Precipitation titration
part 1

Dr. Mai Ramadan

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  Ksp

- **Argenometry:**

  Moher's-, Volhard's- and Fajan's methods

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- **Examples and Problems**

Introduction

A precipitation titration is accompanied by formation of precipitate (sparingly soluble salts).

The common **subtypes** are argenometry and mercurimetry

Introduction

Solubility product constant: K_{sp}

$$AgCl\,(s) \longleftrightarrow Ag^{+} + Cl^{-}$$

$$K_{sp} = [Ag^{+}]\,[Cl^{-}]$$

$$Ag_2CrO_4\,(s) \longleftrightarrow 2\,Ag^{+} + CrO_4^{-2}$$

$$K_{sp} = [Ag^{+}]^2\,[CrO_4^{-2}]$$

Indicators

Moher's Method : Coloured precipitate

Titrant: $AgNO_3$

Analyte: Cl^- and Br^- but not I^-

Indicator: K_2CrO_4 solution

Media: is neutral or slightly acidic.

Not basic: to prevent precipitation of Ag^+ (write equations)

Not strongly acidic: to prevent chromate-dichromate equilibrium to detect end point (**why**)

End point: **Red precipitate** Ag_2CrO_4

$$2\,Ag^+ + CrO_4^{-2} \longrightarrow Ag_2CrO_4\,(s)$$

Moher's Method : Analysis of chloride ion

1. Analyte solution + chromate (Yellow colored)

2. AgCl (White ppt)

3. At end point slight excess Ag+ form Ag_2CrO_4 (Red ppt) AgCl is present

3. After end point large excess Ag+ form

Moher's Method : Analysis of chloride ion

See video for titration on you tube

https://youtu.be/ODnPyAy-Z54

Indicators

Moher’s Method : Colored precipitate

$$2\ CrO_4^{-2} + 2\ H_3O^+ \longrightarrow Cr_2O_7^{-2} + 3\ H_2O$$

$$3\ Cr_2O_7^{-2} + 2\ H_3O^+ \longrightarrow 2\ Cr_3O_{10}^{-2} + 3\ H_2O$$

$$4\ Cr_3O_{10}^{-2} + 2\ H_3O^+ \longrightarrow 3\ Cr_4O_{13}^{-2} + 3\ H_2O$$

Indicators

Volhard's method : Colored solution

Analyte: Br^-, I^-, possible **Cl^-** specific condition.

Titrant: KSCN , NH4SCN

Media: acidic (Ag^+ ? , Fe^{+3} ?)

$AgNO_3$: A known amount is added to analyte followed by titration of $Ag^+_{unreacted}$

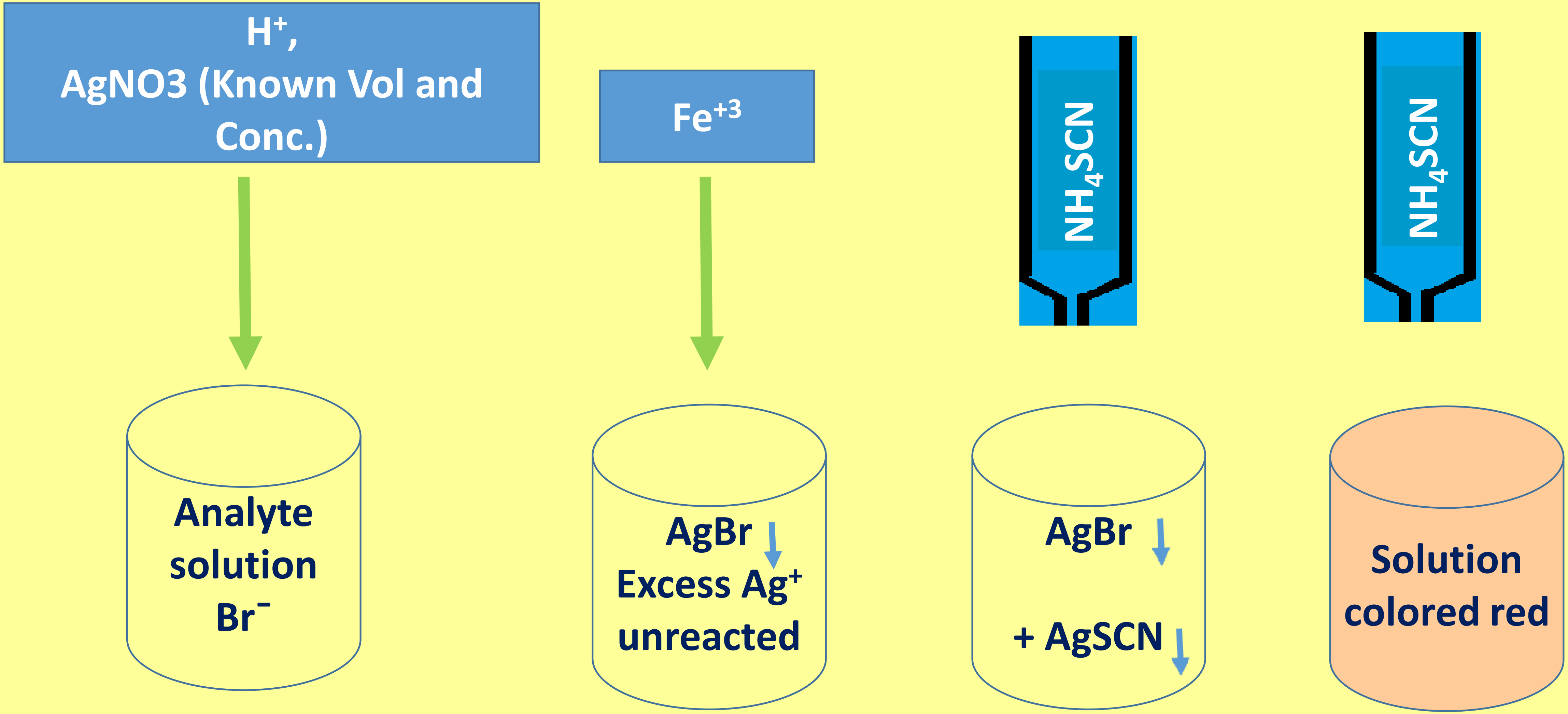
$$Ag^+ + SCN^- \longrightarrow AgSCN\ (s)$$

Indicator : $NH_4Fe(SO_4)_2.12\ H_2O$

End point: **Bloody red colour** of the solution.

$$Fe^{+3} + 3\ SCN^- + 3\ H_2O \longrightarrow [Fe\ (SCN)_3(H_2O)_3]$$

Volhard method : Analysis of bromide



Indicators

Volhard method : Colored solution

Ksp of AgCl is larger than AgSCN.

$$AgCl\ (s) + SCN^- \longrightarrow AgSCN\ (s) + Cl^-$$

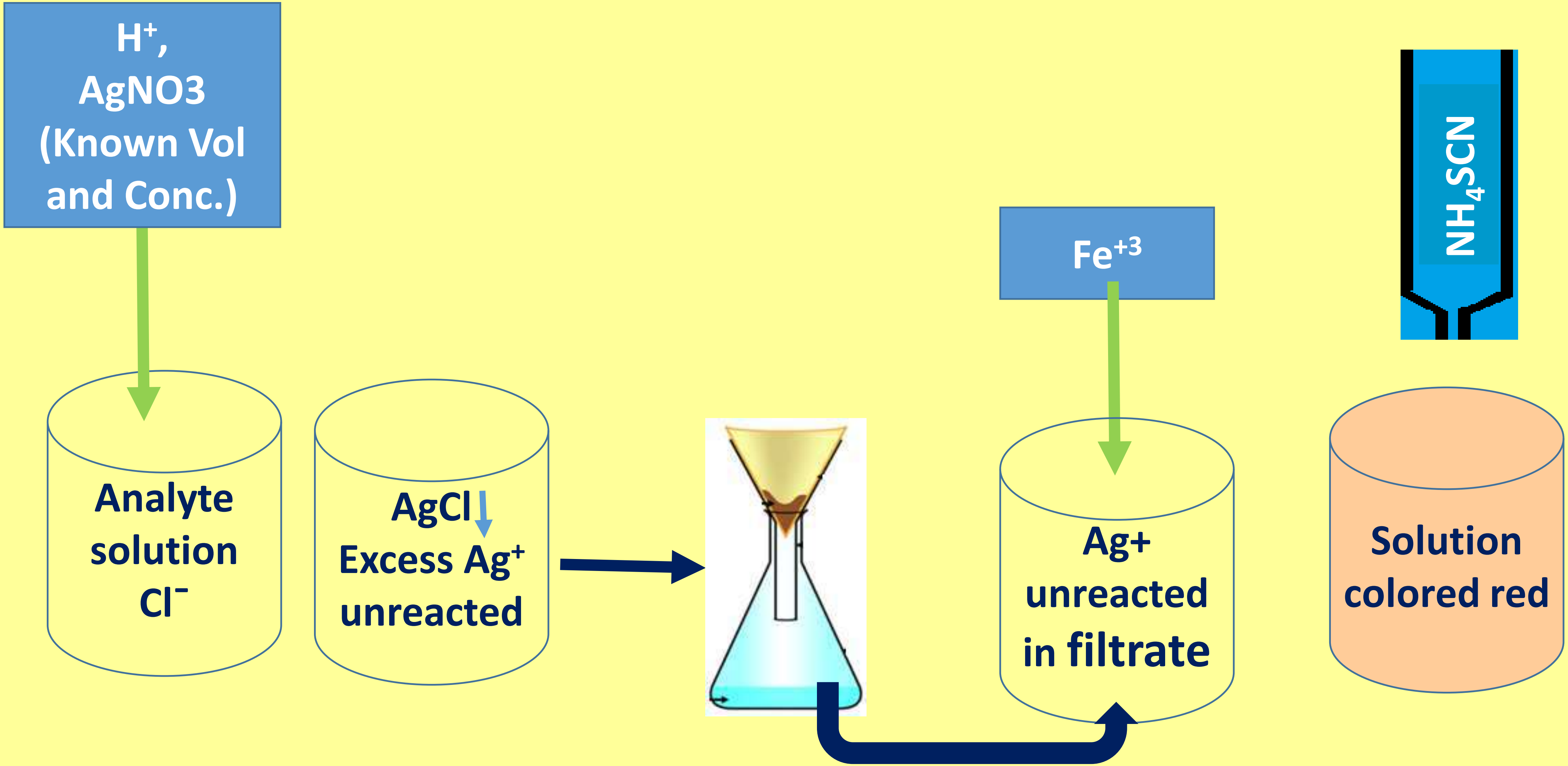
The above reaction lead to an overconsumption of the titrant SCN^- during back titration.

The solution: Specific condition

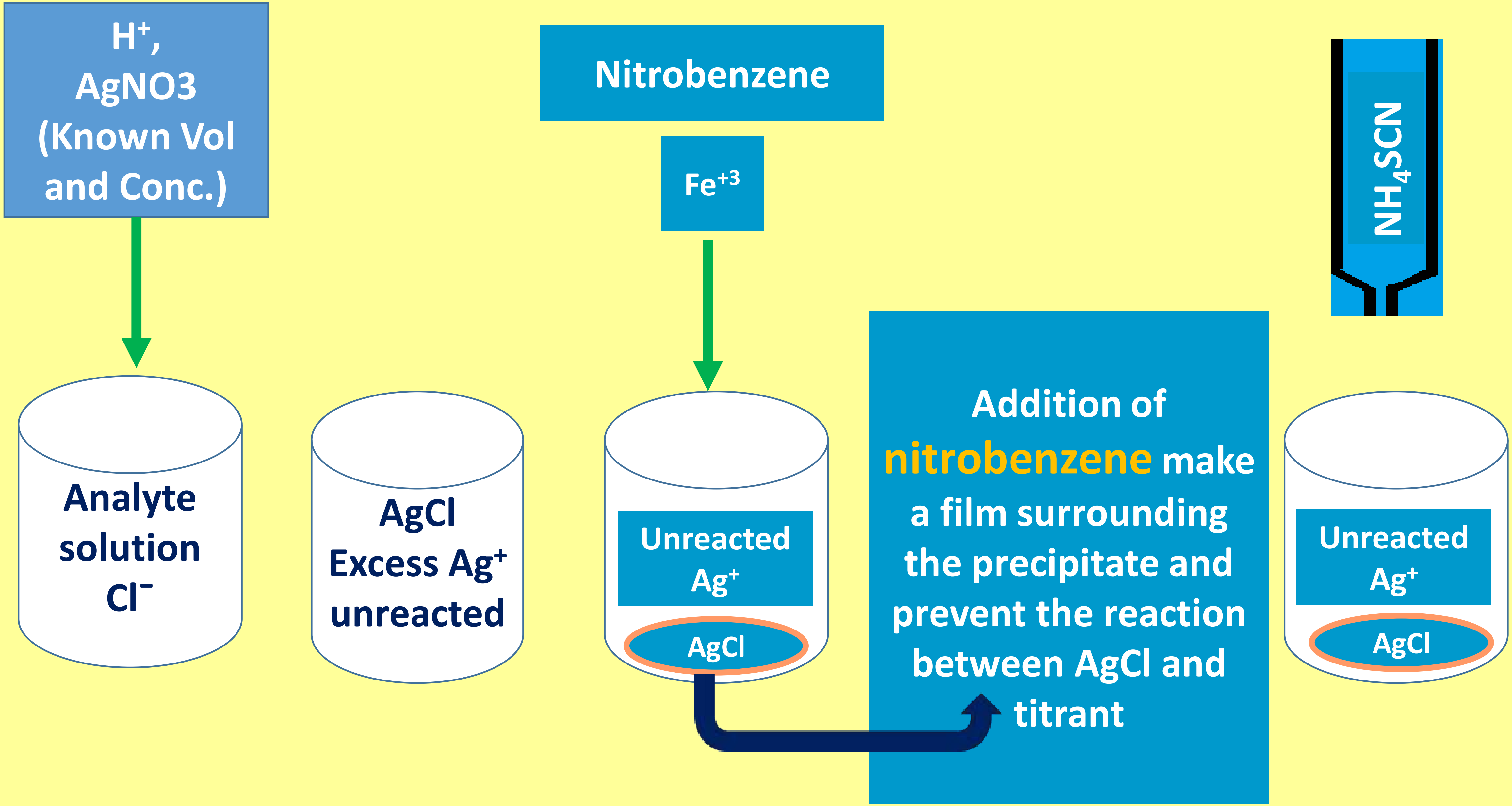
1. Add organic solvent to coat the precipitate AgCl and keep isolated from titration media e.g .CHCl3, CCl4, nitrobenzene

2. Filtrate AgCl then backtitrate the filtrate.

Modified volhard's method : Chloride analysis



Modified volhard's method :Chloride analysis



Precipitation titration part 2

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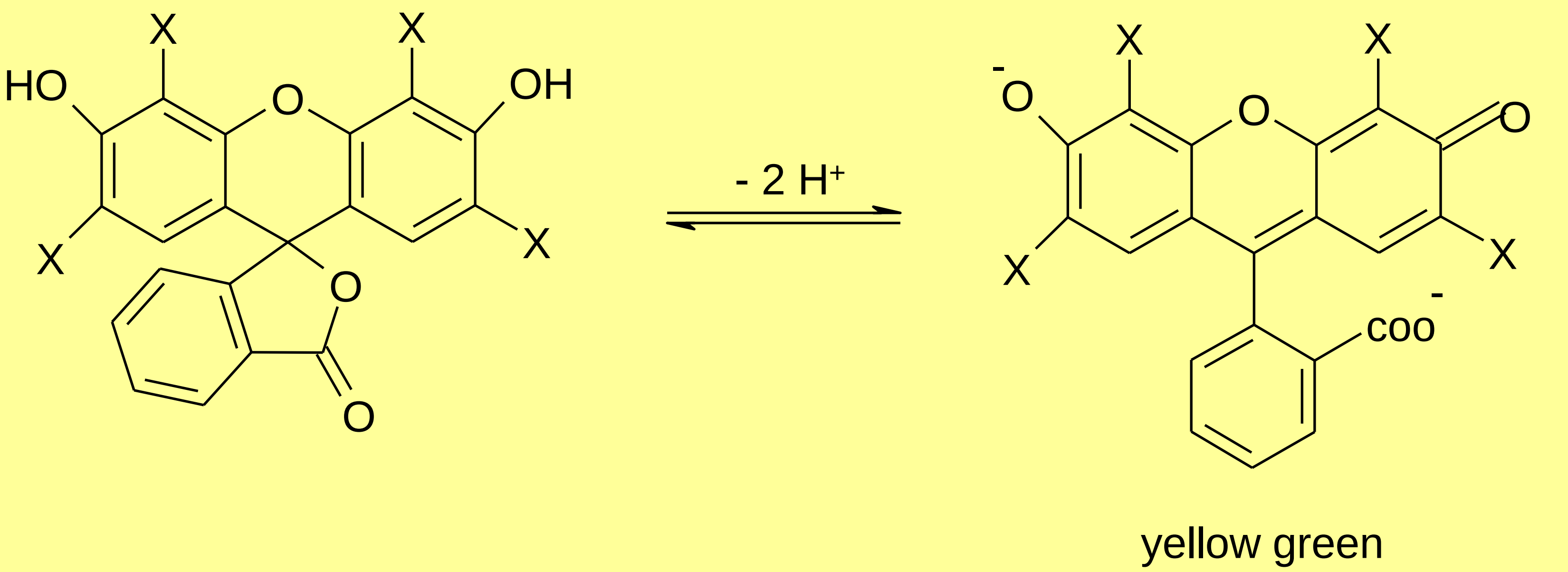
Indicators

Fajans' method : Adsorption indicator

The indicator causes coloration of the precipitate after being adsorped on the surface of precipitate.

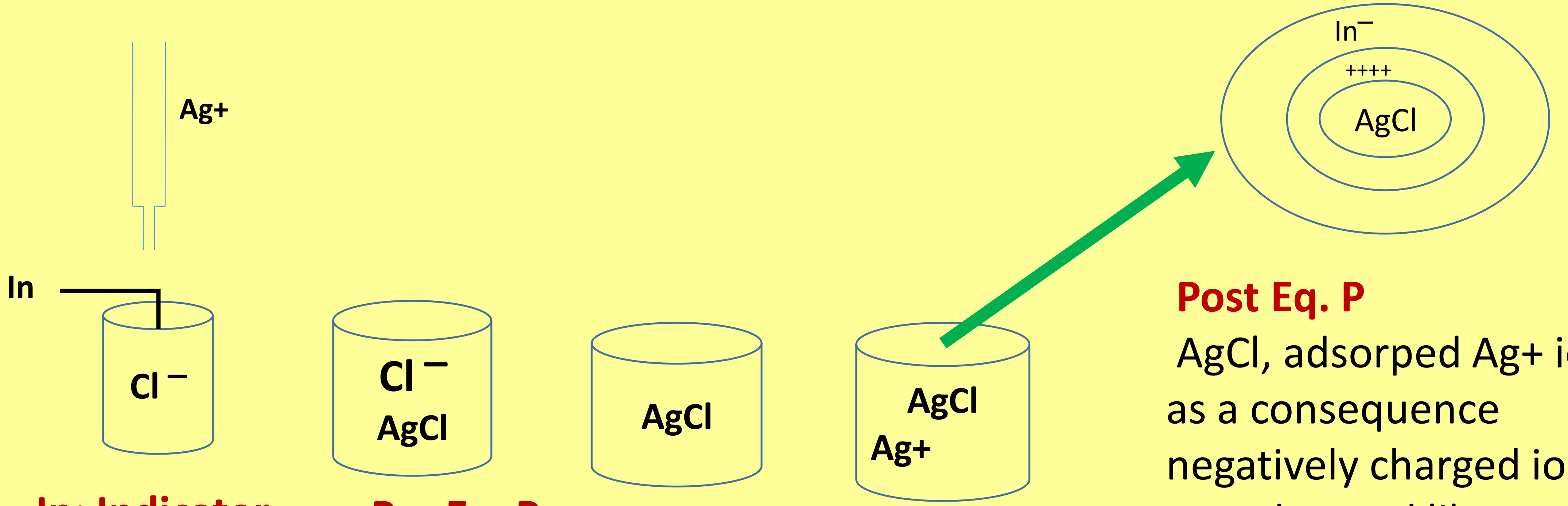
Example: Fluorescein (Cl^-) and eosin for (Br^- and I^-).



X = H, Fluorescein
X = Br, Eosin

Indicators

Fajans' method : Adsorption indicator



In: Indicator, Flourescinate anion

Pre Eq. P
Excess Cl^-

Eq. P
Only AgCl

Post Eq. P
AgCl, excess Ag+

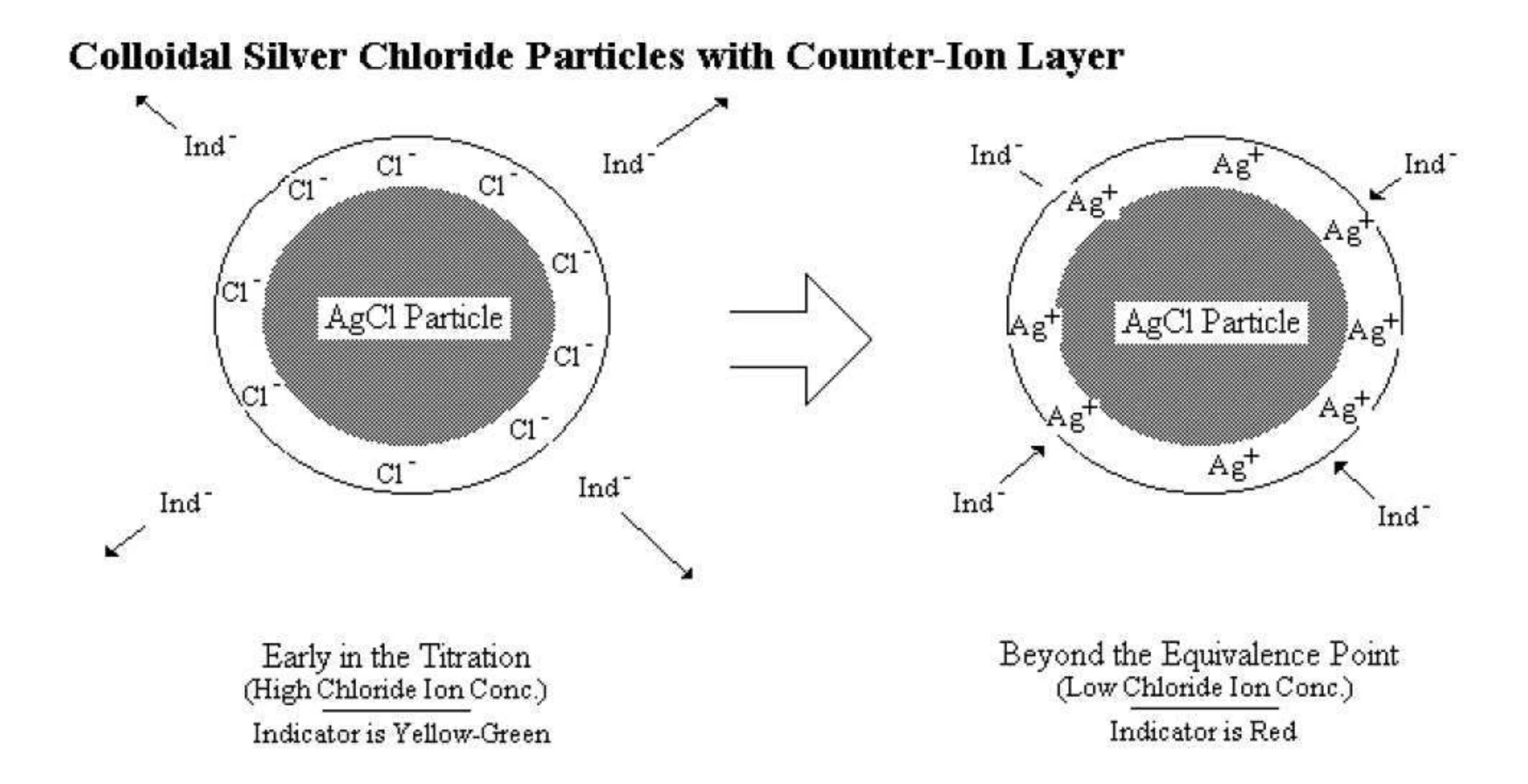
Post Eq. P

AgCl, adsorped Ag+ ion, as a consequence negatively charged ions are adsorped like indicator

Ag flourescinate layers colored AgCl with a red color.

Indicators

Fajans' method : Adsorption indicator



Indicators

Fajans' method : Adsorption indicator

Ag fluoresceinate is not a precipitate.The colour is disturbed by addition of chloride ions due to **desorption** of fluoresceinate.

The adsorption affinity of particles to indicator must be smaller than that of analyte ions.

This affinity is decrease in the following order
I^-,CN^-> SCN^- >Br^-> eosin > Cl^-> Ac^- > fluorescein> NO_3^- > ClO_4^-.

Indicators

Fajans' method : Adsorption indicator

Adsorption indicators were first described by K. Fajans, a Polish chemist in 1926.

Titrations involving adsorption indicators are rapid, accurate, and reliable, but their application is limited to the few precipitation titrations that form **colloidal precipitates rapidly**.

Fajans Titration

(a) (b) (c)

Fajan's method of chloride with $AgNO_3$ using flourescine
(a): Indicator before beginning titration (b): AgCl precipitate before end point (c): indicator adsorbed on precipitate after end point

Fajans' method : Analysis of chloride

See video in you tube channel

https://youtu.be/rEKtsaofmXM

Application of precipitation titration

Species analyzed	Notes
	Volhard Method
Br^-, I^-, SCN^-, CNO^-, AsO_4^{3-}	Precipitate removal is unnecessary.
Cl^-, PO_4^{3-}, CN^-, $C_2O_4^{2-}$, CO_3^{2-}, S^{2-}, CrO_4^{2-}	Precipitate removal required.
BH_4^-	Back titration of Ag^+ left after reaction with BH_4^-: $BH_4^- + 8Ag^+ + 8OH^- \rightarrow 8Ag(s) + H_2BO_3^- + 5H_2O$
K^+	K^+ is first precipitated with a known excess of $(C_6H_5)_4B^-$. Remaining $(C_6H_5)_4B^-$ is precipitated with a known excess of Ag^+. Unreacted Ag^+ is then titrated with SCN^-.
	Fajans Method
Cl^-, Br^-, I^-, SCN^-, $Fe(CN)_6^{4-}$	Titration with Ag^+. Detection with dyes such as fluorescein, dichlorofluorescein, eosin, bromophenol blue.
F^-	Titration with $Th(NO_3)_4$ to produce ThF_4. End point detected with alizarin red S.
Zn^{2+}	Titration with $K_4Fe(CN)_6$ to produce $K_2Zn_3[Fe(CN)_6]_2$. End-point detection with diphenylamine.
SO_4^{2-}	Titration with $Ba(OH)_2$ in 50 vol% aqueous methanol using alizarin red S as indicator.
Hg_2^{2+}	Titration with NaCl to produce Hg_2Cl_2. End point detected with bromophenol blue.
PO_4^{3-}, $C_2O_4^{2-}$	Titration with $Pb(CH_3CO_2)_2$ to give $Pb_3(PO_4)_2$ or PbC_2O_4. End point detected with dibromofluorescein (PO_4^{3-}) or fluorescein ($C_2O_4^{2-}$).

Precipitation titration part 3

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Problems

Suppose a method using argenometry for determination of K+?
(Hint look to the table on the previous slide)

1. Add to K+ solution a known amount (Volume and concentration of tetraphenyl boron----------- a ppt will be formed (Write balance equation)

2. Add a known amount of Ag+ to the above solution.
Unreacted tetraphenyl boron reacts with Ag+ (Write balance equation)

3. Titrate the unreacted Ag+ with SCN^- standard solution (Write balance equation)

Problems

Argenometry for determination of K+?

No. mole $B(C_6H_5)_4^-$ (total) = Known

No. mole Ag^+ (total) = Known

1. $K^+ + B(C_6H_5)_4^-{}_{reacted} \longrightarrow KB(C_6H_5)_4$

2. $Ag^+{}_{reacted} + B(C_6H_5)_4^-{}_{unreacted} \longrightarrow AgB(C_6H_5)_4$

3. $Ag^+{}_{unreacted} + SCN^- \longrightarrow AgSCN$

No. mole SCN^- (Titrant) = Volume * Conc.

Problems

A silver nitrate solution contains 14.77 g of primary standard $AgNO_3$ in 1.00 L. What volume of this solution will be needed to react with

(a) 0.2631 g of NaCl?

(b) 64.13 mg of Na_3AsO_4?

(c) 50.00 mL of 0.01808 M H_2S?

(d) 0.3462-g sample $ZnCl_2$ assayed 74.52% (w/w)?

Problems

b)

Conc.(M) $AgNO_3 = \frac{14.77\ (g)}{169.87\ (g/mol)} * \frac{1}{1\ (L)} = 0.087\ (M)$

64.13 mg of Na_3AsO_4?

$3\ Ag^+ + Na_3AsO_4 \longrightarrow Ag_3AsO_4 + 3\ Na^+$

No mmol $Ag^+ = \frac{3\ mol\ Ag^+}{1\ mol\ Na_3AsO_4} *$ no mmol $Na_3AsO_4 =$

$= \frac{3 * 64.13\ mg}{1 * 207.889\ (mg/mmol)} = 0.925\ (mmol)$

Conc (M) * Vol (mL) = 0.925 (mmol)

Vol = 10.63 (mL)

Problems

d)

0.3462-g sample $ZnCl_2$ assayed 74.52% (w/w)?

$$2\ Ag^+ + ZnCl_2 \longrightarrow 2\ AgCl + Zn^{+2}$$

$$\text{No mmol } Ag^+ = \frac{2 \text{ mol } Ag^+}{1 \text{ mol } ZnCl_2} * \text{ no mol } ZnCl_2 =$$

74.52 g $ZnCl_{2}$ ---------------------------- 100 g powder

---------------------------- 0.3462 g

Wt of $ZnCl_2$ = **0.258 g**

$$\text{No mmol } Ag^+ = \frac{2 * 0.258\ g}{1 * 136.29 (g/mol)} = 0.0038 \text{ (mol)}$$

Conc (M) * Vol (L) = 0.0038 (mol)

Vol = 0.044 (L)

Problems

Fajans titration of a 0.7908-g sample required 45.32 mL of 0.1046 M $AgNO_3$. Express the results of this analysis in terms of the percentage of:

(a) Cl^-.

(b) $BaCl_2 . H_2O$.

(c) $ZnCl_2 . 2NH_4Cl$ (243.28 g/mol).

Problems

A 2.00 L sample of mineral water was evaporated to a small volume following which K^+ was precipitated with excess sodium tetraphenyl boron:

$$K^+ + NaB(C_6H_5)_4 \longrightarrow KB(C_6H_5)_4\ (s) + Na^+$$

The precipitate was filtered, washed and re-dissolved in acetone. The analysis was completed by a Moher titration that required 43.85 mL of 0.03941 M $AgNO_3$

$$KB(C_6H_5)_4 + Ag^+ \longrightarrow AgB(C_6H_5)_4\ (s) + K^+$$

Calculate the K^+ concentration (ppm) in water sample?

Problems

No mmol Ag^+ = 43.85 (mL) * 0.03941(M) = 1.728 (mmol)

No mmol Ag^+ = no mmol $KB(C_6H_5)_4$ = no mmol K^+
= 1.728 (mmol)

$$\text{Conc } K^+ \text{ (ppm)} = \frac{\text{Wt of K+ (mg)}}{\text{Vol (L)}} = \frac{\text{no mmol * AW}}{\text{Vol (L)}} =$$

$$= \frac{1.728 \text{ (mmol)} * 39 \text{ (mg/mmol)}}{2.0 \text{ (L)}} = 33.7 \text{ (ppm)}$$

Precipitation titration part 4

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Problems

The phosphate in a 4.258 g sample of plant food was precipitated as Ag_3PO_4 through the addition of 50 ml of (0.0820 M) $AgNO_3$. The solid was filtered and washed, following which **the filtrate and washings were diluted to exactly 250 ml.** Titration of a 50.0 ml aliquot of this solution required a 4.64 ml back titration with 0.0625 M KSCN. Express the result of analysis in terms of **the percentage of P_2O_5. (MW P_2O_5 = 141.99)**

$$3\,Ag^{+} + PO_4^{-3} \longrightarrow Ag_3PO_4\,(s)$$

Hint: titration with SCN^- is for Ag+ unreacted remaining in filtrate.

Solution : 1.47%

Problems

??????
% P_2O_5 in sample

Problems

No mmol Ag^+ (total) = 50 (mL) * 0.0820 (M) = 4.1 (mmol)

No mmol Ag^+(unreacted) = no mmol KSCN = 4.64 (mL) * 0.0625(M)
= 0.29 (mmol)

No mmol Ag^+(unreacted) 0.29 (mmol) -------------------- 50 mL
? -------------------- 250 mL

No mmol Ag^+(unreacted) = 1.45 (mmol)

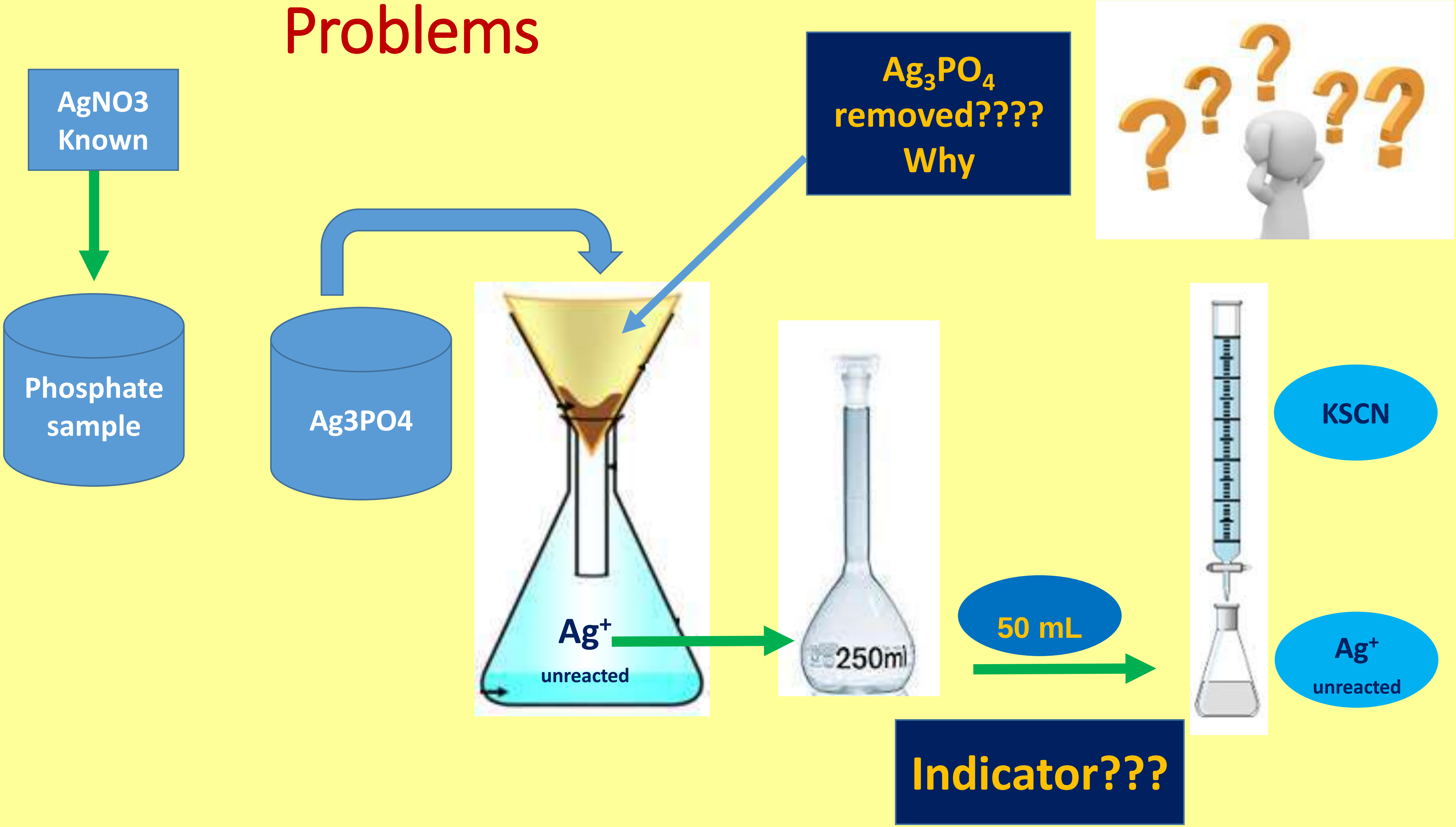
No mmol Ag^+ (reacted) = Total – unreacted = 2.65 (mmol)

$$\text{No mmol } PO_4^{-3} = \frac{1 \text{ mol } PO_4^{-3}}{3 \text{ mol } Ag^+} * \text{no mmol } Ag^+\text{(reacted)} = 0.88 \text{ (mmol)}$$

$$\text{No mmol } P_2O_5 = \frac{1 \text{ mol } P_2O_5}{2 \text{ mol } PO_4^{-3}} * \text{no mmol } PO_4^{-3} = 0.44 \text{ (mmol)}$$

$$\% P_2O_5 = \frac{0.44 * 10^{-3} \text{ (mol)} * 141.99 \text{ (g/mol)}}{4.258 \text{ (g)}} * 100 = 1.47\%$$

Problems



AgNO3
Known
Phosphate
sample
Ag3PO4
Ag_3PO_4
removed????
Why
Ag^+
unreacted
250ml
50 mL
KSCN
Ag^+
unreacted
Indicator???

Problems

The monochloroacetic acid ($ClCH_2COOH$) preservative in a 100 ml of a carbonate beverage was extracted into diethylether and then return to aqueous solution as $ClCH_2COO^-$ by extraction with 1 M NaOH. This aqueous solution is acidified and treated with 50 ml of 0.04521 M $AgNO_3$. The reaction is

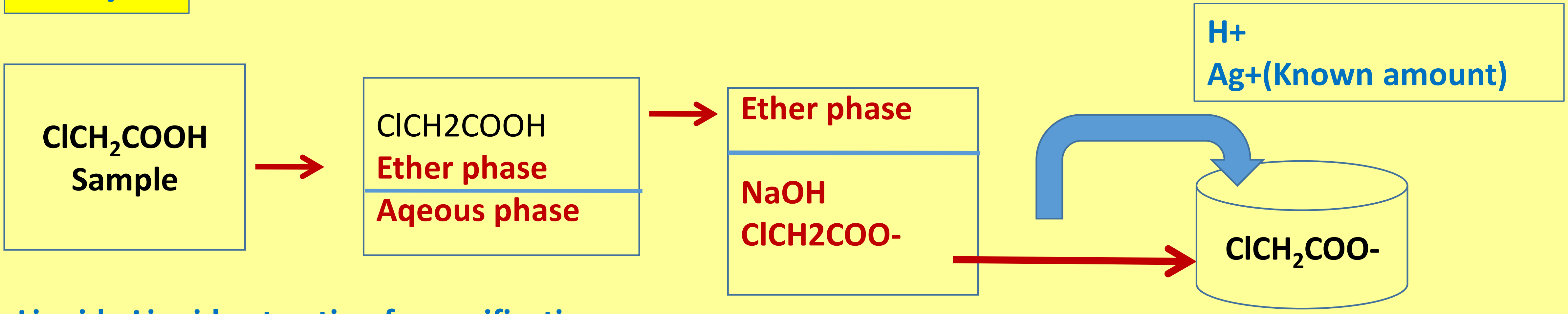
$$ClCH_2COOH + Ag^+ + H_2O \longrightarrow HOCH_2COOH + H^+ + AgCl\,(s)$$

After filtration of AgCl, titration of filtrate and washings required 10.43 ml of an NH_4SCN solution. Titration **of blank** taken through the entire process used 22.98 ml of NH_4SCN. Calculate the weight in mg $ClCH_2COOH$ in the sample.

Blank: is a sample with **no analyte.**

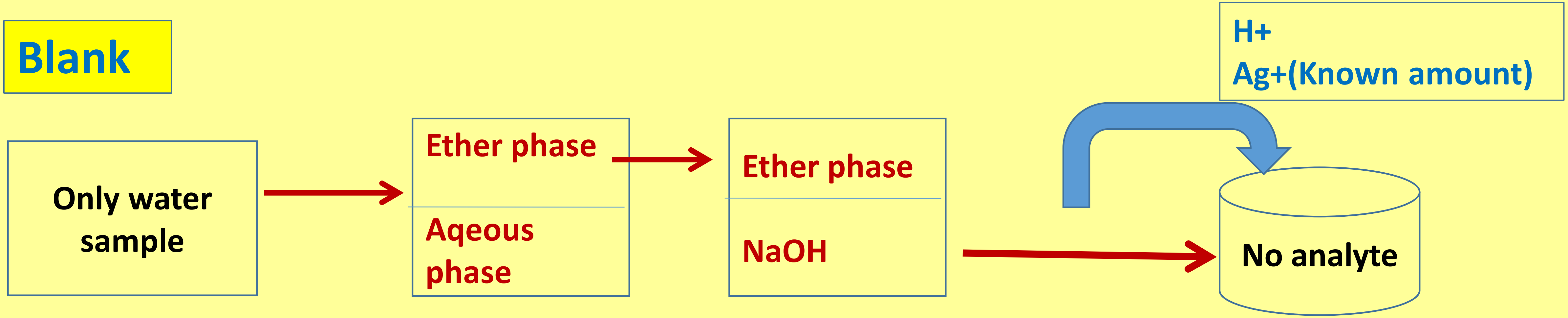
Solution: 117 mg

Sample



Liquid - Liquid extraction for purification

Blank



Remember: AgCl is filtered before back-titration with SCN^-

Problems

Blank

No mmol Ag^+ (total) = 50 (mL) * 0.04521 (M) = 2.2605 (mmol)

No mmol Ag^+ (total) = no mmol NH_4SCN = 22.98 (mL) * Conc. (M)=

$$\text{Conc (M) } NH_4SCN = \frac{2.2605 \text{ (mmol)}}{22.98 \text{ (mL)}} = 0.098 \text{ (M)}$$

Problems

No mmol Ag^+ (total) = 50 (mL) * 0.04521 (M) = 2.2605 (mmol)

No mmol Ag^+(unreacted) = no mmol NH_4SCN =10.43 (ml) * 0.098 (M)
= 1.022 (mmol)

No mmol Ag^+(reacted) = Total – unreacted = 1.2385 (mmol)

No mmol $ClCH_2COOH$ = no mmol Ag^+(reacted) = 1.2385 (mmol)

Wt of $ClCH_2COOH$ in sample = no mmol * MW =

= 1.2385 (mmol) * 94.45 (mg/mmol)= **117 (mg)**

Problems

Examples: 13-2

Problems Chapter 13:

1, 2, 3, 7, from 9 to 18, from 21 to 25, 27, 28.