EDTA Titrations

EDTA

Complexing agent

Acts as ligand- tightly binds metal ions at six different points of interaction

$EDTA + M^{n+} \leftrightarrow EDTA \cdot M^{n+}$ Formation Constant, K_f is large

EDTA can be used as a titrant to measure concentration of metals/ every element

Detecting endpoint

Use indicator

Indicators are complexing agents that bind to metals, but less strongly than EDTA. Choose indicator based color change/pH range and binding constant to analyte. Table 13-13

$IND \cdot Mn+ + EDTA \leftrightarrow EDTA \cdot M^{n+} + IND$

Wine red blue

Erichrome black T

The nature of EDTA

Polyprotic system

H_6Y^{2+}
H_5Y^{+}
H_4Y
H_3Y-
H_2Y^{2-}
HY^{3-}
Y^{4-}

Kf is defined (somewhat arbitrarily) as $[MY^{n-4}]/([M^{n+}][Y^{4-}])$. It is therefore pH dependent

Conditional Formation Constant
$K`_f = \alpha_{Y4} \cdot K_f$

Calculate the free $[Mg^{2+}]$ in a 0.010 M MgY^{2-} solution at pH 12 and pH 6.

Log $K_f(Mg^{2+}) = 8.79$

$K_f(Mg^{2+}) = 6.17*10^8$
$K`f(Mg,pH12) = (0.98)*(\ 6.17*10^8) = 6.04*10^8 = [MgY^{2-}]/([Mg^{2+}][EDTA])$

	MgY^{2-} ↔	Mg^{2+} +	EDTA
Initial	0.010	0	0
Final	0.010-x	x	x

$6.04*10^8 = (0.010-x)/x^2$

$x = 4.07*10^{-6}$ M

$K`f(Mg,pH6) = (2.3*10^{-5})*(\ 6.17*10^8) = 1.42*10^4 = [MgY^{2-}]/([Mg^{2+}][EDTA])$

	MgY^{2-} ↔	Mg^{2+} +	EDTA
Initial	0.010	0	0
Final	0.010-x	x	x

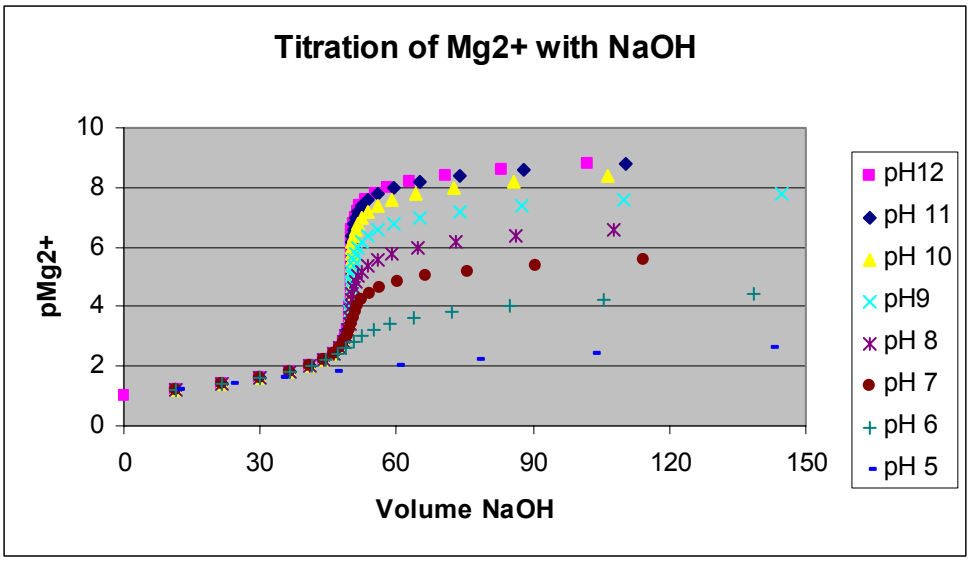
$1.42*10^4 = (0.010-x)/x^2$

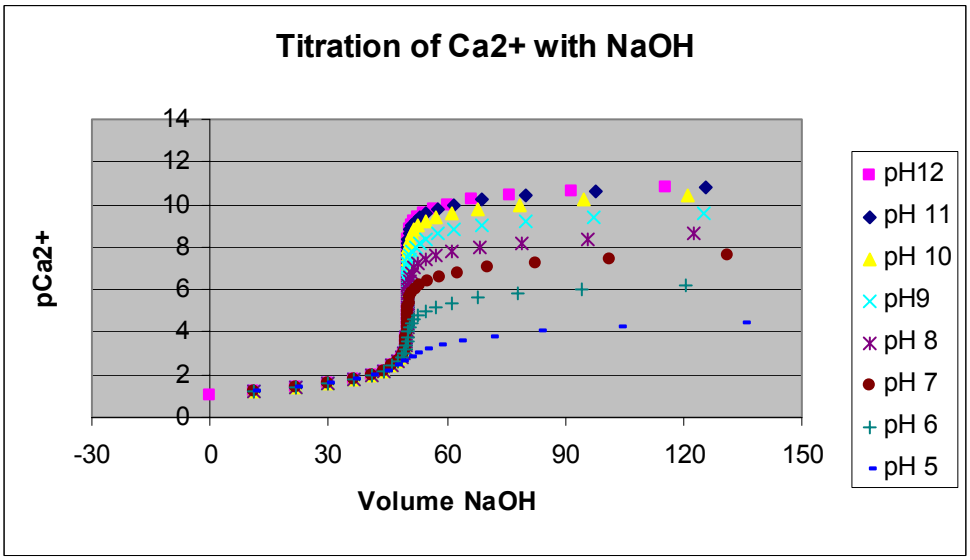
$x = 8.05*10^{-4}$ M

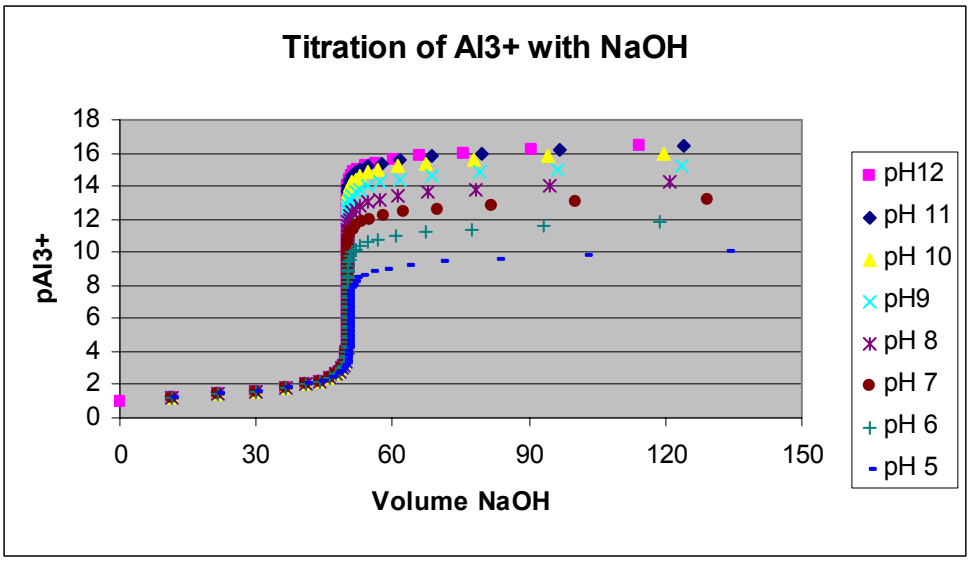
The POINT!!

At the equivalence point of an EDTA titration all of the free metal is converted to it EDTA complexed form, and the above equilibrium is the pertinent reaction. If Kf' is too small, it will be difficult to detect a sharp endpoint to the titration. Therefore, most EDTA titration are buffered to pH >10 to give greater Kf`.

Metal ion	Log Kf
Mg^{2+}	8.79
Ca^{2+}	10.69
Al^{3+}	16.3


Titration of Mg2+ with NaOH
pMg2+
Volume NaOH
0
2
4
6
8
10
0
30
60
90
120
150
pH12
pH 11
pH 10
pH9
pH 8
pH 7
pH 6
pH 5


Titration of Ca2+ with NaOH
pCa2+
Volume NaOH
0
2
4
6
8
10
12
14
-30
0
30
60
90
120
150
pH12
pH 11
pH 10
pH9
pH 8
pH 7
pH 6
pH 5



Techniques

Direct

Back

If analyte precipitates ($Al(OH)_3$) in the absence of EDTA, if complexation with EDTA is too slow, if metal does not freely dissociate from the indicator.

Displacement (for metals without suitable indicator)

Titrate with MgEDTA to displace metal, releasing Mg2+

Then, titrate Mg^{2+} with EDTA

Indirect

Anions; precipitate anions (SO_4^{2-}) with excess cation (Ba^{2+}), wash precipitate, boil with excess EDTA at pH 10. Excess EDTA back titrated with Mg2+

Masking

Selectivity; Mask some ions so that others can be determined free of interferences.

Cyanide masks Cd^{2+}, Zn^{2+}, Hg^{2+}, Co^{2+}, Cu^{+}, Ag^{+}, Ni^{2+}, Pd^{2+}, Pt^{2+}, Fe^{2+}, and Fe^{3+} but not Mg^{2+}, Ca^{2+}, Pb^{2+}, Mn^{2+}