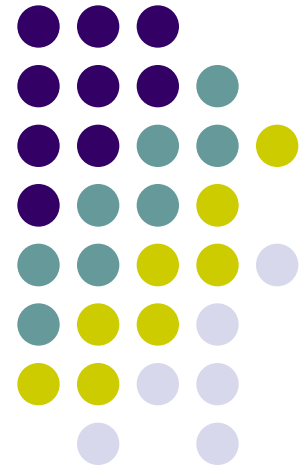
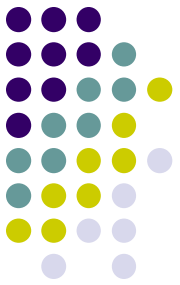


Chapter 16.

Applications of neutralization titrations.





◉ Reagents for Neutralization Reactions

strong acid or base : eq. point에서 명확한 pH 변화 有

.standard soln. 제조(acid)

물은 용액의 경우 매우 안정(HCl)

0.1N HCl → 1 hr 동안 boiling로 해도 농도의 loss

0.5N HCl → 10 min 동안 boiling로 해도 농도의 loss

HClO₄, H₂SO₄ → 사용. HNO₃ → 산화성으로 인해 不用

① dilution → base로 standardization

② less frequently → careful density measurement

③ by distillation of the concentrated reagent ;

(constant boiling HCl) ← 대기압에 따라 농도변화

acid 1 eq. 을 갖는 distillate의 공기 중의 무게

g constant boiling HCl

----- = 164.673 + 0.02039 P

equivalent

(P : 670 ~ 780 mmHg)



◎ Standardization of acids

1) sodium carbonate ; purified sodium hydrogen carbonate을 270 ~ 300 °C에서 1hr 동안 가열.



2 step으로 처리.

1 step ; pH 8.4 부근

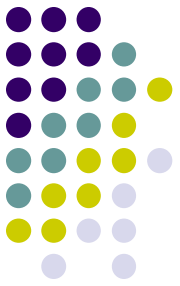
2 step ; pH 4.0 부근 → always used for standardization

(pH 변화 크기 때문)

BCG, methyl orange

$\text{H}_2\text{CO}_3 \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}$; HCO_3^- , CO_3^{2-} 의 buffer 파괴 boiling

* 적정 시 용액 boiling → CO_2 제거



◎ Other primary standards for acids.

- ① Tris-(hydroxymethyl)aminomethane $(\text{HOCH}_2)_3\text{CNH}_2 \rightarrow \text{TRIS}$ or HAM.
- ② sodium tetraborate ③ mercury(II) oxide ④ calcium oxide.

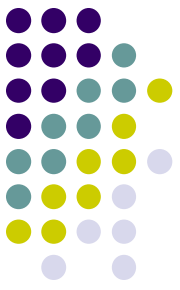
◎ preparation of standard solutions of base

NaOH ; (or KOH, $\text{Ba}(\text{OH})_2$) \rightarrow the soln must be standardized.

* glass, atmosphere에 장기간 접촉치 않는 한 안정.

NaOH + glass \rightarrow silicate 形成

보관 : polyethylene bottle or glass bottle that has been coated with paraffin.

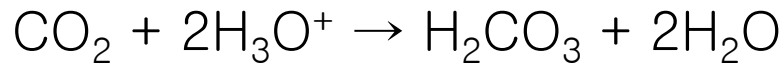


◎ Effect of CO₂ upon standard base solns.

Na, K, Ba의 수산화물 → atmospheric CO₂와 avidly react

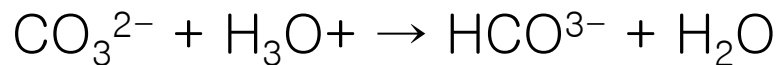


base의 standardized soln에 의한 CO₂의 흡수는 그것의 acid titer를 반드시 변화 시키지는 않는다.



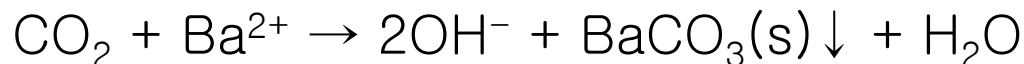
∴ CO₃ 형성에 사용된 acid의 양과 同一 한 base 량 → no error

basic transition indicator 사용(pp) → 이 때 H₃O⁺ 1개가 사용



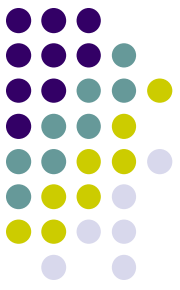
base의 effective normality 감소 → Carbonate error 유발

Ba(OH)₂ 사용하면 CO₂ 흡수하여 ppt 생성



Carbonate error

용액 제조에 사용된 고체 reagent가 대기중의 CO₂ 흡수 →
carbonate 상당량 존재



* carbonate free OH⁻ soln 제조법

① Ba(OH)₂의 경우 ; BaCl₂ or BaNO₃ 등 첨가 → sparingly soluble carbonate 감소

KOH, NaOH의 경우, Ba salt 사용 ← 약점 有

② NaOH 용액 ; 50% aqueous soln 제조 → Na₂CO₃의 very low solubility 利用.

supernatant liquid → decant하여 희석 후 사용

위 용액 제조시 증류수 묶어서 식힌 후 사용

Arrangement for the storage of standard base solutions.

→ CO₂ 흡착제 : soda lime, or astroite

적정 중의 CO₂ 흡수 : beaker, test tube로 뚜껑

standard soln : 1주일 內 사용할 경우 → polyethylene botte에 마개를 사용하며 可能

buret → teflon stopcock 사용이 좋다.



- Standardization of bases.

Weak organic acids 사용

- ① Potassium hydrogen phthalate $\text{KHC}_8\text{H}_4\text{O}_4$

장점 : high equivalent를 갖는 nonhygroscopic crystalline solid.

- ② Other acid : solubility in water is limited → ethanol에 녹임

- ③ potassium hydrogen iodate, $\text{KH}(\text{IO}_3)_2$

: high equivalent weight strong acid

- Typical Applications of Neutralization Titrations, inorganic, organic, biological species (산, 염기의 속성을 갖는) 중화 적정에서 2 type의 end point 결정법.

- ① indicator ② pH meter



◉ Elemental analysis

Carbon, nitrogen, chlorine, bromine, sulfur, phosphorus & fluorine

→ inorganic acid or base로 convert시켜 측정

Nitrogen ; proteins, synthetic drugs, fertilizers urea, portable water supplies

. organic N 측정

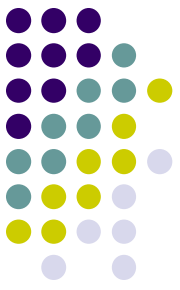
① Dumas method : virtually all organic N compound에 적용

powdered copper(II) oxide와 sample mixing →
combustion tube에서 igniting (sample → CO_2 , H_2O , N_2 ,
nitrogen oxides)

↳ hot Cu를 통과 → N_2 로 변화

ignition products → CO_2 stream에 의해
Swept (highly concentrated KOH 용액이 들어 있는 분량으로 CO_2 ,
 H_2O , SO_2 , HX 흡수

N_2 는 흡수치 없음 → buret으로부터 부분적으로 liquid를 치환
→ volume 측정



② Kjeldahl method (1883)

protein N₂ in grains, meats & other biological materials.

sample → hot, conc - H₂SO₄ 로 산화 → excess of strong base로 처리

↳ C → CO₂ , H₂ → H₂O로 산화

bound N₂ → NH₄⁺ 로 convert

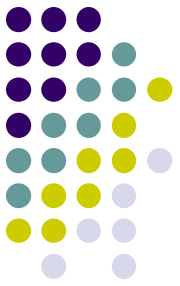
*N₂ 가 amine or amide 등의 proteineous matter이면 정량적으로 NH₄⁺로 변화可

*N₂ 가 nitro, azo & azoxy group이면 → elemental state or nitrogen oxide로 convert.

이런 경우, low results → reducing agent로 sample 전처리 要

ex) salicylic acid, sodium thiosulfate adding

certain aromatic heterocyclic compounds (pyridine, its derivatives) → resistant to complete oxidation by H₂SO₄ oxidation process → an hour, or more maybe needed.



* Gunning method

neutral salt(K_2SO_4) 加 \rightarrow b.p 상승(H_2SO_4)

주의) ig salt concentration 大 $\rightarrow NH_4 +$ ion oxidation

* perchloric acid, potassium permanganate.

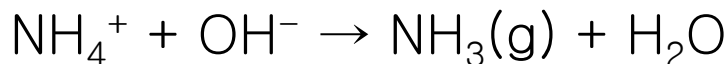
hydrogen peroxide의 경우 $\rightarrow NH_4 +$ ion이 부분적으로 NO_2 로 산화하므로 fail.

① oxidation step 촉매 ; Hg, Cu, selenium

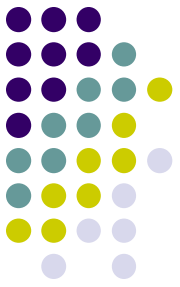
Kjeldahl flask : oxidation

distillation

after oxidation \rightarrow cooling \rightarrow dilution with $H_2O \rightarrow$
basic



Chapter 17. Complex formation titrations (complexometric methods)



$M^+ + \text{electron pair donor} \rightarrow \text{complex ion, coordination comp.}$

↳ ligand(최소 1 pair의 unshared electron 존재)

ex) H_2O , NH_3 , Cl^-

coordination number : 배위권에서 중심원자와 결합하고 있는 주게 원자의 수. ex) 6, 4, 2

. 배위물

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

negative : $CuCl_4^{2-}$

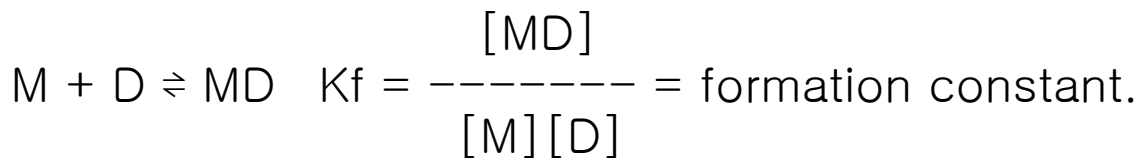
neutral : $Cu(NH_2CH_2COO)_2$

chelates ; is produced when a metal ion coordinates with two donor groups of a single ligand.

여러 자리 ligand

bidentate, terdentate, Quadri-, quinque, sexadentate

1) 4자리배위 금속이온 M + quadridentate ligand D와 반응





2) M + bidentate B M + 2B ⇌ MB₂

.two step

$$M + B \rightleftharpoons MB \quad K_1 = \frac{[MB]}{[M][B]}$$

$$MB + B \rightleftharpoons MB_2 \quad K_2 = \frac{[MB_2]}{[MB][B]}$$

$$\beta_2 = K_1 K_2 = \frac{[MB]}{[M][B]} \times \frac{[MB_2]}{[MB][B]} = \frac{[MB_2]}{[M][B]^2}$$

3) M + unidentate A

M + 4A ⇌ MA₄, K₁, K₂, K₃, K₄ 有

fig 11-1 참조. complex formation titrations

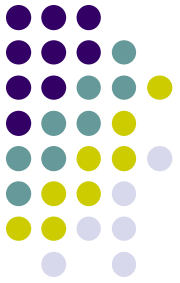
Curve A ; single step

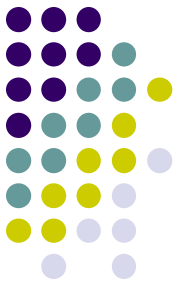
Curve B ; MB₂ two step. K₁ = 10¹², K₂ = 10⁸

Curve C ; MB₄. K₁ = 10⁸, K₂ = 10⁶, K₃ = 10⁴, K₄ = 10²

polydentate ligand + unidentate 보다 적정에 有利

- ◉ Titrations with inorganic complexing reagents.
Hg(II)로 I⁻ ion 정량법 (1834年) was reported.

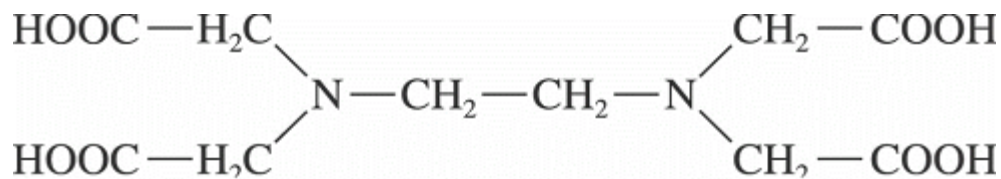




• titrations with aminopolycarboxylic acids.

carboxylic acid groups를 갖는 tertiary amines → stable chelates를 form.

Schwargenbach in 1945 → 분석시약으로서 위치 인식 [EDTA (ethylenediaminetetraacetic acid)에 의한 M 정량]



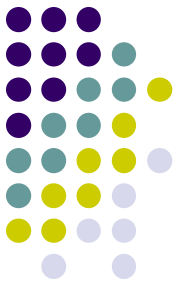
$$K_1 = 1.0 \times 10^{-2}, K_2 = 2.1 \times 10^{-3}, K_3 = 6.9 \times 10^{-7}, K_4 = 5.5 \times 10^{-11}$$

有用 → sexadentate ligand.

ab, H_4Y , H_3Y^- , H_2Y^{2-} , HY^{3-} , Y^{4-}

H_4Y , $\text{NaH}_2\text{Y} \cdot 2\text{H}_2\text{O}$ → are available in reagent quality.

↳ 130 ~ 145 °C 에서 ↳ 80 °C 에서 drying (50% 상대습도 中, for several days) drying(base에서)



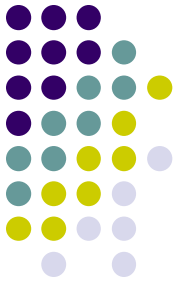
- ◎ composition of EDTA soln, as a function of pH.
relative amount each species in a given soln →
pH에 의존 → α value plotting이 有

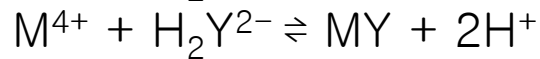
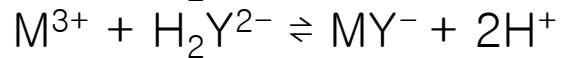
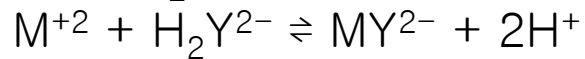
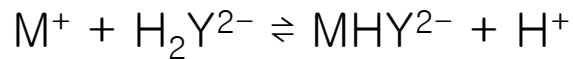
Fig. pH vs EDTA의 α value
 H_2Y^{-2} : predominant species in pH 3 ~ 6
 HY^{3-} ; pH 6 ~ 10, Y^{4-} ; pH 10 이상

◉ complexes of EDTA and Metal Ions

EDTA 장점 : 1:1 complex 형성.(cation의 charge에 무관)

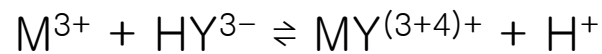
(pH 3 ~ 6에서)



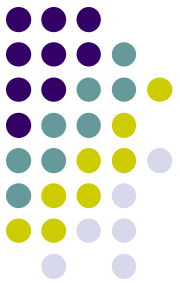
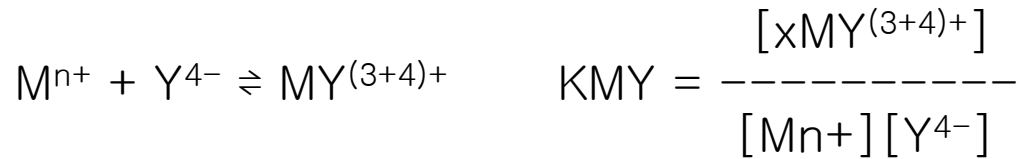


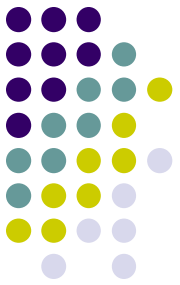
great stable in moderately basic solns

neutral



Formation constants for EDTA complexes.





◎ derivation of EDTA titration curves.

.effect of pH.

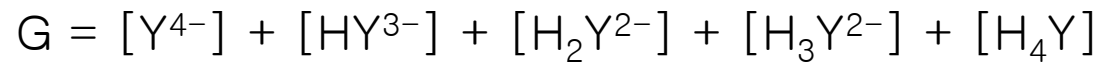
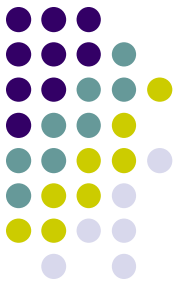
calcium. Mg → alkaline medium

Zn, Ni → moderately acid solus.

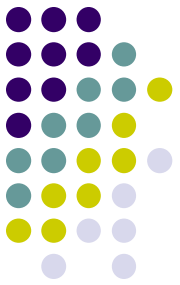
EDTA → buffer soln에서行해야 한다.

$$\alpha_4 = \frac{[Y^{4-}]}{G}$$

G : uncomplexed EDTA의 total com.


$$K_1 K_2 K_3 K_4$$

$$\alpha_4 = \frac{K_1 K_2 K_3 K_4}{[H^+]^4 + K_1 [H^+]^3 + K_1 K_2 [H^+]^2 + K_1 K_2 K_3 [H^+] + K_1 K_2 K_3 K_4}$$



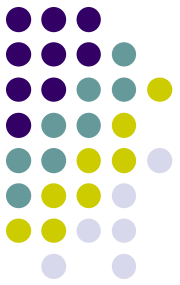
Values for α_4 EDTA

α_4 G = $[Y^{4-}]$ 를 $M^{n+} + Y^{4-} \rightleftharpoons MY(n^{-4})^+$ 에 代入
 $[MY(n^{-4})^+]$

$$K_{MY} = \alpha_4 K_{MY} = \frac{[MY(n^{-4})^+]}{[M^{n+}]G}$$

K'_{MY} = conditional or effective formation constant.

α_4 가 적용가능한 pH에서의 평형상수



ex) Derive a curve for the titration ;

50.0ml of 0.01F Ca^{2+} + 0.0100F EDTA pH:10 으로 buffering.

1) calculation of conditional constant ;

$$K'_{\text{CaY}} = \alpha_4 K_{\text{CaY}} = (3.5 \times 10^{-1})(5.0 \times 10^{10}) = 1.75 \times 10^{10}$$

2) preequivalence point values for pCa.

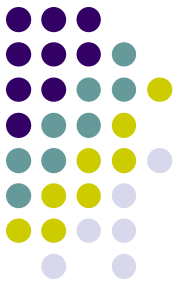
$[\text{Ca}^{2+}]$ = the untitrated excess of the ion + dissociation of the complex [=G]

after 25ml 加. $G \ll$ uncomplexed Ca^{+1} ion의 농도

$$[\text{Ca}^{2+}] = \frac{50.0 \times 0.0100 - 25.0 \times 0.0100}{75.0} + \underline{G} \equiv 3.33 \times 10^{-3}$$

↳ 무시

$$\text{pCa} = -\log 3.33 \times 10^{-3} = 2.48$$



3) equivalence point pCa ; 0.00500F in CaY²⁻

[Ca²⁺] → CaY²⁻의 해리에 의한 것 뿐

$$\because [\text{Ca}^{2+}] = G$$

$$[\text{CaY}^{2-}] = 0.00500 - [\text{Ca}^{2+}] \equiv 0.00500$$

the conditional formation constant for CaY²⁻ at pH10.

$$\frac{[\text{CaY}^{2-}]}{[\text{Ca}^{2+}] G} = 1.75 \times 10^{10}$$

$$\frac{0.00500}{[\text{Ca}^{2+}]^2} = 1.75 \times 10^{10}$$

$$[\text{Ca}^{2+}] = 5.35 \times 10^{-7} \quad \text{pCa} = 6.27$$

4) postequivalence point pCa

CaY²⁻의 당량점에서의 농도 + EDTA(excess)
60.0ml 加 ;

$$F_{CaY^{2-}} = \frac{50.0 \times 0.0100}{110} = 4.55 \times 10^{-3}$$

$$F_{EDTA} = \frac{10.0 \times 0.0100}{110} = 9.1 \times 10^{-4}$$

$$[CaY^{2-}] = 4.55 \times 10^{-3} - [Ca^{2+}] \equiv 4.55 \times 10^{-3}$$

$$G = 9.1 \times 10^{-4} + [Ca^{2+}] \equiv 9.1 \times 10^{-4}$$

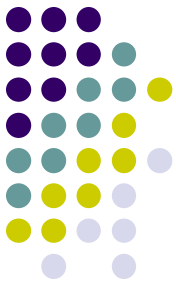
$$\frac{4.55 \times 10^{-3}}{[Ca^{2+}] \times 9.1 \times 10^{-4}} = 1.75 \times 10^{10} = K'_{CaY}$$

$$[Ca^{2+}] = 2.86 \times 10^{-10}$$

$$pCa = 9.54$$

fig 5. pH 6에서 적정곡선

K 값大 → 적정곡선 pM jump 大





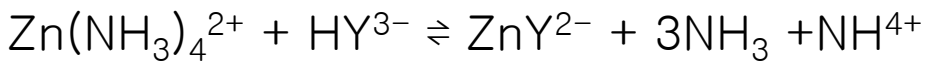
Effect of Other Complexing Agents on EDTA Titrations.

금속에 따라 required pH에서 basic oxide or hydroxide로 침전 생성 가능 → complicate.

이것을 하기 위해 (to keep the metal ion in soln) → auxiliary complexing agent 要

ex) Zn(II) 적정(NH₃ - NH₄Cl buffer 要)

↳ NH₃ → Zn(II)과 soluble ammine complexes → ppt예방



↳ pH뿐 아니라 NH₃의 concentration에 의해서도 좌우.

$$\beta = \frac{[Zn^{2+}]}{C_{Zn}}$$

βZn을 conditional constant에 代入

$$K^7 = \alpha_4 \beta K_{ZnY} = \frac{[ZnY^{2-}]}{C_{ZnG}}$$

NH₃ 농도의 영향 pH9. 참조, 일정 pH에서 착물시약 농도에서 특징적.



end points for EDTA titrations

(metal ion indicators) : organic dyes that form colored chelates with metal ions in a pM range.

(성질)

- ① dyes 자신이 금속 이온과 반응 → 금속 chelate 생성 능력 有
- ② indicator와 금속이온이 만든 금속 킬레이트의 안정도 상수보다 EDTA의 금속 킬레이트의 안정도 상수가 大
- ③ 특이하고 강한 정색 (1/10 배 차이)

ex) E.B.T(enrcchrome black .T.)

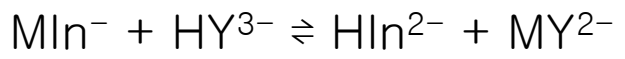
in acidic & modorately basic soln.



red blue

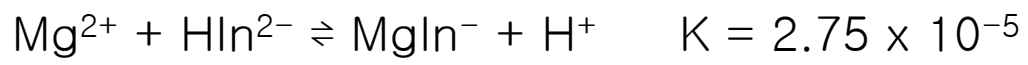
강한 염기성 $HIn^{2-} \rightarrow In^{3-}$ 로 해리(orange)

end point reaction



red blue

(Mg^{2+} 를 EDTA로 정량 時)



blue red

pH 10에서

$$2.75 \times 10^{-5} = \frac{[\text{MgIn}^-][\text{H}^+]}{[\text{Mg}^{2+}][\text{HIn}^{2-}]} \rightarrow 2.75 \times 10^5 = \frac{[\text{MgIn}^-]}{[\text{Mg}^{2+}][\text{HIn}^{2-}]}$$

↙ 적색
↘ 청색

만약 pMg가 4.44 이하 → 청색 ↓↑?

pMg가 6.44 이상 → 적색

pH 7 ~ 11에서 Ca, Mg, Zn, Cd, Hg²⁺, Pb⁺, Mn²⁺ 변색

방해물 : Cu, Co, Ni, Fe → KCN으로 mashing

단점 : 방치하면 천천히 decompose → 보완 → Calmagite.

(기타 시약)

P.V (pyrocatechol violet)

aqueon soln → yellow. strongly acidic → red

basic soln → red - violet

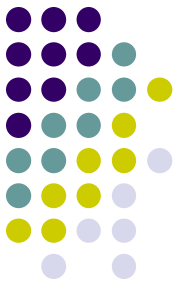
pH 2 ~ 3에서. Bi(청), Th(적)

pH 5 ~ 6에서. Cu(청)

염기성에서. Ni, Co, Mn, Mg, Zn, Cd, Cu(청록)

(Xylenol orange)

(PAN)





◎ titration methods employing EDTA.

① Direct Titration : 25 metal

검출 : 1 indicator, 전류적정, 전압적정 (보조 chelate 加, 완충용액要)

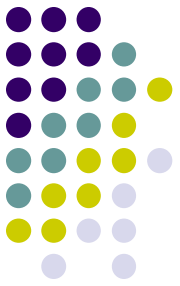
② Back titration

적정 pH에서도 reaction rate 小, or EDTA 加

→ 변색이 생기지 않을 경우(EBT, Calmagite 많이 利用)

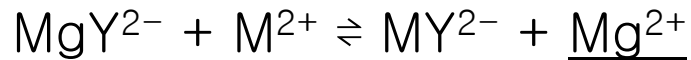
정량금속이온과 반응하는 anion의 존재시

방법 : excess EDTA 加 → pH 조절 → excess EDTA를 $ZnSO_4$, $Th(NO_3)_4$, $MgSO_4$ 등의 metal standard soln으로 액적정.



③ Displacement titration.

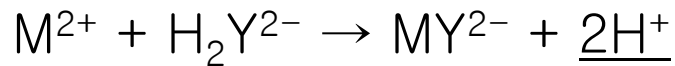
Mn⁺ 용액에 EDTA - Mg (or Zn) excess 용액 加.



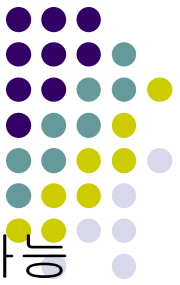
↳ standard base로 적정

④ alkalimetric titration.

excess Na₂H₂Y를 중성의 금속이온에 加



↳ standard base로 적정



◎ scope of complexometric titrations

EDTA 대부분의 금속과 chelating → 선천성 : pH regulation에 의해 가능

pH1의 용액 → M^{2+} 방해없이 M^{3+} 정량가능

pH 에서 EBT 지시약으로 적정 : Mg 방해없이 Cd만 정량 可.

Cd, Co, Cu, Ni, Zn, Pd를 CN^- 로 masking → Mg, Ca 정량.

◎ Determination of water hardness

hardness : the capacity of a water sample to ppt.

주로 Ca, Mg 많이 $CaCO_3$ 당량으로 표시

pH 10에서 Calmagite, Eriochromeblack T를 지시약으로 사용하여 정량.