidentate ligands, chelates, compared to those with monodentate ligands.
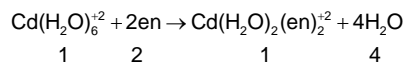
$$Cd(H_2O)_6^{+2} + 4(CH_3)_2NH \rightarrow Cd(H_2O)_2((CH_3)_2NH)_4^{+2} + 4H_2O$$
$$\quad\quad 1 \quad\quad\quad\quad 4 \quad\quad\quad\quad\quad\quad 1 \quad\quad\quad\quad 4$$

$$K_f = 3 \times 10^6$$

$$Cd(H_2O)_6^{+2} + 2en \rightarrow Cd(H_2O)_2(en)_2^{+2} + 4H_2O$$
$$\quad\quad 1 \quad\quad 2 \quad\quad\quad\quad 1 \quad\quad\quad 4$$

$$K_f = 2 \times 10^{10}$$

$en = H_2NCH_2CH_2NH_2$

NTA
Nitrilotriacetic acid

EDTA
Ethylenediaminetetraacetic acid
(also called ethylenedinitrilotriacetic acid)

DCTA
trans-1,2-Diaminocyclohexanetetraacetic acid

DTPA
Diethylenetriaminepentaacetic acid

EGTA
bis-(Aminoethyl)glycolether-*N,N,N',N'*-tetraacetic acid

EDTA, H_4Y, (tetraacetate ion, Y^{-4}) is a widely used chelating (hexadentate) ligand. <u>One step process</u>, i.e. no intermediate species.
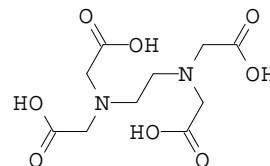
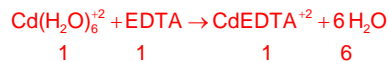Hexadentate EDTA generate the titration curves with sharp end points.
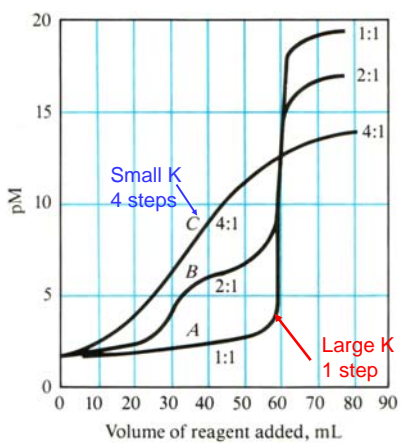
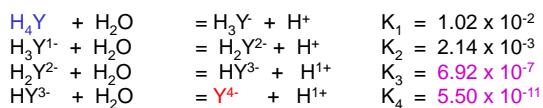$$Cd(H_2O)_6^{+2} + 4(CH_3)_2NH \rightarrow Cd(H_2O)_2((CH_3)_2NH)_4^{+2} + 4H_2O$$
$$\quad 1 \qquad\qquad 4 \qquad\qquad\qquad 1 \qquad\qquad 4$$
$$K_f = 3 \times 10^6$$

$$Cd(H_2O)_6^{+2} + 2en \rightarrow Cd(H_2O)_2(en)_2^{+2} + 4H_2O$$
$$\quad 1 \qquad 2 \qquad\qquad 1 \qquad\qquad 4$$
$$K_f = 2 \times 10^{10}$$

$$Cd(H_2O)_6^{+2} + EDTA \rightarrow CdEDTA^{+2} + 6H_2O$$
$$\quad 1 \qquad 1 \qquad\qquad 1 \qquad\qquad 6$$
$$K_f > 10^{16}$$

Y^{4-}

$+ Mn^{2+} \rightarrow$

EDTA^{4-}

○ Mn ○ O ● C ○ N

Small K
4 steps

Large K
1 step

EDTA dissociation constants: weak acidity.

H_4Y	$+ H_2O$	$= H_3Y^-$	$+ H^+$	$K_1 =$	1.02×10^{-2}
H_3Y^{1-}	$+ H_2O$	$= H_2Y^{2-}$	$+ H^+$	$K_2 =$	2.14×10^{-3}
H_2Y^{2-}	$+ H_2O$	$= HY^{3-}$	$+ H^{1+}$	$K_3 =$	6.92×10^{-7}
HY^{3-}	$+ H_2O$	$= Y^{4-}$	$+ H^{1+}$	$K_4 =$	5.50×10^{-11}

Further, it is insoluble. At pH~7, $[Y^{-4}]$ - insignificant.

At pH >10; $[Y^{-4}]$ - significant, dominates.
$Y^{-4} = EDTA^{-4}$

Fractional Composition
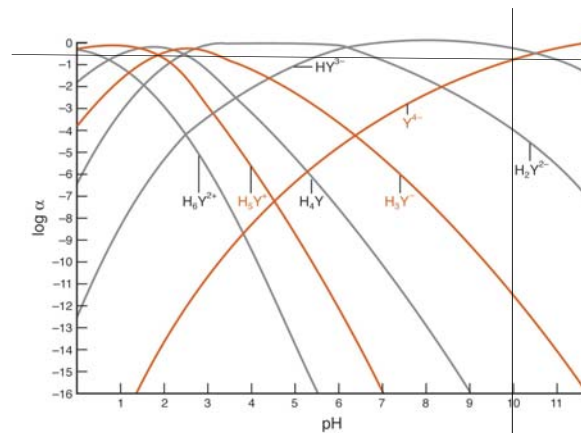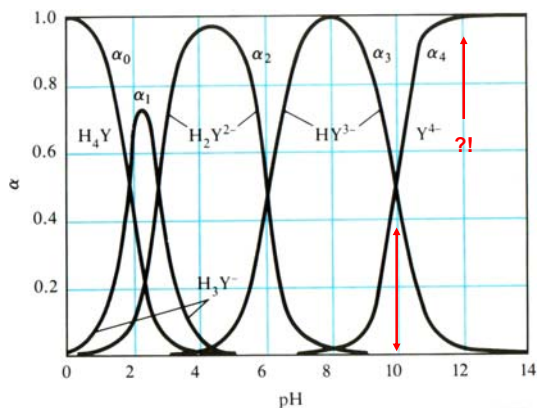
Table 13-1	Values of α_{Y4-} for EDTA at 20°C and $\mu = 0.10$ M
pH	α_{Y4-}
0	1.3×10^{-23}
1	1.9×10^{-18}
2	3.3×10^{-14}
3	2.6×10^{-11}
4	3.8×10^{-9}
5	3.7×10^{-7}
6	2.3×10^{-5}
7	5.0×10^{-4}
8	5.6×10^{-3}
9	5.4×10^{-2}
10	0.36
11	0.85
12	0.98
13	1.00
14	1.00

Generic reaction:

$$H_4Y + M^{+n} \rightleftarrows MY^{+n-4} + 4H^+$$
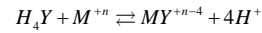
$$K_f' = \frac{[MY^{+n-4}][H^+]^4}{[H_4Y][M^{+n}]}$$

Effective K'_f = f(pH)
Conditional equilibrium constant.

Small [H⁺], large pH of medium; leads to large K_f'.

The formation constant of EDTA complexes are pH dependent.

At buffer pH > 10, EDTA exists mostly in the Y^{-4} form.

(At lower pH, Y^{-4} combines with H⁺ ions, thus at low pH, Y^{-4} is in competition for H⁺ and metal ions.)
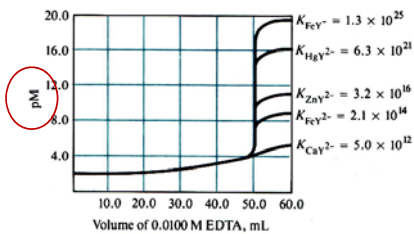
The affinity of different metal ions to Y^{-4} is vastly different. Therefore for each ion there is a _minimum pH_ needed for the formation of an analytically _satisfactory_ complexation.

The minimum pH required to override the competition of Y^{-4} to protons and seek a given metal ion M^{+n} can be determined.
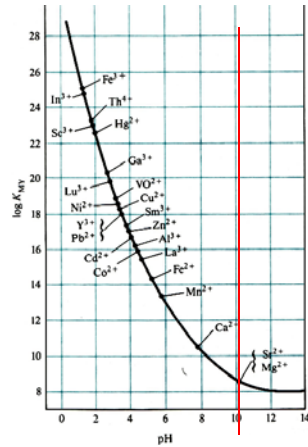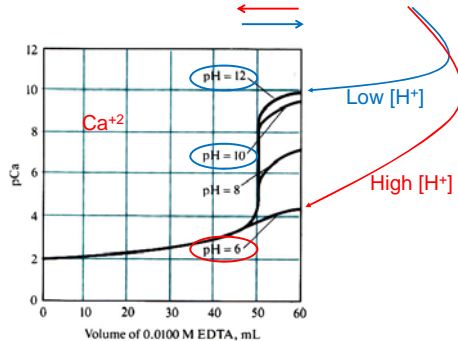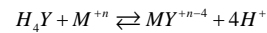

Minimum pH required for quantification i.e. K sufficiently large.

Functional/effective K'_f =f(pH)

$K_{FeY^-} = 1.3 \times 10^{25}$
$K_{HgY^{2-}} = 6.3 \times 10^{21}$
$K_{ZnY^{2-}} = 3.2 \times 10^{16}$
$K_{FeY^{2-}} = 2.1 \times 10^{14}$
$K_{CaY^{2-}} = 5.0 \times 10^{12}$

Volume of 0.0100 M EDTA, mL

@ pH=6

Functional/effective K'_f =f(pH)

$$H_4Y + M^{+n} \rightleftarrows MY^{+n-4} + 4H^+$$

Ca⁺²

pH = 12
pH = 10
pH = 8
pH = 6

Low [H⁺]

High [H⁺]

Volume of 0.0100 M EDTA, mL

Functional/effective $K'_f = f(pH)$

@ pH=6
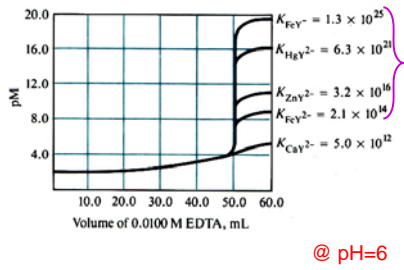
Table 13-2 Formation constants for metal-EDTA complexes

| Ion	log K_f	Ion	log K_f	Ion	log K_f
Li^+	2.79	Mn^{3+}	25.3 (25°C)	Ce^{3+}	15.98
Na^+	1.66	Fe^{3+}	25.1	Pr^{3+}	16.40
K^+	0.8	Co^{3+}	41.4 (25°C)	Nd^{3+}	16.61
Be^{2+}	9.2	Zr^{4+}	29.5	Pm^{3+}	17.0
Mg^{2+}	8.79	Hf^{4+}	29.5 ($\mu = 0.2$)	Sm^{3+}	17.14
Ca^{2+}	10.69	VO^{2+}	18.8	Eu^{3+}	17.35
Sr^{2+}	8.73	VO_2^+	15.55	Gd^{3+}	17.37
Ba^{2+}	7.86	Ag^+	7.32	Tb^{3+}	17.93
Ra^{2+}	7.1	Tl^+	6.54	Dy^{3+}	18.30
Sc^{3+}	23.1	Pd^{2+}	18.5 (25°C,	Ho^{3+}	18.62
Y^{3+}	18.09		$\mu = 0.2$)	Er^{3+}	18.85
La^{3+}	15.50	Zn^{2+}	16.50	Tm^{3+}	19.32
V^{2+}	12.7	Cd^{2+}	16.46	Yb^{3+}	19.51
Cr^{2+}	13.6	Hg^{2+}	21.7	Lu^{3+}	19.83
Mn^{2+}	13.87	Sn^{2+}	18.3 ($\mu = 0$)	Am^{3+}	17.8 (25°C)
Fe^{2+}	14.32	Pb^{2+}	18.04	Cm^{3+}	18.1 (25°C)
Co^{2+}	16.31	Al^{3+}	16.3	Bk^{3+}	18.5 (25°C)
Ni^{2+}	18.62	Ga^{3+}	20.3	Cf^{3+}	18.7 (25°C)
Cu^{2+}	18.80	In^{3+}	25.0	Th^{4+}	23.2
Ti^{3+}	21.3 (25°C)	Tl^{3+}	37.8 ($\mu = 1.0$)	U^{4+}	25.8
V^{3+}	26.0	Bi^{3+}	27.8	Np^{4+}	24.6 (25°C, $\mu = 1.0$)
Cr^{3+}	23.4				

NOTE: The formation constant is the equilibrium constant for the reaction $M^{n+} + Y^{4-} \rightleftharpoons MY^{n-4}$. Values in table apply at 20°C, and ionic strength 0.1 M, unless otherwise noted.
SOURCE: A. E. Martell and R. M. Smith, Critical Stability Constants, Vol. 1 (New York: Plenum Press, 1974), pp. 204–211.

Mg(II) and Ca(II) K'_f; 6.16×10^8 , 4.8×10^{10} at pH = 10.

Titrated separately, Mg(II) and Ca(II) can be quantitated. Difference in K values does not permit analysis *for each ion separately* when in a mixture in *one* titration procedure. (because of the non-appearance of two sigmoids, one after another)

Total hardness (Ca(II) + Mg(II)) determination, feasible however.

The optimum pH for Ca(II) analysis is 10, but pH as low as 8 gives acceptable titration curves because of large K'_f.
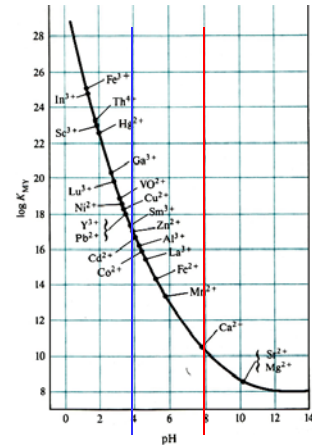
Minimum pH required for quantification i.e. K sufficiently large.

At high pH (=10, basic) some M^{+n} ions _precipitate_ as hydroxides, and in such cases direct titration is not possible.

Ex. Zn(II); Strategy - before buffering the solution add ammonia to form $Zn(NH_3)_4^{+2}$ complex ion, and titrate vs EDTA. $K_{zn\text{-}EDTA}^{-2} > K_{zn(NH3)4}^{+2}$.

However, this modification drastically changes the pZn value, shortening the pZn change at the end point, less sharper end point.

If K_f value is sufficiently large, affinity of Y^{-4} for M^{+n} is significant, then even at pH=6 yields acceptable titration curves (Fe(III)).
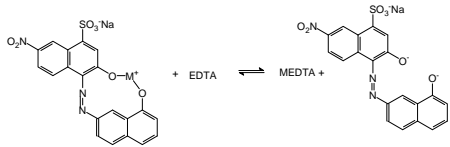
Color Indicators for EDTA titrations:

Metal ion complexometric indicator – a weaker chelating agent than EDTA. e,.g. Eriochrome Black T.
(H_2In^-, type; may be used as an acid - base indicator, too)

Eriochrome Black T
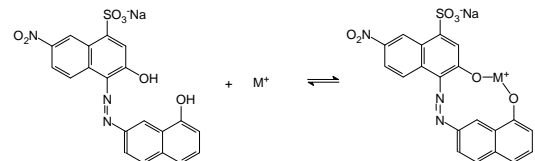
Color 1
Before end point

4

Color 1   Color 2

Just after end point

$+$ EDTA $\rightleftharpoons$ MEDTA $+$

Table 13-3 Common metal ion indicators

Name	Structure	pK_a	Color of free indicator	Color of metal ion complex
Eriochrome black T		$pK_2 = 6.3$ $pK_3 = 11.6$	H_2In^- red HIn^{2-} blue In^{3-} orange	Wine red
Calmagite		$pK_2 = 8.1$ $pK_3 = 12.4$	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		$pK_2 = 2.32$ $pK_3 = 2.85$ $pK_4 = 6.70$ $pK_5 = 10.47$	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

PREPARATION AND STABILITY:
Eriochrome black T: Dissolve 0.1 g of the solid in 7.5 mL of triethanolamine plus 2.5 mL of absolute ethanol; solution is stable for months; best used for titrations above pH 6.5.
Calmagite: 0.05 g/100 mL, H_2O; solution is stable for a year in the dark.
Murexide: Grind 10 mg of murexide with 5 g of reagent NaCl in a clean mortar; use 0.2–0.4 g of the mixture for each titration.
Xylenol orange: 0.5 g/100 mL, H_2O; solution is stable indefinitely.
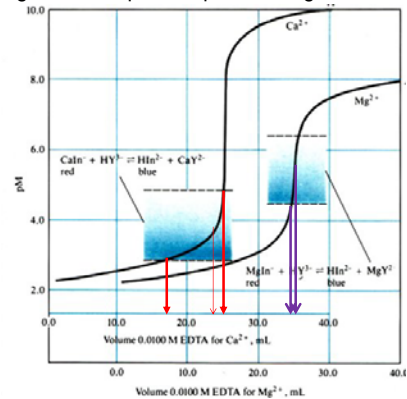Pyrocatechol violet: 0.1 g/100 mL; solution is stable for several weeks.

Which ion gives a sharper end point? Mg^{+2}

Types of EDTA titrations: Direct titration:

unknown M^{+n} + indicator (or ISE for M^{+n})

   $\downarrow$ + buffer; titrate with std. EDTA

   titrate (1 mol M^{+n} = 1 mol EDTA)

Sharpening of end point of Ca^{+2} vs EDTA:

a. unknown Ca^{+2}+indicator+trace of Mg^{+2}
   $\downarrow$ + buffer; titrate with std. EDTA
   determine end point. V mL

b. Indicator + trace of Mg^{+2} (blank titration)
   $\downarrow$ +water +buffer; titrate with std. EDTA
   determine end point. V' mL

Volume for Ca(II) = (V-V') mL

possible because $K_{Mg(II)-EDTA} < K_{Ca(II)-EDTA}$

Back titration:

used when,
a. suitable metal ion indicator not available.
b. M^{+n} and EDTA *reaction* is slow.
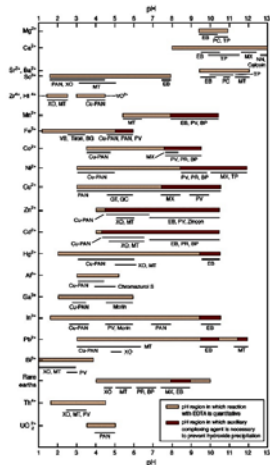c. M^{+n} forms ppt. at titration conditions.

unknown M^{+n} + known *excess* vol. std. EDTA

   $\downarrow$ + buffer; titrate unreacted EDTA vs std. Mg^{+2} or std. Zn^{+2}

find end point $\Rightarrow$ unreacted EDTA.

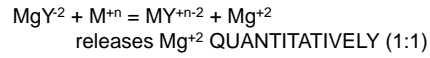Calculate EDTA consumed in the reaction vs M^{+n}.

requirement: $[MgEDTA]^{-2}$ or $[ZnEDTA]^{-2}$ less stable
Than the $[MEDTA]^{+n}$ complex.

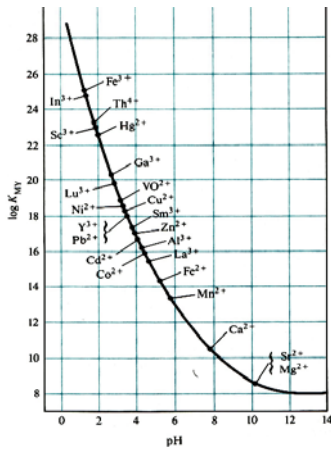Displacement reaction (use of an auxilliary agent MgY^{-2} or ZnY^{-2}:

Prepare MgY^{-2} (or ZnY^{-2}) solution (pH=10)
Add exc. of MgY^{-2} to a measured vol. of unknown M^{+n} solution.
($K_{Mg-Y} < K_{M-Y}$)

$MgY^{-2} + M^{+n} = MY^{+n-2} + Mg^{+2}$
releases Mg^{+2} QUANTITATIVELY (1:1)

titrate "*freed*" *Mg^{+2} produced* vs std. EDTA.
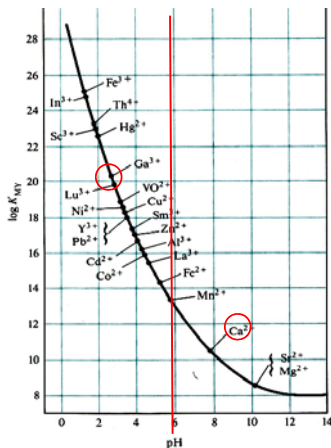(1mol M^{+n} = 1mol Mg^{+2})

requirement: $[MgEDTA]^{-2}$ or $[ZnEDTA]^{-2}$ less stable
than $[MEDTA]^{+n}$ complex.

Minimum pH required
for quantification

Scope: Selectivity toward different metals is achieved
by pH control.

Masking agents may be used to 'remove' interfering ions
from the reaction sphere via formation of stable complexes
with auxiliary ligand.

Minimum pH required
for quantification