

Gravimetry

Dr. Mai Ramadan

Gravimetry

Definition:

It is a method based on measurement of weight of an analyte or a compound containing the analyte. (Analysis by weighing)

Types:

Precipitation method

Volatilization method

Gravimetry

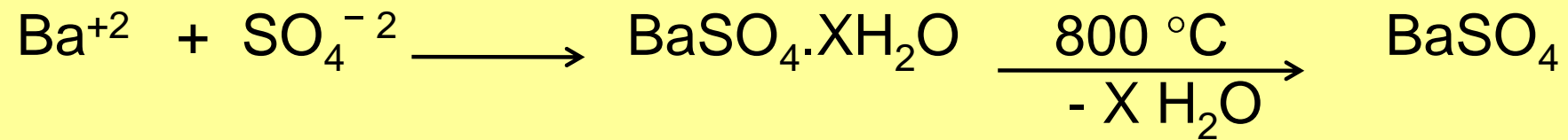
Precipitation method:

The species to be determined is precipitated by a reagent that yields a sparingly soluble product (or a product of known composition, or a product that can be converted to one of known composition).

Precipitation method

Examples:

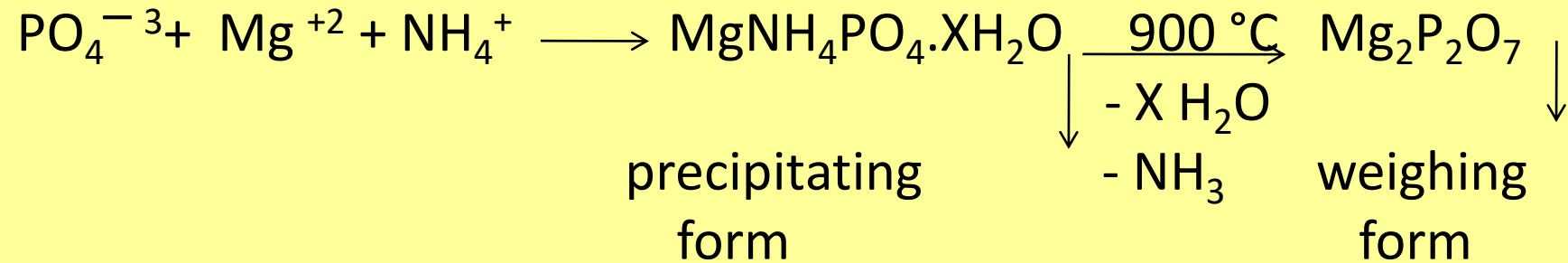
Determination of barium is performed by precipitation using sulfate as precipitating agent. The precipitate is BaSO_4 which remains after ignition up to $800\text{ }^\circ\text{C}$ as BaSO_4



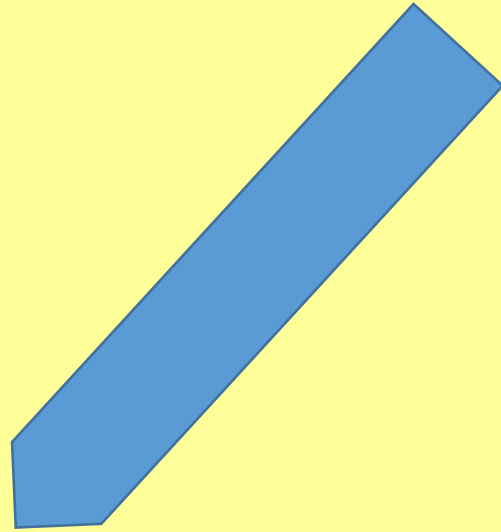
Precipitation method

Examples:

To precipitate phosphate $\text{Mg}^{+2}/\text{NH}_3$ buffer is added



Precipitation method



**Precipitating
form**



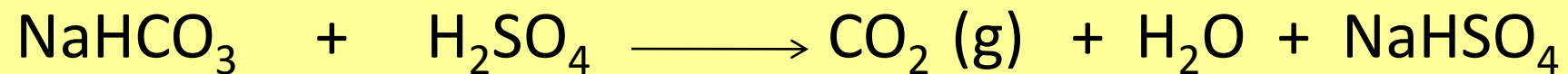
**Weighing
form**

Gravimetry

Volatilization method:

The analyte (or its decomposition products) are volatilized at a suitable temperature. The volatilized species are collected and weighed directly or weighed by difference.

Example:



$$\text{Wt CO}_2 = X_t - X_o$$

X_t: wt of media after absorption

X_o: original weight of media

Steps of precipitation method

Sample preparation

Addition of precipitating solution

Digestion

Filtration

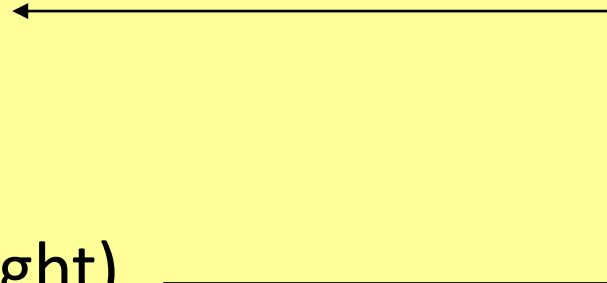
Washing

Drying or ignition

Cooling down in desiccator

Weighing \longrightarrow (constant weight) \longleftarrow

Calculation



Steps of precipitation method

Sample preparation

The sample should be weighed, grounded and then dissolved. pH adjustment could be needed.

Addition of precipitating agent

This stage is critical for the precipitate, since it influences its physical properties.

Precipitating agent should be added hot, diluted, slowly and under stirring.

Steps of precipitation method

Digestion: the precipitate is allowed to stand in the presence of the mother liquor at elevated temp. or by room temp. and large particles grow at the expense of small ones.

Digestion improves the purity and filtrability of both colloidal and crystalline ppt.

This process includes the dissolution and recrystallization of small particles which results in bridging between particles to form a larger, easily filtrable one.

Steps of precipitation method

Filtration:

separation of the precipitate from the mother liquor.

Filtration should be accelerated using Buchner funnel.

The media employed for filtration are:

Filter paper:

It has a very small ash content, retain the smallest particles of precipitate (Porosity) and permit rapid filtration.

Steps of precipitation method

Sintered-glass filtering crucible:

It is made of resistance glass and have a porous disc
(*various porosity indicated from 0-5, see Tab.*)

It should not be heated above 200°C.

Don,t use for strongly alkaline

Porosity	0	1	2	3	4	5
Pore diameter (µm)	200-250	100-120	40-50	20-30	5-10	1-2

Porcelain filtering crucible: porous filter base, can be heated to higher temprature.

Steps of precipitation method

Washing:

to remove impurities adsorbed on the surface after filtration using distilled water for several times.

Drying and ignition

Drying:

removes the solvent(s) of the mother liquid from which the precipitate was formed. For Temp. up to 250 °C a thermostatically controlled electric oven is used.

Steps of precipitation method

Ignition:

converts the precipitate to a known composition called the *weighing form*. For higher Temp. a muffle furnace is used.

Drying/ignition behavior

Consider calcium oxalate

Around 145 °C, calcium oxalate exists as $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$.

Around 225 °C, calcium oxalate exists as CaC_2O_4 .

Around 500 °C, calcium oxalate exists is converted to CaCO_3 .

Above 900 °C, calcium carbonate is converted to CaO .

Steps of precipitation method

Ignition:

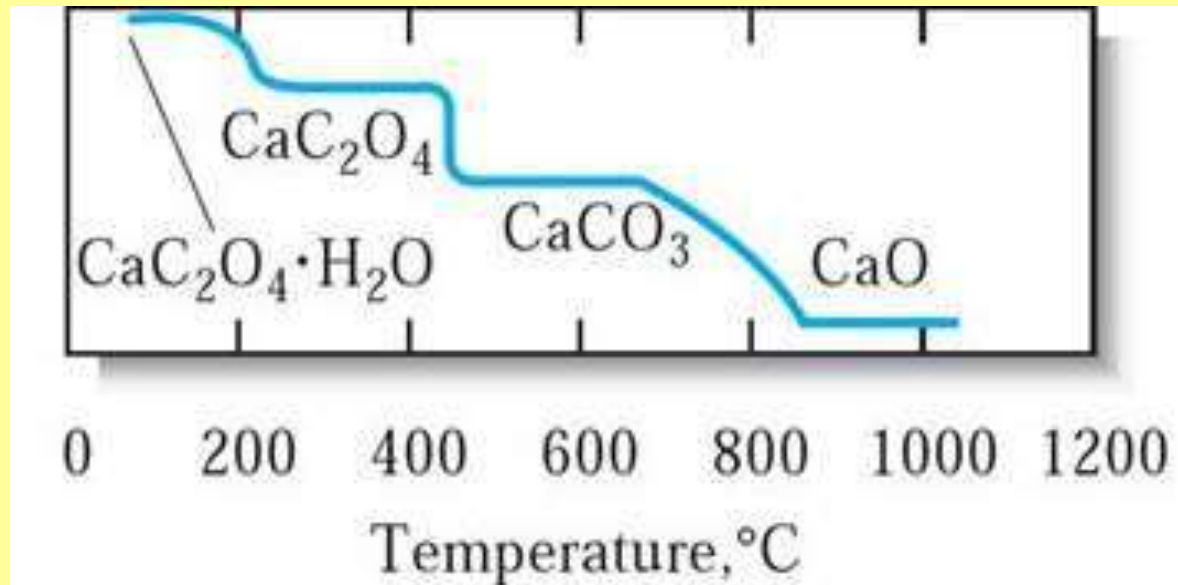


Figure 4-7 Effect of temperature on precipitate mass.

Steps of precipitation method

Cooling in desiccator:

The ppt should be put in desiccator after drying or ignition.

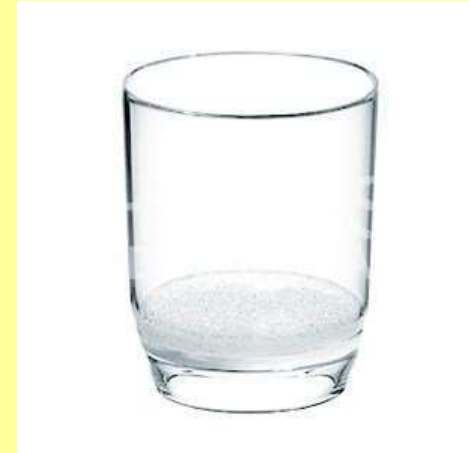
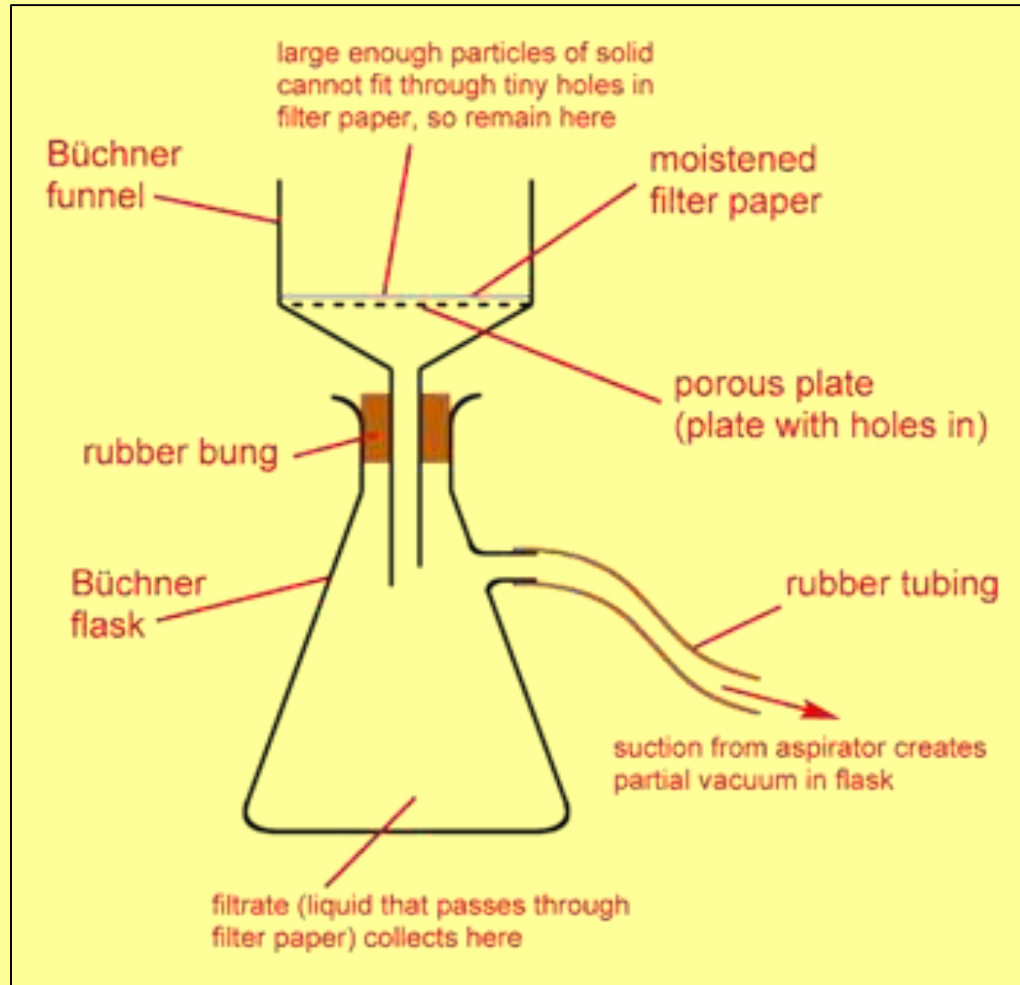
Weighing:

Using a digital calibrated balance. Drying process is repeated until the weight is not more changed.

Calculation:

It will be discussed later.

Steps of precipitation method



Glass filtering crucible



Desiccator

Formation of precipitate

Two steps are involved in this process:

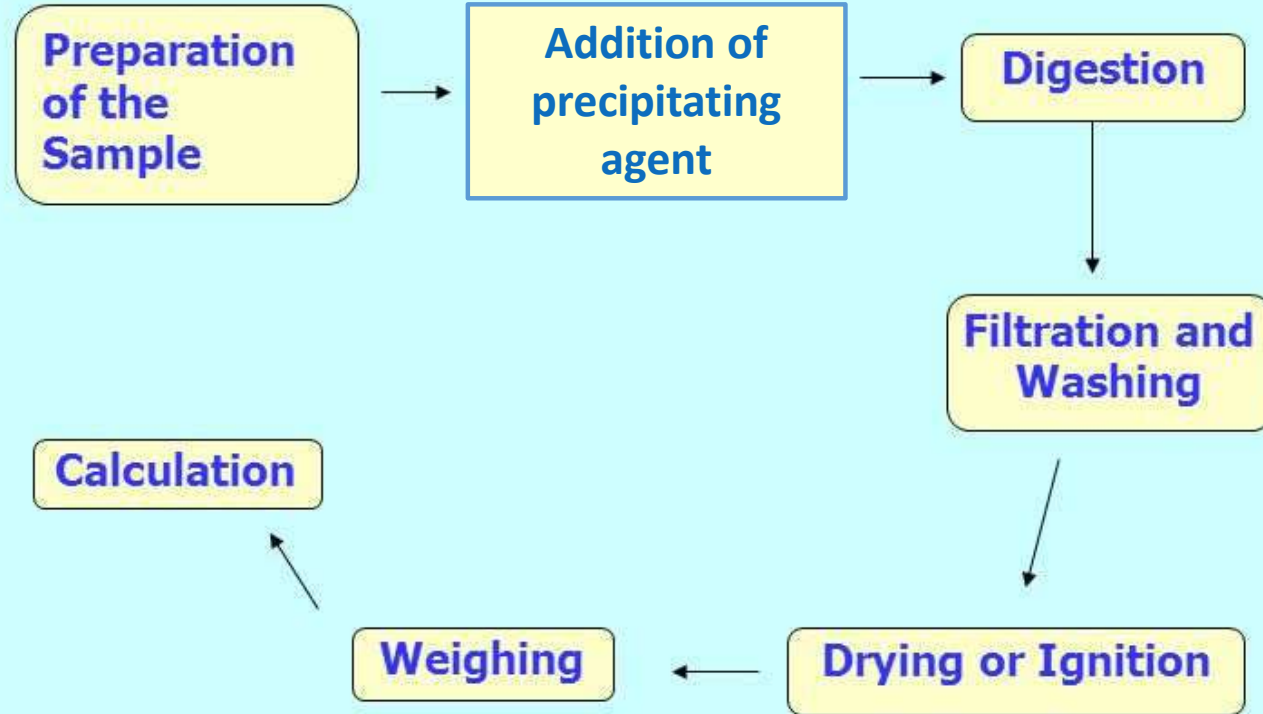
- 1. *Nucleation*:** Formation of the smallest precipitate particles in a supersaturated solution, which are capable of spontaneous growth.
- 2. *Particle Growth*:** Deposition of ions/molecules on the surface of the solid, nucleated particles.

To obtain particles with the best characters (large pure crystals) then form your precipitate slowly using warm, dilute solution with stirring then allow it to digest without stirring.

Gravimetry

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STEPS OF A GRAVIMETRY ANALYSIS



Mechanisms of Co-precipitation

Co-precipitation: is the precipitation of an otherwise soluble substance along with the insoluble material.

Mechanisms of Co-precipitation

1. Surface adsorption
2. Inclusion (mixed crystal formation, Isomorphous)
3. Occlusion
4. Postprecipitation

Mechanisms of Co-precipitation

Surface adsorption

it is a process in which a substance is held on the surface of a solid.

It can be removed by washing and digestion.

Inclusion (mixed crystal formation, Isomorphous)

Ions of the same charge and size are trapped within crystal lattice.

K^+ replaces NH_4^+ in $MgNH_4PO_4$, Sr^{+2} in $BaSO_4$ and Mn^{+2} in CdS .

Mechanisms of Co-precipitation

Occlusion

In this process material that is not part of crystal structure is trapped in a pocket of a rapidly growing precipitate .

Both occlusion and occlusion can not be improved by washing. Digestion and re-precipitation can remove such impurities.

Mechanisms of Co-precipitation

Postprecipitation: CaC_2O_4 & Mg^{+2}

The precipitate causes a localized high concentration of unwanted species, when the precipitate allowed to stand in contact with the mother liquor.

To avoid post-precipitation a rapid filtration and removal of undesired ions before the precipitation are required.

Colloidal precipitate

Colloidal particles : According to particle size

$\geq 10^{-5}$

$10^{-5} - 10^{-7}$

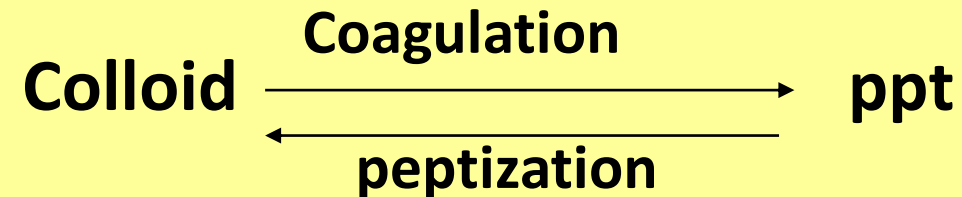
$\leq 10^{-7}$ cm

suspension

colloid

solution

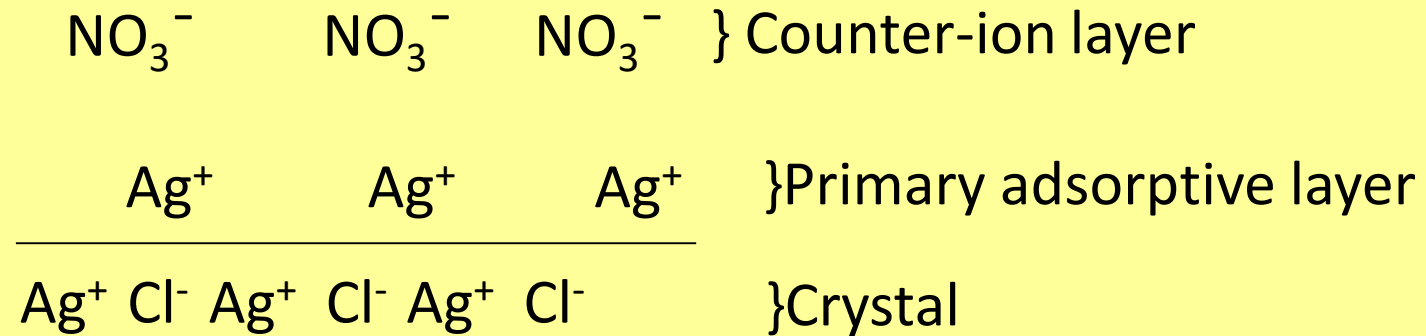
Colloidal particles do not settle out. Filtration is difficult due to plugging of pores in the filter, or passing through the filter.



Coagulation is accomplished by: Stirring, heating and by adding of an electrolyte

Colloidal precipitate

For example: precipitation of Cl^- with an excess of AgNO_3



Colloidal precipitate

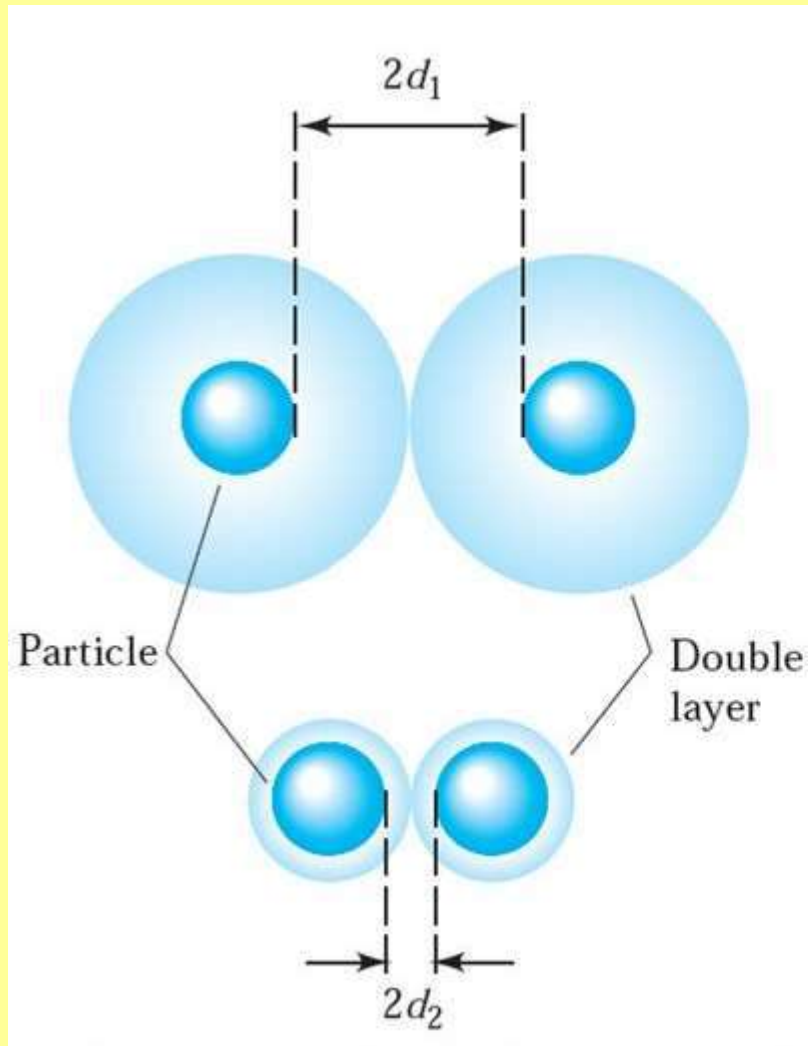


Figure 4-4 The electric double layer of a colloid consists of a layer of charge adsorbed on the surface of the particle (the primary adsorption layer) and a layer of opposite charge (the counterion layer) in the solution surrounding the particle. Increasing the electrolyte concentration has the effect of decreasing the volume of the counterion layer, thereby increasing the chances for coagulation.

Precipitation from homogenous solution

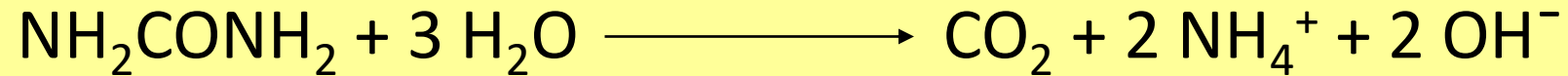
It is a technique in which a precipitating agent is generated in a solution of the analyte by a slow chemical reaction.

The relative supersaturation is kept low.

The precipitating agent is formed homogeneously and reacts immediately with the analyte.

Precipitation from homogenous solution

Example: Urea for Fe (III) and Al (III)



Others: ethyl oxalate, trimethyl phosphate, dimethyl sulfate,

Thioacetamide (see table 5-3)

Precipitation from homogenous solution



Methods for Homogeneous Generation of Precipitating Agents			
Precipitating Agent	Reagent	Generation Reaction	Elements Precipitated
OH ⁻	Urea	$(\text{NH}_2)_2\text{CO} + 3\text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{NH}_4^+ + 2\text{OH}^-$	Al, Ga, Th, Bi, Fe, Sn
PO ₄ ³⁻	Trimethyl phosphate	$(\text{CH}_3\text{O})_3\text{PO} + 3\text{H}_2\text{O} \rightarrow 3\text{CH}_3\text{OH} + \text{H}_3\text{PO}_4$	Zr, Hf
C ₂ O ₄ ²⁻	Ethyl oxalate	$(\text{C}_2\text{H}_5)_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O} \rightarrow 2\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{C}_2\text{O}_4$	Mg, Zn, Ca
SO ₄ ²⁻	Dimethyl sulfate	$(\text{CH}_3\text{O})_2\text{SO}_2 + 4\text{H}_2\text{O} \rightarrow 2\text{CH}_3\text{OH} + \text{SO}_4^{2-} + 2\text{H}_3\text{O}^+$	Ba, Ca, Sr, Pb
CO ₃ ²⁻	Trichloroacetic acid	$\text{Cl}_3\text{CCOOH} + 2\text{OH}^- \rightarrow \text{CHCl}_3 + \text{CO}_3^{2-} + \text{H}_2\text{O}$	La, Ba, Ra
H ₂ S	Thioacetamide*	$\text{CH}_3\text{CSNH}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CONH}_2 + \text{H}_2\text{S}$	Sb, Mo, Cu, Cd
DMG†	Biacetyl + hydroxylamine	$\text{CH}_3\text{COCOCH}_3 + 2\text{H}_2\text{NOH} \rightarrow \text{DMG} + 2\text{H}_2\text{O}$	Ni
HOQ‡	8-Acetoxyquinoline§	$\text{CH}_3\text{COOQ} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{HOQ}$	Al, U, Mg, Zn

Precipitating agents

Precipitating agents



Inorganic

See table (5-4)

Notice:

precipitating form and
weighing form

Organic

Chelating agent: 8-OHquinoline,
Dimethylglyoxime

Salt formation: $\text{NaB}(\text{C}_6\text{H}_5)_4$

Inorganic precipitating agents

Some Inorganic Precipitating Agents	
Precipitating Agent	Element Precipitated*
$\text{NH}_3(aq)$	Be (BeO), Al (Al_2O_3), Sc (Sc_2O_3), Cr (Cr_2O_3)†, Fe (Fe_2O_3), Ga (Ga_2O_3), Zr (ZrO_2), In (In_2O_3), Sn (SnO_2), U (U_3O_8)
H_2S	Cu (CuO)†, Zn (ZnO or ZnSO_4), Ge (GeO_2), As (<u>As_2O_3</u> or As_2O_5), Mo (MoO_3), Sn (SnO_2)†, Sb (<u>Sb_2O_3</u> , or Sb_2O_5), Bi (Bi_2S_3)
$(\text{NH}_4)_2\text{S}$	Hg (<u>HgS</u>), Co (Co_3O_4)
$(\text{NH}_4)_2\text{HPO}_4$	Mg ($\text{Mg}_2\text{P}_2\text{O}_7$), Al (AlPO_4), Mn ($\text{Mn}_2\text{P}_2\text{O}_7$), Zn ($\text{Zn}_2\text{P}_2\text{O}_7$), Zr ($\text{Zr}_2\text{P}_2\text{O}_7$), Cd ($\text{Cd}_2\text{P}_2\text{O}_7$), Bi (BiPO_4)
H_2SO_4	Li, Mn, Sr, Cd, Pb, Ba (all as sulfates)
H_2PtCl_6	K (K_2PtCl_6 or Pt), Rb (<u>Rb_2PtCl_6</u>), Cs (<u>Cs_2PtCl_6</u>)
$\text{H}_2\text{C}_2\text{O}_4$	Ca (CaO), Sr (SrO), Th (ThO_2)
$(\text{NH}_4)_2\text{MoO}_4$	Cd (CdMoO_4)†, Pb (<u>PbMoO_4</u>)

Inorganic precipitating agents

HCl	Ag (AgCl), Hg (Hg ₂ Cl ₂), Na (as NaCl from butyl alcohol), Si (SiO ₂)
AgNO ₃	Cl (AgCl), Br (<u>AgBr</u>), I(<u>AgI</u>)
(NH ₄) ₂ CO ₃	Bi (Bi ₂ O ₃)
NH ₄ SCN	Cu [Cu ₂ (SCN) ₂]
NaHCO ₃	Ru, Os, Ir (precipitated as hydrous oxides, reduced with H ₂ to metallic state)
HNO ₃	Sn (SnO ₂)
H ₅ IO ₆	Hg [Hg ₅ (IO ₆) ₂]
NaCl, Pb(NO ₃) ₂	F (PbClF)
BaCl ₂	SO ₄ ²⁻ (BaSO ₄)
MgCl ₂ , NH ₄ Cl	PO ₄ ³⁻ (Mg ₂ P ₂ O ₇)

Organic precipitating agents



■ Chelating agent

8-hydroxyquinoline

Dimethylglyoxime



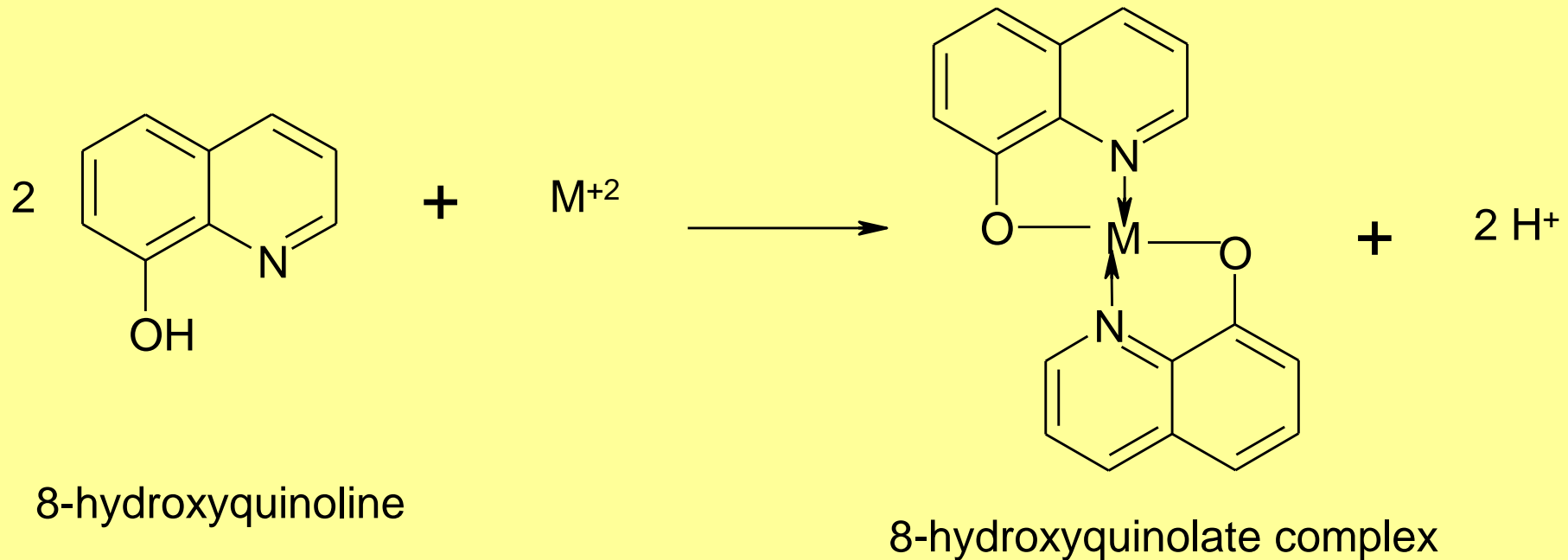
■ Salt formation

Sodium tetraphenylboron

Organic precipitating agents

Chelating agent

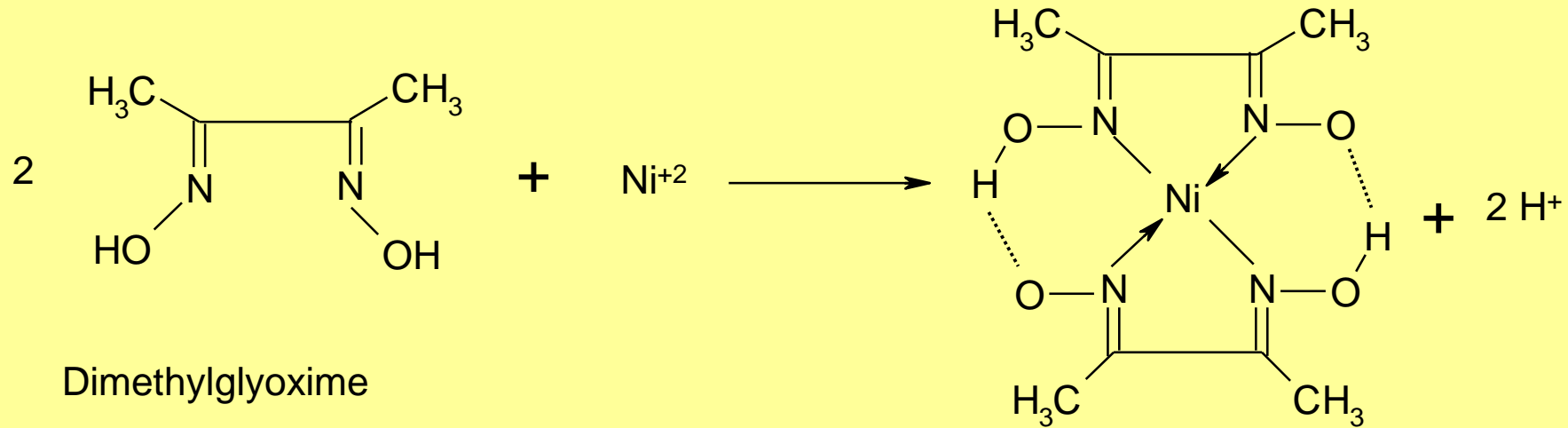
8-hydroxyquinoline: used for Mg^{+2} , Zn^{+2} , Al^{+3} , Cd^{+2} , Cu^{+2} , --



Organic precipitating agents

Chelating agent

Dimethylglyoxime (DMG): for Ni⁺²



Organic precipitating agents

Salt formation:

Sodium tetraphenylboron $\text{NaB}(\text{C}_6\text{H}_5)_4$: for K^+ , NH_4^+ , Cs^+



Gravimetry part 3

Dr. Mai Ramadan

Calculation

Stoichiometry: the weight relationships among reacting chemical species

Mole: one mole of a chemical species is 6.022×10^{23} atoms, molecules, ions or ion pairs.

No. moles = Weight (g)/formula weight (g/mol)

No. millimoles = weight (mg)/formula weight (mg/mmol)

Calculation

Treatment of a 0.400 g sample of impure potassium chloride with an excess of AgNO_3 resulted in the formation of 0.7332 g AgCl . **Calculate the percentage of KCl in the sample.**

(FW AgCl = 143.42, KCl = 74.56)



No. Mol AgCl = weight (g) / MW (g/mol)

No. Mol AgCl = $0.7332 \text{ (g)} / 143.42 \text{ (g/mol)} = 5.112 \times 10^{-3}$
mol

Calculation

$$\text{No. mol KCl} = \frac{1 \text{ mol KCl}}{1 \text{ mol AgCl}} \times \text{No. mol AgCl}$$

$$\text{No. mol KCl} = 5.112 \times 10^{-3} \text{ (mol)}$$

$$\begin{aligned} \text{Wt of KCl} &= \text{no. mol KCl} * \text{MW} = \\ &= 5.112 \times 10^{-3} \text{ (mol)} * 74.56 \text{ (g/mol)} \\ &= 0.3812 \text{ (g)} \end{aligned}$$

$$\% \text{ KCl} = \frac{\text{Wt of KCl (g)}}{\text{Wt of sample (g)}} \times 100 = 95.3\%$$

Stoichiometric factor



You look for no mol. X???????? and no moles W is known

$$\text{No. moles X} = \frac{a}{c} * \text{no. moles W}$$

a & c are no moles of the unknown (X) and no moles of known (W) according to the balanced equation

Calculation

What weight of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (fw = 244.25) is needed to react with 0.1503 g of:

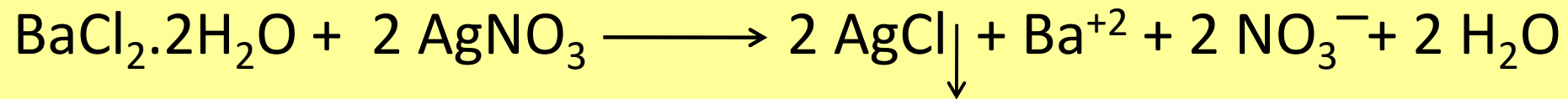
AgNO_3 (fw = 169.9 g)? (AgCl , FW= 143.32)

MgSO_4 ? (BaSO_4)

H_3PO_4 ? ($\text{Ba}_3(\text{PO}_4)_2$)

What is the weight of the resulting precipitate?

Calculation



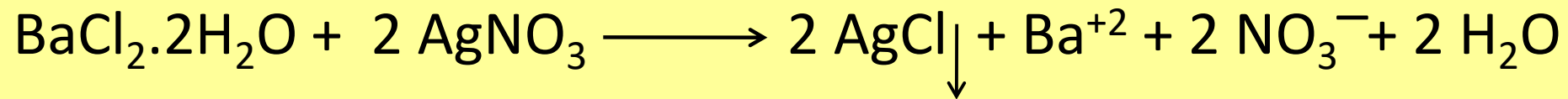
$$\text{No. mol BaCl}_2 \cdot 2\text{H}_2\text{O} = \frac{1 \text{ mol BaCl}_2 \cdot 2\text{H}_2\text{O}}{2 \text{ mol AgNO}_3} \times \text{No. mol AgNO}_3$$

$$\text{No. mol BaCl}_2 \cdot 2\text{H}_2\text{O} = \frac{1}{2} \times \frac{0.1503 \text{ (g)}}{169.9 \text{ (g/mol)}} = 4.4232 \cdot 10^{-4} \text{ (mol)}$$

$$\text{Wt BaCl}_2 \cdot 2\text{H}_2\text{O} = \text{No. mol BaCl}_2 \cdot 2\text{H}_2\text{O} \times \text{MWt}$$

$$\text{Wt BaCl}_2 \cdot 2\text{H}_2\text{O} = 4.4232 \cdot 10^{-4} \text{ (mol)} \times 244.25 \text{ (g/mol)} = 0.1080 \text{ (g)}$$

Calculation



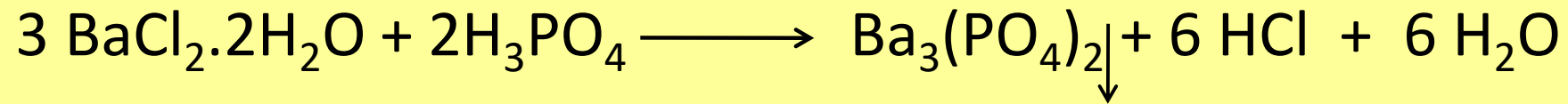
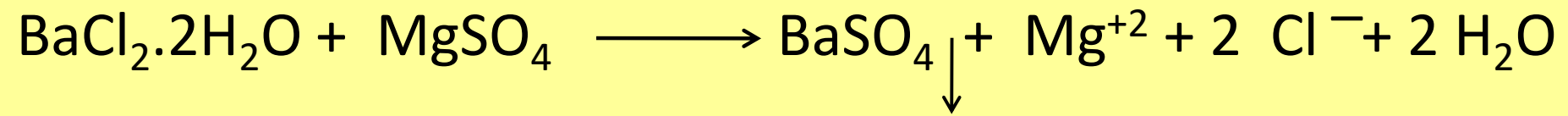
$$\text{No. mol AgCl produced} = \frac{2 \text{ mol AgCl}}{2 \text{ mol AgNO}_3} \times \text{No. mol AgNO}_3$$

$$\text{No. mol AgCl} = \frac{2}{2} \times \frac{0.1503 \text{ (g)}}{169.9 \text{ (g/mol)}} = 8.8464 \times 10^{-4} \text{ (mol)}$$

$$\text{Wt AgCl} = \text{No. mol AgCl} \times \text{MWt}$$

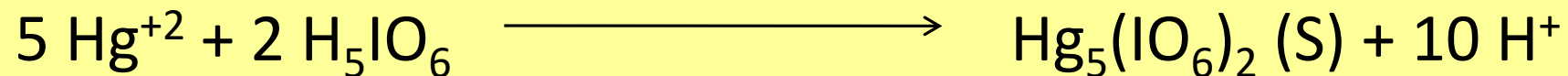
$$\text{Wt AgCl} = 8.8464 \times 10^{-4} \text{ (mol)} \times 143.32 \text{ (g/mol)} = 0.1268 \text{ (g)}$$

Calculation



Calculation

The mercury in a 0.7152 g sample was precipitated with an excess of paraperiodic acid H_5IO_6



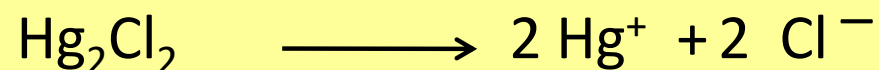
The precipitate was filtered, washed free of precipitating agent, dried and found to weigh 0.3408 g. **Calculate the percentage of Hg_2Cl_2 in the sample**

(FW $\text{Hg}_5(\text{IO}_6)_2 = 1448.76$, $\text{Hg}_2\text{Cl}_2 = 472.09$)

Calculation

$$\text{No. Mol Hg}^{+2} = \frac{5 \text{ mol Hg}^{+2}}{1 \text{ mol Hg}_5(\text{IO}_6)_2} \times \text{No. mol Hg}_5(\text{IO}_6)_2$$

$$\text{No. Mol Hg}^{+2} = \frac{5}{1} \times \frac{0.3408 \text{ (g)}}{1448.76 \text{ (g/mol)}} = 1.176 \times 10^{-3} \text{ (mol)}$$



$$\text{No. Mol Hg}_2\text{Cl}_2 = \frac{1 \text{ mol Hg}_2\text{Cl}_2}{2 \text{ mol Hg}^{+2}} \times \text{no. mol Hg}^{+2} = 5.881 \times 10^{-4} \text{ (mol)}$$

Calculation

$$\text{Wt Hg}_2\text{Cl}_2 = \text{No. Mol Hg}_2\text{Cl}_2 \times \text{MWt}$$

$$\text{Wt Hg}_2\text{Cl}_2 = 5.881 \times 10^{-4} \text{ (mol)} \times 472.09 \text{ (g/mol)} = 0.2777 \text{ (g)}$$

$$\% \text{ Hg}_2\text{Cl}_2 = \frac{\text{Wt of Hg}_2\text{Cl}_2 \text{ (g)}}{\text{Wt of sample (g)}} \times 100 =$$

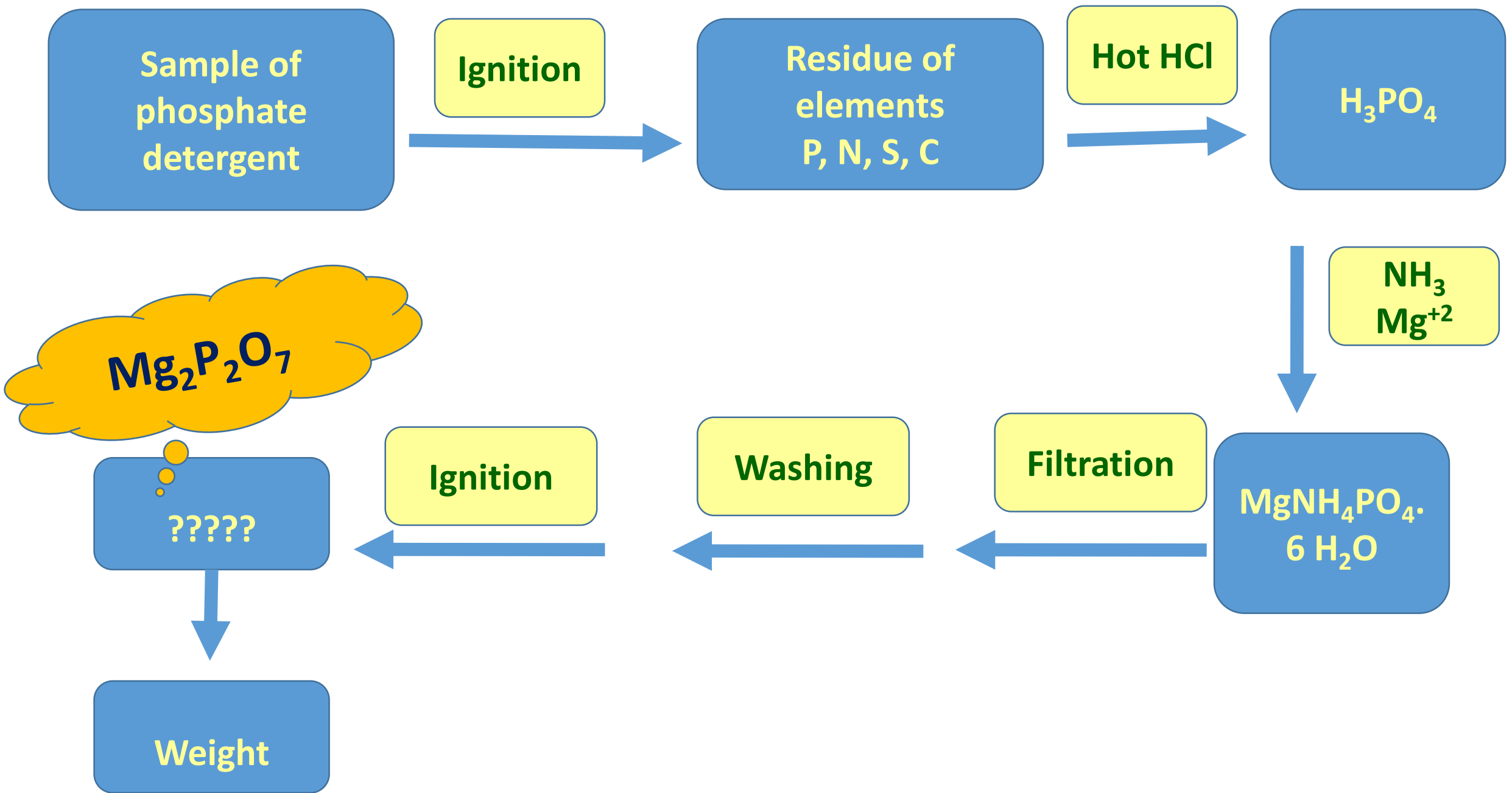
$$\% \text{ Hg}_2\text{Cl}_2 = 38.83\%$$

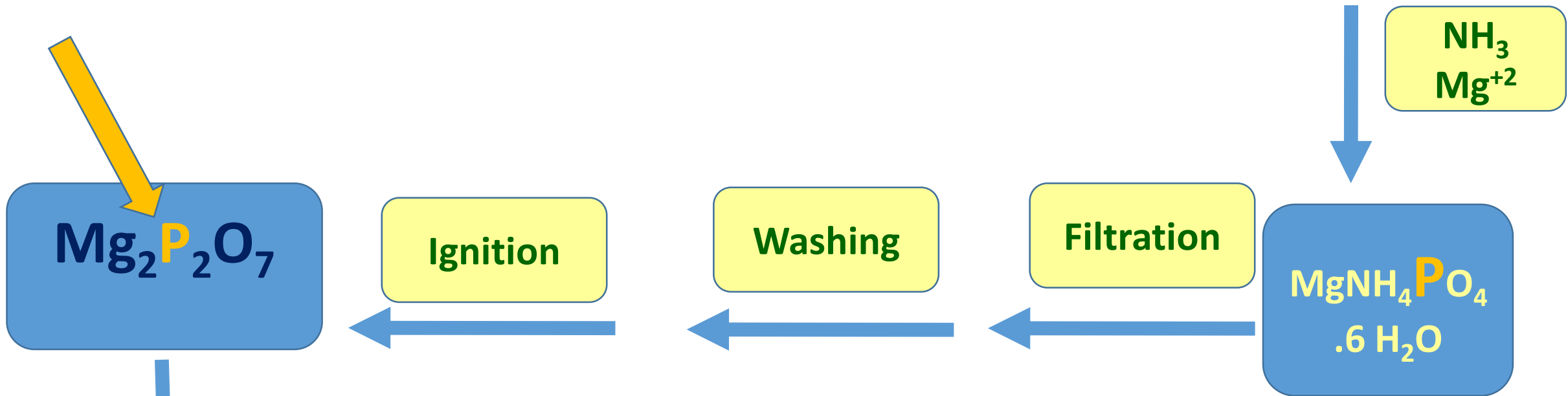
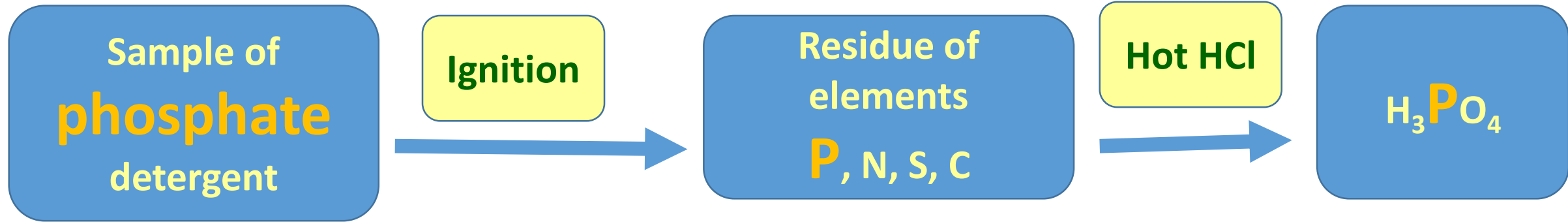
Gravimetry part 4

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Calculation

A 0.3516 g sample of a commercial phosphate detergents was ignited at red heat to destroy the organic matter. The residue was then taken up in hot HCl, which converts the P to H_3PO_4 . The phosphate was precipitated as $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ by addition of Mg^{+2} followed by aq. NH_3 . After being filtered and washed, the precipitate was ignited at $1000\text{ }^\circ\text{C}$ (*what is the weighing form*). The residue weighed 0.2161 g. **Calculate the percent P in the sample** (FW $\text{Mg}_2\text{P}_2\text{O}_7 = 222.57$, $\text{P} = 30.974$)





Wt of residue is known

Calculation

The weighing form is $\text{Mg}_2\text{P}_2\text{O}_7$

MWt of $\text{Mg}_2\text{P}_2\text{O}_7 = 222.57 \text{ (g/mol)}$

$$\text{No. Mol P} = \frac{2 \text{ mol P}}{1 \text{ mol Mg}_2\text{P}_2\text{O}_7} \times \text{No. mol Mg}_2\text{P}_2\text{O}_7$$

$$\text{No. Mol P} = \frac{2 \text{ mol P}}{1 \text{ mol Mg}_2\text{P}_2\text{O}_7} \times \frac{0.2161 \text{ (g)}}{222.57 \text{ (g/mol)}} = 1.9419 \times 10^{-3} \text{ (mol)}$$

$$\begin{aligned} \text{Wt P} &= \text{No. mol P} \times \text{MWt} = \\ &= 1.9419 \times 10^{-3} \text{ (mol)} \times 30.974 \text{ (g/mol)} \\ &= 0.060 \text{ (g)} \end{aligned}$$

Calculation

The source of phosphor in the final ppt $\text{Mg}_2\text{P}_2\text{O}_7$

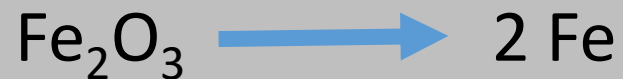
$$\% \text{ P in sample} = \frac{\text{Wt of P (g)}}{\text{Wt of sample (g)}} \times 100 =$$

$$\% \text{ P in sample} = \frac{0.060 \text{ (g)}}{0.3516 \text{ (g)}} \times 100 = 17.11\%$$

An iron ore was analyzed by dissolving a 1.1324-g sample in concentrated HCl. The resulting solution was diluted with water, and the iron(III) was precipitated as the hydrous oxide $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ by the addition of NH_3 . After filtration and washing, the residue was ignited at a high temperature to give 0.5394 g of pure Fe_2O_3 (159.69 g/mol). Calculate (a) the % Fe (55.847 g/mol) and (b) the % Fe_3O_4 (231.54 g/mol) in the sample.

Solution FW of Fe_2O_3 = (159.69 g/mol), AW of Fe = (55.847 g/mol)

$$\text{No. moles Fe}_2\text{O}_3 = \text{Wt} / \text{FW of Fe}_2\text{O}_3 = 3.3778 \times 10^{-3} \text{ mol Fe}_2\text{O}_3$$



$$\text{No moles Fe} = \frac{2 \text{ mol Fe}}{1 \text{ mol Fe}_2\text{O}_3} * \text{mol Fe}_2\text{O}_3 = 6.7556 \times 10^{-3} \text{ mol}$$

$$\text{Wt of Fe} = \text{No. moles Fe} * \text{AW} = 0.37728 \text{ g Fe}$$

$$\% \text{ Fe} = \frac{0.37728 \text{ g Fe}}{1.1324 \text{ g sample}} \times 100\% = 33.32\%$$



$$\text{No moles Fe}_3\text{O}_4 = \frac{1 \text{ mol Fe}_3\text{O}_4}{3 \text{ mol Fe}} * \text{no. mol Fe} =$$

$$\text{No moles Fe} = \frac{2 \text{ mol Fe}}{1 \text{ mol Fe}_2\text{O}_3} * \text{no mol Fe}_2\text{O}_3 =$$

$$\text{No moles Fe}_3\text{O}_4 = \frac{1 \text{ mol Fe}_3\text{O}_4}{3 \text{ mol Fe}} * \frac{2 \text{ mol Fe}}{1 \text{ mol Fe}_2\text{O}_3} * \text{no mol Fe}_2\text{O}_3$$

$$\text{No moles Fe}_3\text{O}_4 = \frac{2 \text{ mol Fe}_3\text{O}_4}{3 \text{ mol Fe}_2\text{O}_3} * \text{no mol Fe}_2\text{O}_3$$

$$\text{No moles Fe}_3\text{O}_4 = \frac{2 \text{ mol Fe}_3\text{O}_4}{3 \text{ mol Fe}_2\text{O}_3} * 3.3778 * 10^{-3} \text{ mol Fe}_2\text{O}_3 \text{ mol} =$$

$$\text{No moles Fe}_3\text{O}_4 = 2.2519 * 10^{-3} \text{ mol}$$

$$\text{wt Fe}_3\text{O}_4 = 2.2519 * 10^{-3} \text{ (mol)} * (231.54 \text{ g/mol}) = 0.52140 \text{ (g)}$$

$$\% \text{ Fe}_3\text{O}_4 = \frac{\text{Wt Fe}_3\text{O}_4 \text{ (g)}}{\text{Wt sample (g)}} * 100\% = 46.04\%$$

Problems

Chapter 5 : Questions no. 12,13,14, 15, 18, 24,25, 26,
27, 28, 30, 38

See also example : 5-3, 5-5