QUALITATIVE ANALYTICAL CHEMISTRY

Qualitative analysis

- Analytical chemistry is the chemistry discipline concerned with the chemical composition of materials. Analytical chemistry also is concerned with developing the tools used to examine chemical compositions.
- Qualitative analysis deals with the detection of the nature of the chemical species in a sample.
- Elemental qualitative analysis is used to separate and detect cations and anions in a sample substance.

Qualitative analysis

- Classical qualitative inorganic analysis is a method of analytical chemistry which seeks to find elemental composition of inorganic compounds. It is mainly focused on detecting ions in an aqueous solution, so that materials in other forms may need to be brought into this state before using standard methods. The solution is then treated with various reagents to test for reactions characteristic of certain ions, which may cause color change, solid forming and other visible changes.[1]
- Qualitative inorganic analysis is that branch or method of analytical chemistry which seeks to establish elemental composition of inorganic compounds through various reagents.

Qualitative analysis

- Evidence, detection
  - Chemical methods
  - „Instrumental“ methods (spectroscopic, electrochemical)
- Observations, evidence
  - Sensoric (crystals, homogeneity, olfactory assessment - smell, colour)
  - Changes depending on physical conditions (heating, coloration of flame)
  - Analytical reactions between examinated substance and analytical reagent (acid-base reactions, precipitation reactions, complex forming reactions, redox reactions, catalytic r.)
- Ionrganic qualitative analysis– ionic reactions

Procedure for qualitative analysis

1. Sampling, sample description
2. Preliminary tests
3. Transfer of sample into solution
4. Detetion of cations in 1/3 of sample solution
5. Detection of anions in 1/3 of sample solution
6. Verification of results in the remaining solution
7. Conclusion of analysis

Guidelines

A) Sample size ⇒ working technique
B) Preliminary tests
C) Only those elements that are expected to be present in solution based on preliminary tests should be tested
D) Results of analyses must agree with observations

Preliminary tests

- Nature of the sample
  - Heating in flame in presence of air
    - Burning (organic substances)
    - volatilization, sublimation (ammonium salts)
    - Melting (salts of alkali metals)
    - Residue after ignition (heavy metlas compounds ⇒ oxides)
    - Flame test – coloration (**Na**, **Ca**, **K**, **Ba**, **Cu**, **B**)
  - Test with H_2SO_4
    - diluted: gas evolution at cold (CO_2 carbonates, NO_2 nitrites) by heat (SO_2 from sulphites and thiosulphates, H_2S sulphides, HX halogenides)
    - concentrated: carbonization of organic substances, oxidation of Br^- and I^- evolution of Br_2 a I_2

Selectivity and implementation of analytical reactions

- According to the degree of selectivity we distinguish analytical reactions:
  - Group r. ≈ group reagents – for separation of cation groups
  - Selective r. ≈ selective reagents – at certain conditions proof of limited groups of cations – detection of one cation require more selective reactions
  - Specific ≈ under prescribed condition only one cation is proved
- Accomplishment of reactions
  - Test tube (5 ml, 1 ml), micro test tube (0,1 ml)
  - Drop (0,3 ml)
  - Microscope 0.01 ml

  $D = P/(V.10^6)$, P = observation limit (μg), V (ml), D = limiting dilution, **$pD = -\log D$**

Detection of cations

- history: Boettger, Fresenius – different properties of sulphides
- reagents: HCl, H_2S, $(NH_4)HS$, $(NH_4)_2CO_3$

1. Insoluble chlorides
2. Sulphides precipitating in acidic
3. Sulphides and hydroxides precipitating from ammoniacal medium
4. Insoluble carbonates
5. Cations that do not precipitate with any of above reagents

This separation is used no more (gaseous sulphane!)

Instead: group reactions preformed parallell in aliquot parts of a sample

DETECTION OF CATIONS, GROUP REACTIONS, SELECTIVE REACTIONS

Cations detection – group reactions

1. **HCl: Ag^+, Hg_2^{2+}, Pb^{2+}**
    - Ag^+: AgCl + hν → Ag (reduction, graying) dissolves in: CN^-, $S_2O_3^{2-}$, NH_3; $AgCl + 2\,NH_3 \rightarrow [Ag(NH_3)^2]^+ + Cl^-$ $[Ag(NH_3)^2]^+ + 2\,H^+ \rightarrow AgCl + Cl^-$
    - Hg_2^{2+}: $Hg_2Cl_2 + 2\,NH_3 \rightarrow Hg + Hg(NH_2)Cl + NH_4^+ + Cl^-$
    - Pb^{2+}: $PbCl_2$ dissolves in hot water
2. **H_2SO_4: Pb^{2+}, Ba^{2+}, Sr^{2+}, Ca^{2+}** white precipitates
3. **H_2S (H^+): Ag^+, Hg_2^{2+}, Pb^{2+}, Hg^{2+}, Cu^{2+}, Cd^{2+}, Bi^{3+}, Sb^{3+}, Sn^{2+}, Sn^{4+}**
    - Coloured sulphides: CdS, Sb_2S_3, SnS_2, others are black
    - H_2S is low dissociated in acidic medium , and therefore, only the least soluble sulphides
    - also disproportionation: $3\,CuS \rightarrow Cu_2S + CuS + S$

Cations detection – group reactions

4. **NH_4HS: Fe^{2+}, Fe^{3+}, Cr^{3+}, Al^{3+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}**
   - Higher degree of dissociation of NH_4HS to S^{2-} than H_2S in acid medium, therefore, more soluble sulphides precipitate
   - NH_4HS precipitates at the same time cations presented at 3) (their sulphides are less soluble)
   - FeS, Fe_2S_3, CoS, NiS – black
   - ZnS – white, MnS – light, oxidation $\Rightarrow$ darkening
   - Cr^{3+}, Al^{3+} - alkaline medium $\Rightarrow$ $Al(OH)_3$ white, transparent, $Cr(OH)_3$ green, sulphides are not formed
   - CoS, NiS – aging, polymerization, unlike other sulphides are insoluble in HCl
   - In excess of NH_4HS are dissolved:

$$Sb_2S_3 + 3\ S^{2-} \rightarrow 2\ SbS_3^{3-}$$

$$SnS_2 + S^{2-} \rightarrow SnS_3$$

after acidification they precipitate again

Cations detection – group reactions

5. **NaOH: Ag^+, Hg_2^{2+}, Pb^{2+}, Hg^{2+}, Cu^{2+}, Cd^{2+}, Bi^{3+}, Sb^{3+}, $Sn^{2+/4+}$, $Fe^{2+/3+}$, Cr^{3+}, Al^{3+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}**
   - Do not precipitate: Ba^{2+}, Sr^{2+}, Ca^{2+} partially, Mg precipitates ~ $pH > 9$; alkali metals; NH_4^+
   - Amorphous slimy precipitates: alkaline salts→ hydroxides
   - In excess of NaOH amphoteric hydroxdes dissolve: $Pb(OH)_2$, $Sb(OH)_3$, $Sn(OH)_2$, $Sn(OH)_4$, $Cr(OH)_3$, $Al(OH)_3$, $Zn(OH)_2$ ⇒ employed for separation of cations
   - Noble metals:

     $Ag^+ \rightarrow Ag_2O$ brown

     $Hg^{2+} \rightarrow HgO$ yellow
   - Dismutation: $Hg_2^{2+} + 2\ OH^- \rightarrow HgO + Hg + H_2O$ (turns black)
   - Oxidation of hydroxides $Mn^{2+/3+}$, $Co^{2+/3+}$ $Fe^{2+/3+}$ discoloration

     Mn: light→ brownish

     Co: light→ brownish

     Fe: světle zelený → reddish brown

Cations detection – group reactions

6. **NH_4OH: Ag^+, Hg^{2+}, Pb^{2+}, Hg^{2+}, Cu^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}, Bi^{3+}, Sb^{3+}, $Sn^{2+/4+}$, $Fe^{2+/3+}$, Al^{3+}, Cr^{3+}**
   - Do not precipitate: alkali metals; Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}
   - In excess of NH_4OH amphoteric hydroxdes do not dissolve : $Pb(OH)_2$, $Sb(OH)_3$, $Sn(OH)_2$, $Sn(OH)_4$, $Cr(OH)_3$, $Al(OH)_3$, $Zn(OH)_2$
   - In excess of NH_4OH soluble ammincomplexes are formed, and therefore hydroxides dissolve Ag^+, Cd^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+} to coloured (Cu^{2+} blue, $Co^{2+/3+}$ oxidation by air – red Co(III) complex) or colourless (Ag, Cd, Zn) complexes
   - $Hg_2^{2+} + X^- + 2\ NH_3 \rightarrow HgNH_2X + NH_4^+ + Hg$

     $Hg^{2+} + X^- + 2\ NH_3 \rightarrow HgNH_2X + NH_4^+$

     $2\ Hg^{2+} + 4\ NH_3 \rightarrow (Hg_2N)^+ + 3\ NH_4^+$ Millon base

Cations detection – group reactions

7. **KI: Ag^+, Hg^{2+}, Pb^{2+}, Hg^{2+}, Cu^{2+}, Bi^{3+}**

- AgI – pale yellow, PbI_2 – yellow, soluble in hot water to colourless solution, HgI_2 – red, Hg_2I_2 – yellow-green, BiI_3 - brownish
- excess of iodide – complex-forming features:
  - $PbI_2 + I^- \rightarrow [PbI_3]^-$
  - $Hg_2I_2 + 2\,I^- \rightarrow [HgI_4\,]^{2-} + Hg$
  - $BiI_3 + I^- \rightarrow [BiI_4]^-$
- hydrolysis:

  $BiI_3 + H_2O \rightarrow$ BiOI (orange) $+ 2\,H^+ + 2\,I^-$
- redox reactions:

  $Cu^{2+} + 4\,I^- \rightarrow 2$ CuI (white) $+ I_2$

  $Hg_2I_2 \rightarrow HgI_2 + Hg$ (graying)

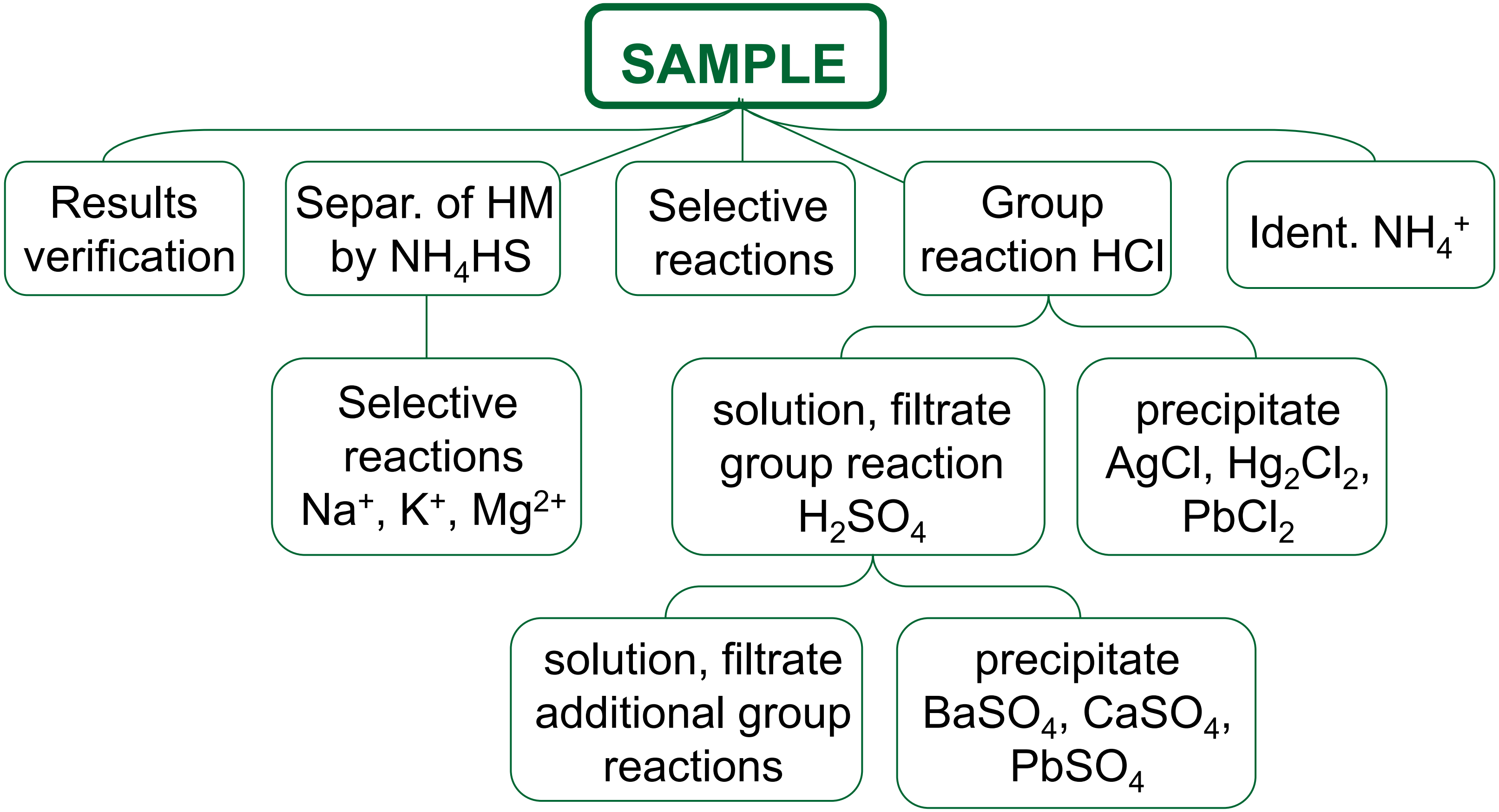
  $2\,Fe^{3+} + 2\,I^- \rightarrow 2\,Fe^{2+} + I_2$ brown colour of solutions by iodine

Cations detection – group reactions

8. **Hydrolytic reactions: Bi^{3+}, $Sn^{2+/4+}$, Sb^{3+}**
   - hydroxocomplexes, basic salts and hydroxides are formed at increasing pH – splitting of H^+ from H_2O in hydration shells of cations
   - hydrolysis:
     - a) by diluting with water
     - b) by addding of acetate buffer HAc/Ac^-, pH 5
   - significant hydrolysis – in teh form of chlorides:

$$Bi^{3+} + H_2O + Cl^- \rightarrow BiOCl + 2H^+$$

Separation of cations



SAMPLE

Results verification

Separar. of HM by NH_4HS

Selective reactions

Group reaction HCl

Ident. NH_4^+

Selective reactions Na^+, K^+, Mg^{2+}

solution, filtrate group reaction H_2SO_4

precipitate $AgCl$, Hg_2Cl_2, $PbCl_2$

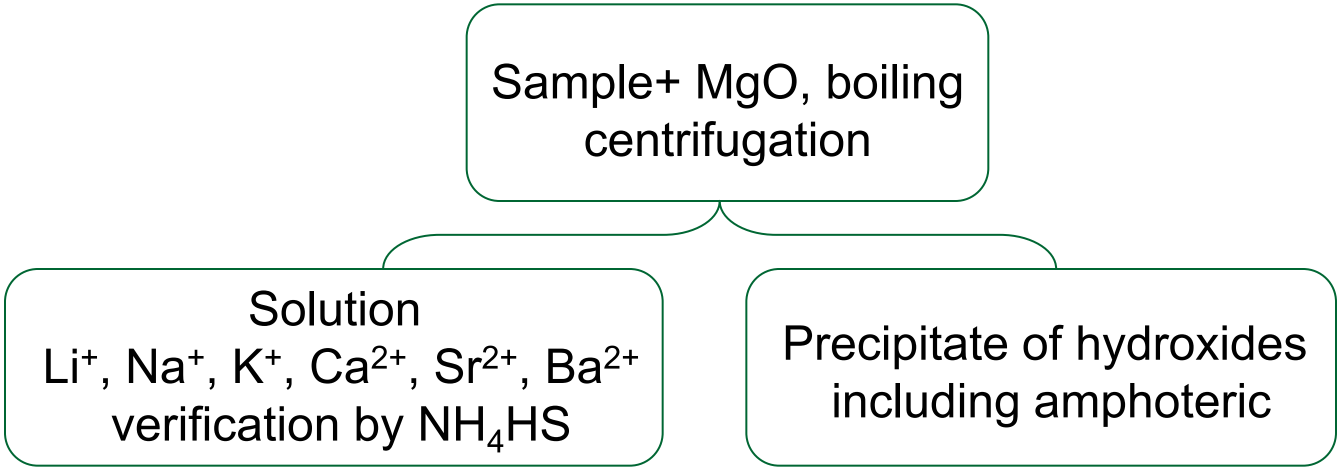
solution, filtrate additional group reactions

precipitate $BaSO_4$, $CaSO_4$, $PbSO_4$

Separation of cations – Selective reactions

- Removing of cations of heavy metals HM
  - $NH_4HS \Rightarrow$ precipitation of sulphides
  - MgO, var $\Rightarrow MgO + H_2O \rightarrow Mg(OH)_2$

$$Me^{2+} + Mg(OH)_2 \rightarrow Me(OH)_2 + Mg^{2+}$$

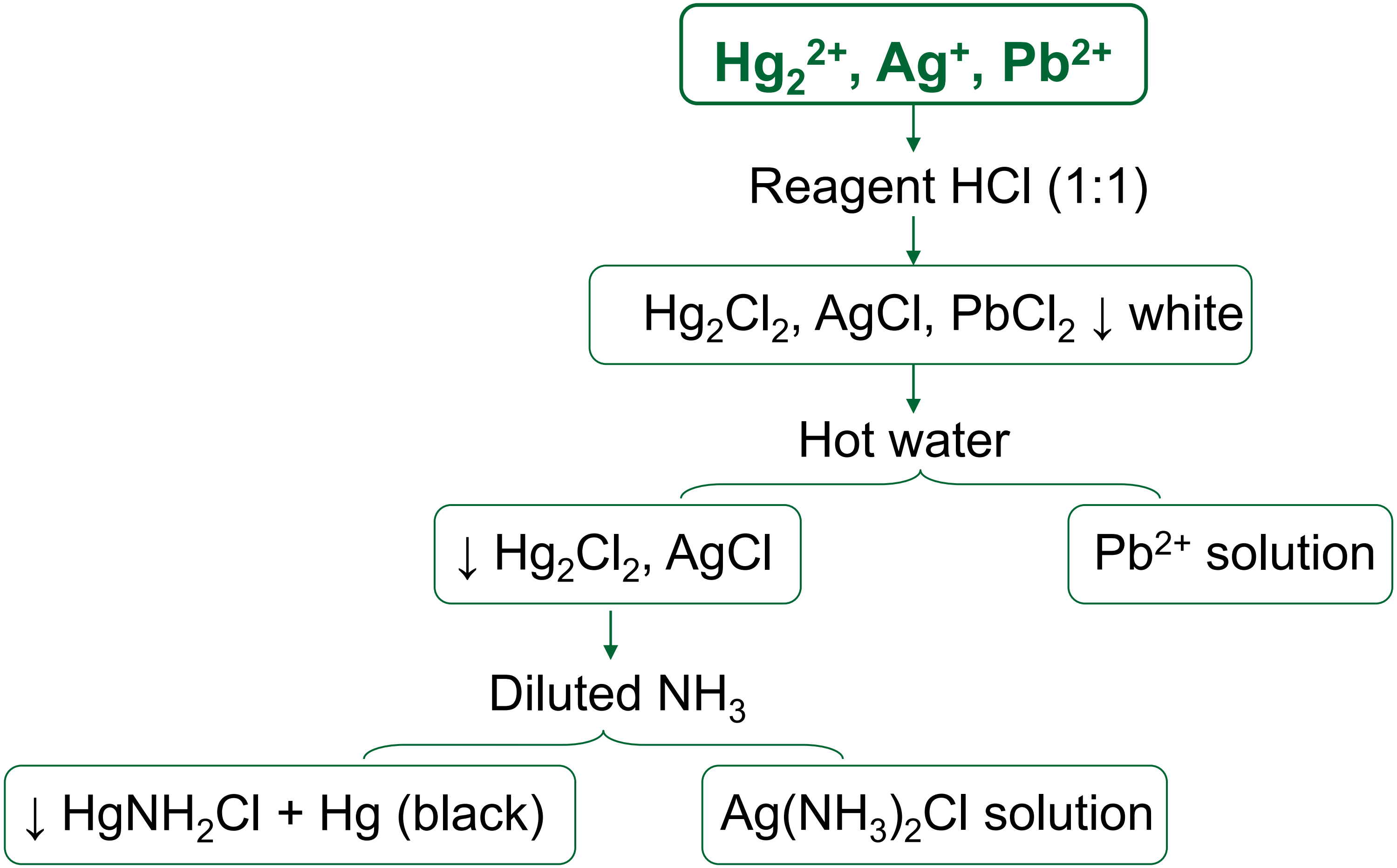


Sample+ MgO, boiling
centrifugation

Solution
Li^+, Na^+, K^+, Ca^{2+}, Sr^{2+}, Ba^{2+}
verification by NH_4HS

Precipitate of hydroxides
including amphoteric

Group of poorly soluble chlorides



Hg_2^{2+}, Ag^+, Pb^{2+}

Reagent HCl (1:1)

Hg_2Cl_2, AgCl, $PbCl_2$ ↓ white

Hot water

↓ Hg_2Cl_2, AgCl

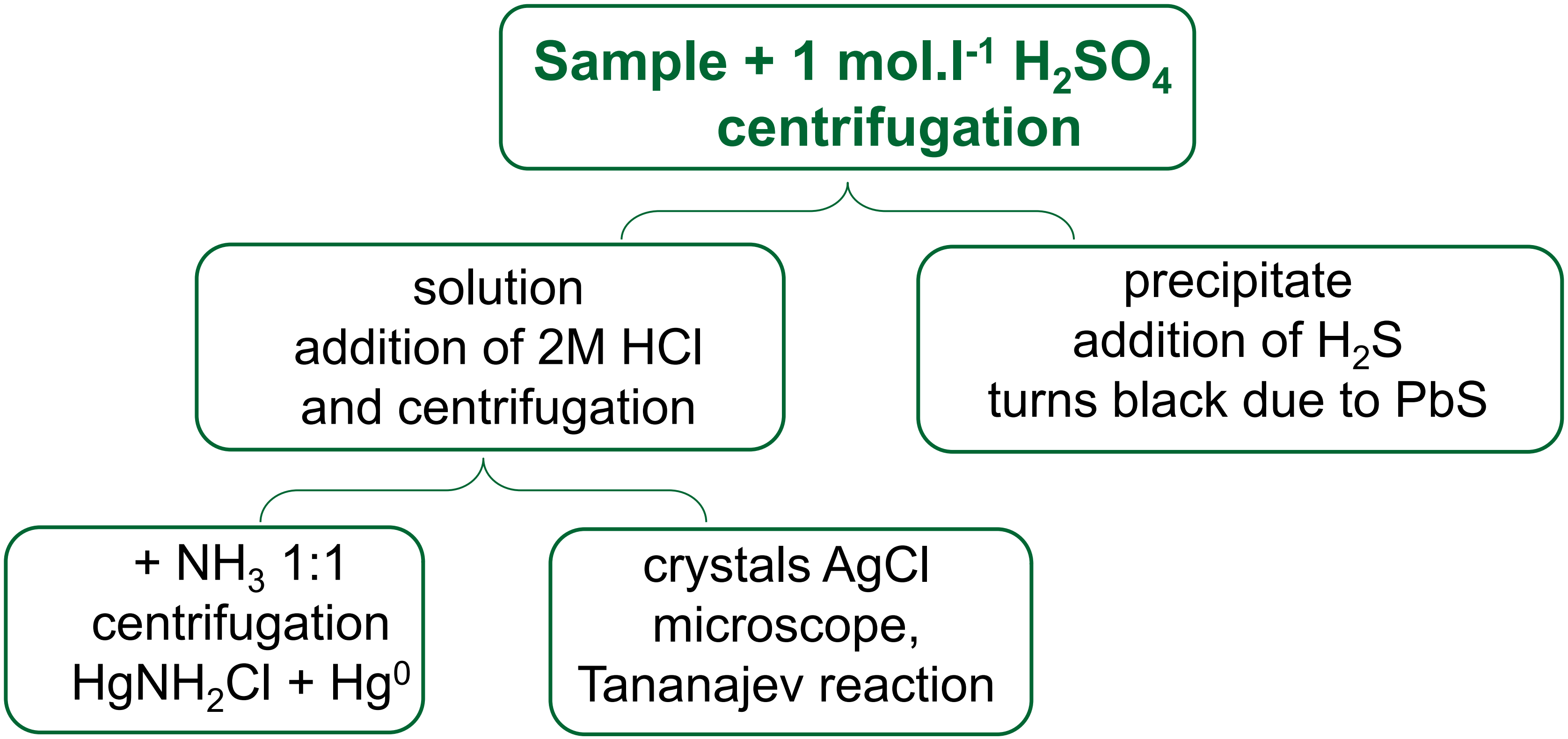
Pb^{2+} solution

Diluted NH_3

↓ $HgNH_2Cl$ + Hg (black)

$Ag(NH_3)_2Cl$ solution

Selective reactions of cations forming poorly soluble chlorides



Sample + 1 mol.l^{-1} H_2SO_4
centrifugation

solution
addition of 2M HCl
and centrifugation

precipitate
addition of H_2S
turns black due to PbS

+ NH_3 1:1
centrifugation
$HgNH_2Cl + Hg^0$

crystals AgCl
microscope,
Tananajev reaction

Selective reactions of cations forming poorly soluble chlorides

- **Hg_2^{2+}:**
  1. $Hg_2Cl_2 + 2\ NH_3 \rightarrow NH_4Cl + HgNH_2Cl \downarrow$ bílá + $Hg^0 \downarrow$ (grey precipitate)
  2. $Hg_2^{2+} + 2\ I^- \rightarrow Hg_2I_2 \downarrow$ yellow-green
     (turns black by resulting Hg)
  3. $Hg_2^{2+} + CrO_4^- \rightarrow Hg_2CrO_4 \downarrow$ červenohnědá
  4. catalytic oxidation of Al^0 (Hg_2^{2+}, Hg^{2+}, Hg^0),
     interferes Cu^{2+}, Bi^{3+}, As^{III}

Selective reactions of cations forming poorly soluble chlorides

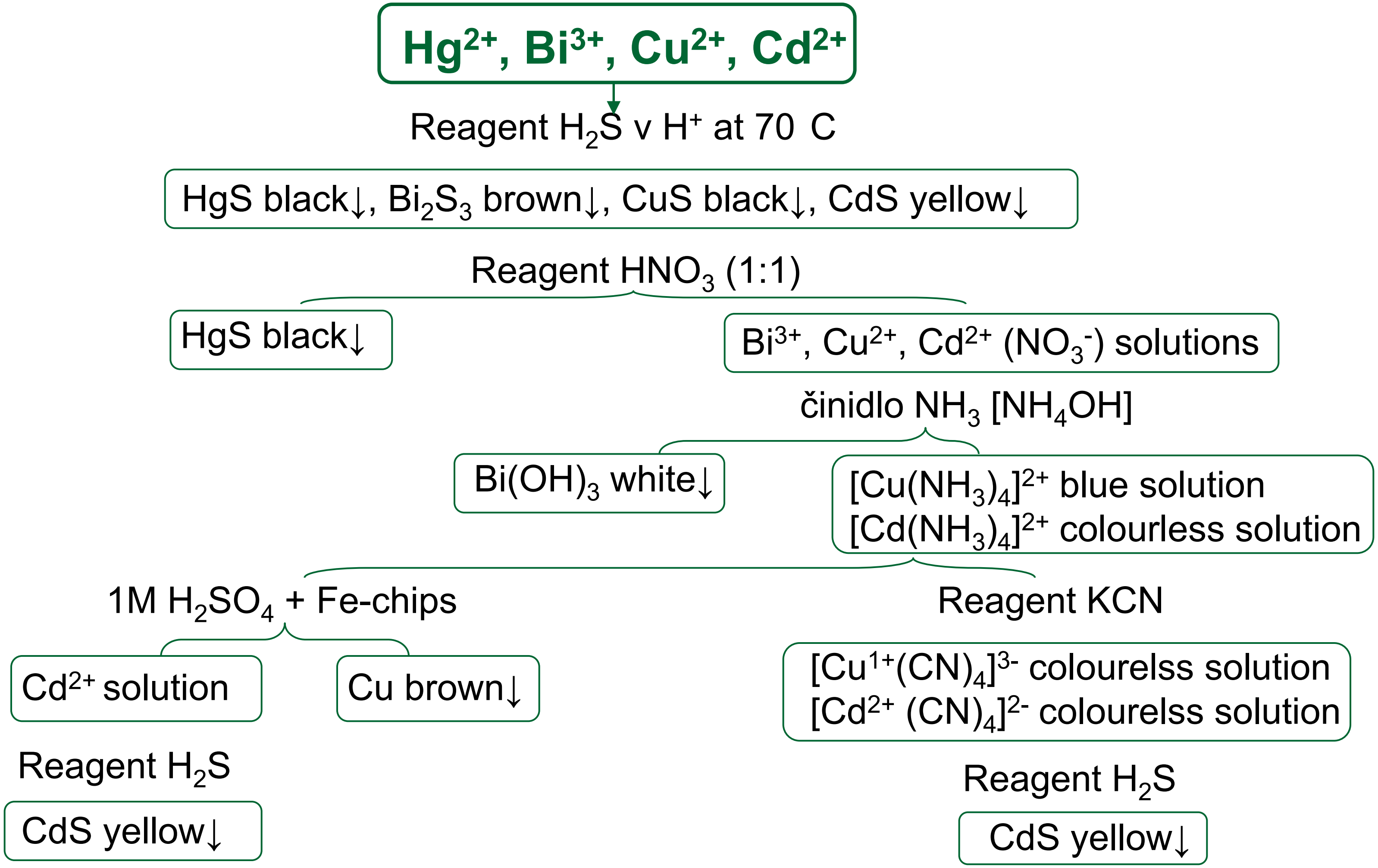
- **Ag^+:**

1. $AgCl + 2\ NH_4OH \leftrightarrow Ag(NH_3)^{2+} + 2H_2O + Cl^-$,
   evolution of NH_3 ⇒ precipitation of AgCl – microscope
2. $Ag^+ + Br^- \rightarrow AgBr \downarrow$ yellowish (in NH_3 only bleaches, does not dissolve)
3. $Ag^+ + I^- \rightarrow AgI \downarrow$ yellow (no reaction with NH_3)
4. $2\ Ag^+ + CrO_4^- \rightarrow Ag_2CrO_4 \downarrow$ red-brown
5. Redox Tananajev reaction
   $Mn(OH)_2 + 2\ Ag^+ + 2\ OH^- \rightarrow 2\ H_2O + MnO_2 \downarrow$ brown $+ 2\ Ag \downarrow$ black
6. Ag^+ + rhodamine + $H^+ \rightarrow$ žlutooranžová ↓

Selective reactions of cations forming poorly soluble chlorides

- **Pb^{2+}:**
  1. $Pb^{2+} + H_2SO_4 \rightarrow PbSO_4 \downarrow$ white $+ 2H^+$;
     $PbSO_4 + 3\ NaOH \rightarrow Pb(OH)_3^- + SO_4^{2-} + 3\ Na^+$; difference from $BaSO_4$
  2. $PbSO_4 + S^{2-} \rightarrow PbS + SO_4^{2-} \downarrow$ black; oddělení Ba^{2+} od Pb^{2+}: $NH_4OH \rightarrow Pb(OH)_2$; Ba^{2+}, $2\ OH^-$
  3. $PbSO_4 + K_2CrO_4 \rightarrow PbCrO_4 \downarrow$ yellow $+ 2\ K^+ + SO_4^{2-}$
  4. $Pb^{2+} + 2\ I^- \rightarrow PbI_2 \downarrow$ yellow (golden rain),
     in excess of I^- converts to $[PbI_4]^{2-}$ - colourless solution
  5. Pb^{2+} + difenylthiokarbazone $\rightarrow$ red$\downarrow$

Sulphides precipitating from acid medium



Hg^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}

Reagent H_2S v H^+ at 70 C

HgS black↓, Bi_2S_3 brown↓, CuS black↓, CdS yellow↓

Reagent HNO_3 (1:1)

HgS black↓

Bi^{3+}, Cu^{2+}, Cd^{2+} (NO_3^-) solutions

činidlo NH_3 [NH_4OH]

$Bi(OH)_3$ white↓

$[Cu(NH_3)_4]^{2+}$ blue solution
$[Cd(NH_3)_4]^{2+}$ colourless solution

1M H_2SO_4 + Fe-chips

Cd^{2+} solution

Cu brown↓

Reagent H_2S

CdS yellow↓

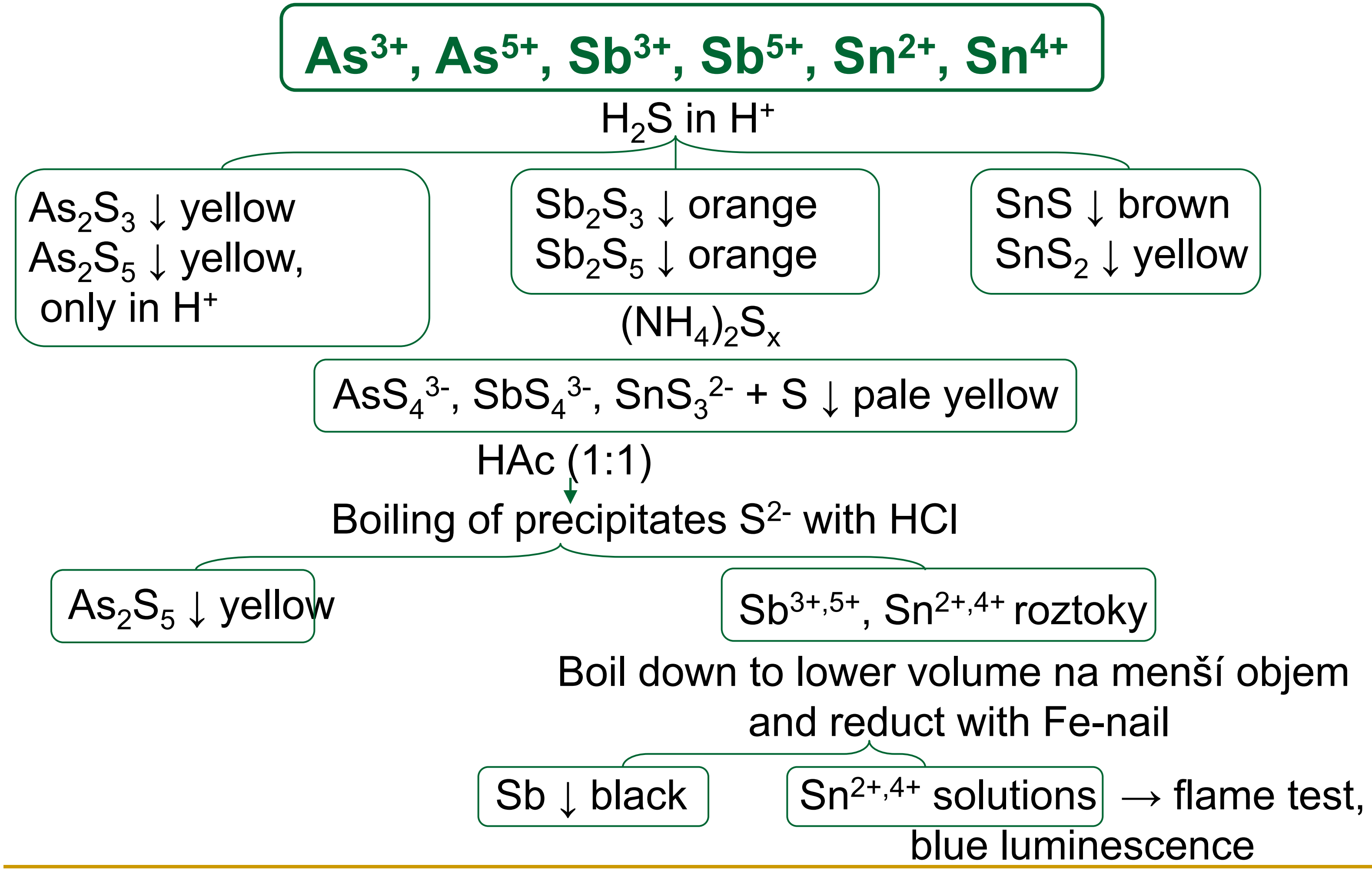
Reagent KCN

$[Cu^{1+}(CN)_4]^{3-}$ colourelss solution
$[Cd^{2+}(CN)_4]^{2-}$ colourelss solution

Reagent H_2S

CdS yellow↓

Sulphides precipitating from acid medium and soluble in $(NH_4)_2S_x$



As^{3+}, As^{5+}, Sb^{3+}, Sb^{5+}, Sn^{2+}, Sn^{4+}

H_2S in H^+

As_2S_3 ↓ yellow
As_2S_5 ↓ yellow,
only in H^+

Sb_2S_3 ↓ orange
Sb_2S_5 ↓ orange

SnS ↓ brown
SnS_2 ↓ yellow

$(NH_4)_2S_x$

AsS_4^{3-}, SbS_4^{3-}, SnS_3^{2-} + S ↓ pale yellow

HAc (1:1)

Boiling of precipitates S^{2-} with HCl

As_2S_5 ↓ yellow

$Sb^{3+,5+}$, $Sn^{2+,4+}$ roztoky

Boil down to lower volume na menší objem
and reduct with Fe-nail

Sb ↓ black

$Sn^{2+,4+}$ solutions → flame test,
blue luminescence

Selective reactions of cations forming low soluble sulphides in acid (2M HCl)

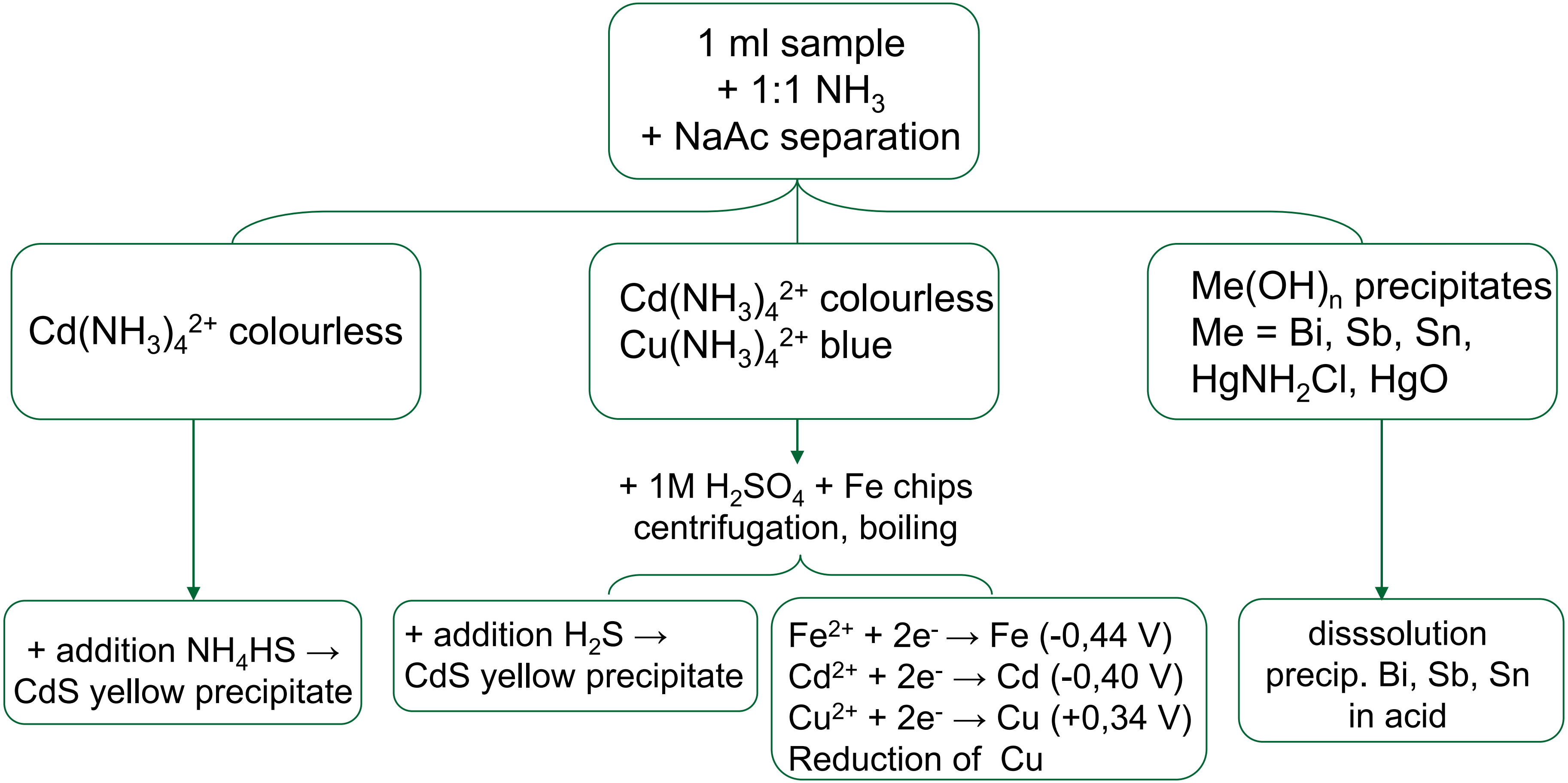
$$H_2S + H_2O \leftrightarrow HS^- + H_3O^+$$
$$HS^- + H_2O \leftrightarrow S^{2-} + H_3O^+$$

- HgS black
- CuS black
- Bi_2S_3 brown
- CdS yellow
- Sb_2S_3 orange-red
- SnS brown
- SnS_2 yellow
  - SnS_2 soluble in excess of NH_4HS to SnS_3^{2-}
- As_2S_3 yellow, As_2S_5 yellow, only in H^+

- ammonia-based separation

$$Hg^{2+}, Cu^{2+}, Cd^{2+}, Sn^{2+}, Sn^{IV}, Sb^{3+}, Bi^{3+}$$

Selective reactions of cations forming low soluble sulphides in acid (2M HCl)



1 ml sample
+ 1:1 NH_3
+ NaAc separation

$Cd(NH_3)_4^{2+}$ colourless

+ addition NH_4HS → CdS yellow precipitate

$Cd(NH_3)_4^{2+}$ colourless
$Cu(NH_3)_4^{2+}$ blue

+ 1M H_2SO_4 + Fe chips
centrifugation, boiling

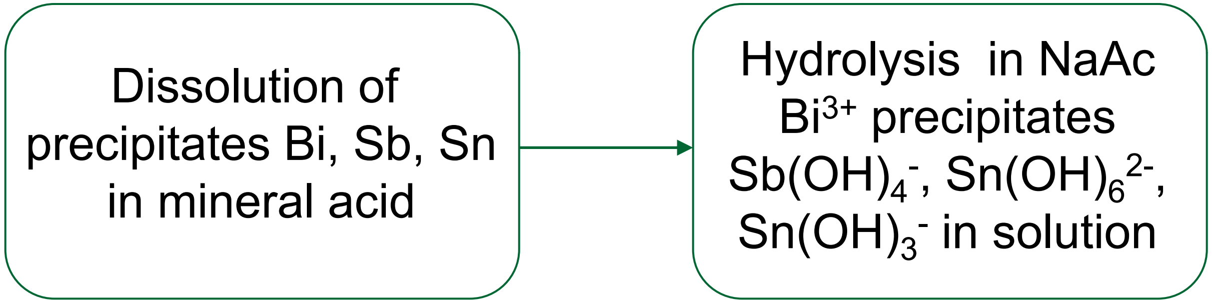
+ addition H_2S → CdS yellow precipitate

$Fe^{2+} + 2e^- \rightarrow Fe$ (-0,44 V)
$Cd^{2+} + 2e^- \rightarrow Cd$ (-0,40 V)
$Cu^{2+} + 2e^- \rightarrow Cu$ (+0,34 V)
Reduction of Cu

$Me(OH)_n$ precipitates
Me = Bi, Sb, Sn,
$HgNH_2Cl$, HgO

disssolution precip. Bi, Sb, Sn in acid

Selective reactions of cations forming low soluble sulphides in acid (2M HCl)



Dissolution of precipitates Bi, Sb, Sn in mineral acid

Hydrolysis in NaAc
Bi^{3+} precipitates
$Sb(OH)_4^-$, $Sn(OH)_6^{2-}$, $Sn(OH)_3^-$ in solution

- **Hg^{2+}**

1. Reaction with $SnCl_2$:
   $Sn^{2+} + 2\,Hg^{2+} + 2\,Cl^- \rightarrow Hg_2Cl_2\downarrow$ white (turns gray /black) + Sn^{IV}
   removing of interfering Pb^{2+}, Ag^+, Hg_2^{2+} by addition of 2M HCl
2. Catalytic oxidation of Al
3. Reaction with KI : $Hg^{2+} + 2\,I^- \rightarrow HgI_2$ red precipitate
   $HgI_2 + 2\,I^- \rightarrow [HgI_4]^{2-}$ soluble complex, interferes Bi^{3+} by $BiI_3 + I^- \rightarrow [BiI_4]^-$ yellow solution, elimination by adding Cu^{2+}, disprop. CuI (white), sorption of HgI_2 on CuI, BiI_3 dissolves
4. Hg^{2+} + difenylthiokarbazone + $OH^- \rightarrow$ red-orange solution

Selective reactions of cations forming low soluble sulphides in acid (2M HCl)

- **Cu^{2+}**

1. Reaction with $K_4[Fe(CN)_6]$:
   $Cu^{2+} + [Fe(CN)_6]^{4-} \rightarrow Cu_2[Fe(CN)_6]\downarrow$ red-brown = *Hatschett brown* precipitate of variable composition $CuK_2[Fe(CN)_6]$, $Cu_2K[Fe(CN)_6]$ in neutral or weak acid medium; precipitate is soluble in NH_3 and in diluted mineral acids; interferes Fe^{3+} (Berlin blue), removed by NH_3
2. Reaction with Kupral (Sodium diethyldithiocarbamate trihydrate)

   $(C_2H_5)_2NCSSNa.3H_2O$, results in brown precipitate of chelate 1:2, extraction to chloroform $CHCl_3$ trichloromethane, low soluble chelates interfere, reaction is selective in NH_3 leachate and when masking with EDTA
3. Cu^{2+} + salicylaldoxim + $H^+ \rightarrow$ pale yellow↓ (salicylaldehyde oxime)

   $C_6H_4CH{=}NOH\text{-}2\text{-}OH$.

Selective reactions of cations forming low soluble sulphides in acid (2M HCl)

- **Cd^{2+}**
  1. Reaction with gaseous H_2S or by addition of sulphane water forms yellow precipitate CdS
     after separation of HM: interfere Hg, Ag, Pb, Cu, Bi, Sb, Sn, ammonia separation, in solution remains Ag^+, Cu^{2+}, Cd^{2+}, reduction of Ag^+, Cu^{2+} by means of Fe
  2. $Cd^{2+} + 2\ OH^- \rightarrow Cd(OH)_2 \downarrow$ white

- **Bi^{3+}**
  1. Reaction with thiourea ⇒ yellow soluble complex (pH < 1) $\{Bi[S=C(NH_2)_2]_3\}^{3+}$; interferes Sb^{3+} , elimination by oxidation to Sb^V by $KMnO_4$ and Sb^V masking by F^-
  2. Reduction by $3\ Sn^{II} + 2\ Bi^{3+} \rightarrow 2\ Bi^0 + 3\ Sn^{IV}$, bismuth = black metal; interfere Ag^+, Hg_2^{2+} - removing by 2M HCl, interferes Hg^{2+}, than detection of Bi^{3+} by hydrolysis to BiOCl

Selective reactions of cations forming low soluble sulphides in acid (2M HCl)

- **Sb^{3+}**
  1. Sb^{3+} hydrolytically separated by means of NaAc, then reduction by Fe in acid medium → black pulverized antimony and H_2; interferes Cu^{2+}, this is eliminated by removing of hydrolysates
  2. after oxidation by $KMnO_4$ to Sb^V coloured ion associate with crystal violette is formed $\{SbCl_6^-; B^+\}$ extraction to benzene
  3. $Sb^{3+} + Na_2S_2O_3 \rightarrow \downarrow$ red precipitate of antimony vermilion
  4. Marsh-Liebig test, antimony mirror does not move with heat

- **Sn^{2+}, Sn^{4+}**
  1. Luminescence reaction in flame – blue emission of SnCl, interferes Cu^{2+} - green flame, therefore prior to test is reduced by Fe

Group of other sulphides and hydroxidů precipitated by ammonium hydrogensulphide

Co^{2+}, Ni^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Al^{3+}, Zn^{2+}, Cr^{3+}

Reagent $(NH_4)_2S$ v NH_4Cl and NH_4OH medium

CoS black↓, NiS black ↓, FeS black ↓, Fe_2S_3 brownish ↓, MnS flesh-pink↓,
$Al(OH)_3$ white↓, ZnS white↓, $Cr(OH)_3$ grey-blue-green ↓

činidlo HCl (1:4)

CoS ↓ black, NiS ↓ black

H_2O_2 (5%) + H^+

$CoSO_4$, $NiSO_4$ solutions

Fe^{2+}, Fe^{3+}, Mn^{2+}, Al^{3+}, Zn^{2+}, Cr^{3+} (Cl^-) solutions

NaOH (20%) + H_2O_2 (5%)

$Fe(OH)_3$ ↓ reddish brown
$Mn(OH)_2$ ↓ reddish brown

CrO_4^{2-} yellow solution
AlO_3^{3-} $[Al(OH)_4]^-$ cl. solution
ZnO_2^{2-} $[Zn(OH)_4]^{2-}$ cl. solution

+ 1 drop of H_2O_2
+ 1M H_2SO_4
+ extr. izoamylalcohol

blue extract Cr^{3+}

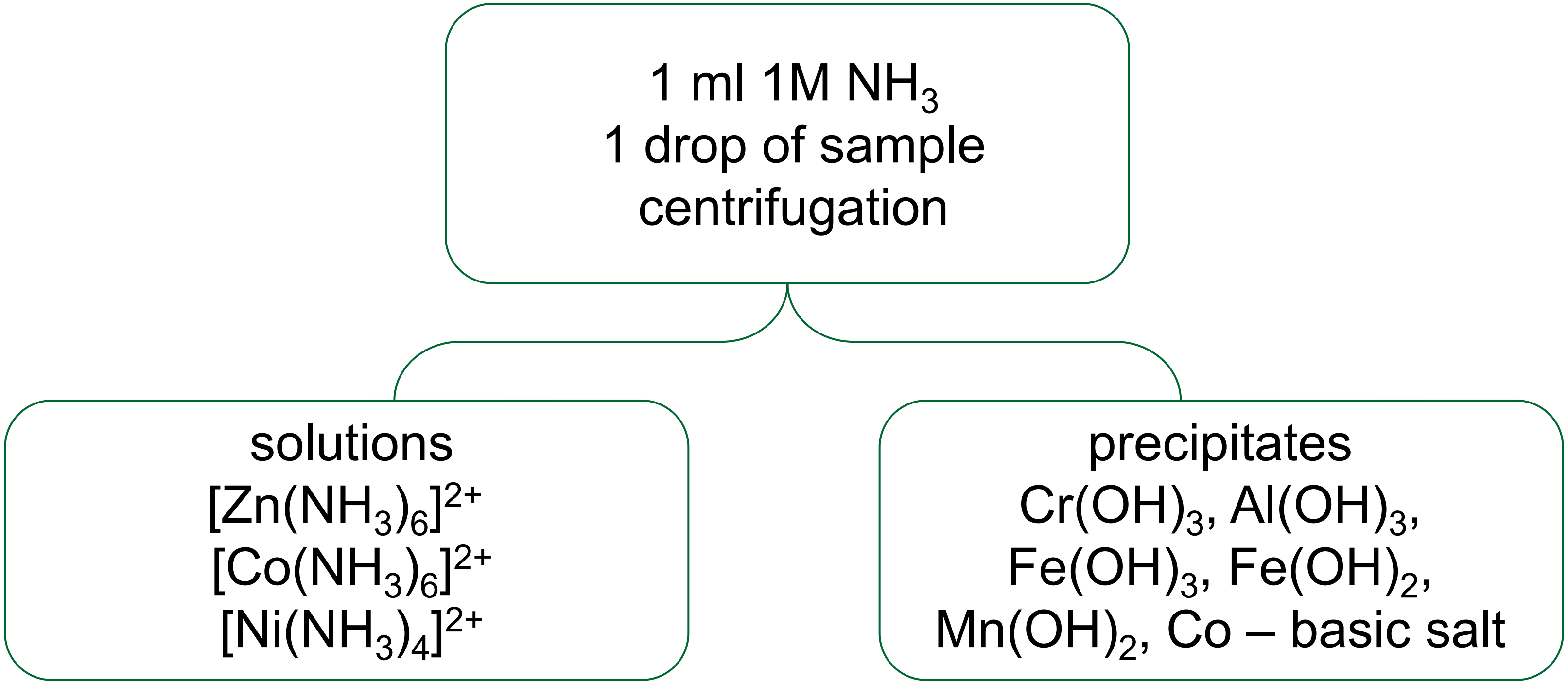
+ 1 drop of alizarine
+ 2M CH_3COOH

red solution Al^{3+}

+ 20% HCl
+ $[Fe(CN)_6]^{3-}$

yellow-green↓ Zn^{2+}

Selective reactions of Co^{2+}, Ni^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Al^{3+}, Zn^{2+}, Cr^{3+}



1 ml 1M NH_3
1 drop of sample
centrifugation

solutions
$[Zn(NH_3)_6]^{2+}$
$[Co(NH_3)_6]^{2+}$
$[Ni(NH_3)_4]^{2+}$

precipitates
$Cr(OH)_3$, $Al(OH)_3$,
$Fe(OH)_3$, $Fe(OH)_2$,
$Mn(OH)_2$, Co – basic salt

Selektivní reakce kationů Co^{2+}, Ni^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Al^{3+}, Zn^{2+}, Cr^{3+}

- **Fe^{3+}**
  1. s thiokyanatanem $(SCN)^-$ v kyselém prostředí
     $Fe^{3+} + SCN^- \rightarrow$ červené komplexy $[Fe(SCN)]^{2+}$, $[Fe(SCN)_2]^+$…
     $Fe[Fe(SCN)_6]$ typický krvavě červený roztok; ruší fluoridy
  2. s $K_4[Fe(CN)_6]$ v kys. prostředí vzniká sraženina nebo koloidní roztok Berlínské modři $K\{Fe^{III}[Fe^{II}(CN)_6]\}$ respektive $Fe^{III}{}_4[Fe^{II}(CN)_6]_3$; ruší Cu^{2+} ve velkém nadbytku
  3. s kyselinou sulfosalicylovou v kys. prostř. vzniká fialový roztok rozpustného chelátu; ruší fluoridy a dihydrogenfosforečnany
  4. $Fe^{3+} + 3\,NH_3 + 3\,H_2O \rightarrow 3\,NH_4^+ + Fe(OH)_3 \downarrow$ rezavě hnědá, v nadbytku NH_3 nerozpustná
- **Fe^{2+}**
  1. s 1,10-fenanthrolinem při pH 2-9 vzniká stabilní červený chelát
  2. s kynoželezitanem $K_3[Fe(CN)_6]$ vzniká Berlínská modř
  3. bezvodé soli Fe^{2+} jsou bílé, hydratované světle zelené: $FeSO_4.7H_2O$, $(NH_4)Fe(SO_4)_2.6H_2O$ (Mohrova sůl) a $FeCl_2.4H_2O$

Selektivní reakce kationů Co^{2+}, Ni^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Al^{3+}, Zn^{2+}, Cr^{3+}

- **Al^{3+}**
  1. s alizarinem S (1,2-dihydroxyantrachinon-3-sulfonan) vzniká červený lak – chelát AlL, povrchově adsorbován na $Al(OH)_3$ v NH_3 prostředí, ruší: Fe^{3+}, Cu^{2+} - oddělení pomocí NaOH
  2. s kvercetinem – vzniká zeleně fluoreskující, ve vodě málo rozpustný Al - chelát při pH 1-4, ruší: Zn^{2+} a Sb^{3+} – nepatrná fluorescence, maskování: F^-

- **Cr^{3+}**
  1. s peroxidem H_2O_2 v alkalickém prostředí za varu → CrO_4^{2-} žlutý roztok, po okyselení přechází s přebytečným peroxidem na nestálý modrý peroxid $Cr^{VI}O_5$, ruší: Mn^{2+} - alkalické dělení
  2. $Cr^{3+} + 3\ NH_3 + 3\ H_2O \rightarrow 3\ NH_4^+ + Cr(OH)_3 \downarrow$ šedozelená

Selektivní reakce kationů Co^{2+}, Ni^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Al^{3+}, Zn^{2+}, Cr^{3+}

- **Zn^{2+}**
  1. s kyanoželeznatanem $K_4[Fe(CN)_6]$ v prostředí 1M HCl vzniká bílá sraženina $K_2Zn[Fe(CN)_6]$; ruší Fe^{3+}, Cu^{2+}, Mn^{2+}, Ni^{2+} a Co^{2+} - dělení v 10% NaOH
  2. s difenylthiokarbazonem v alkalickém prostředí vzniká zelený roztok, vytřepáním v roztoku CCl_4 přechází na purpurovou červeň

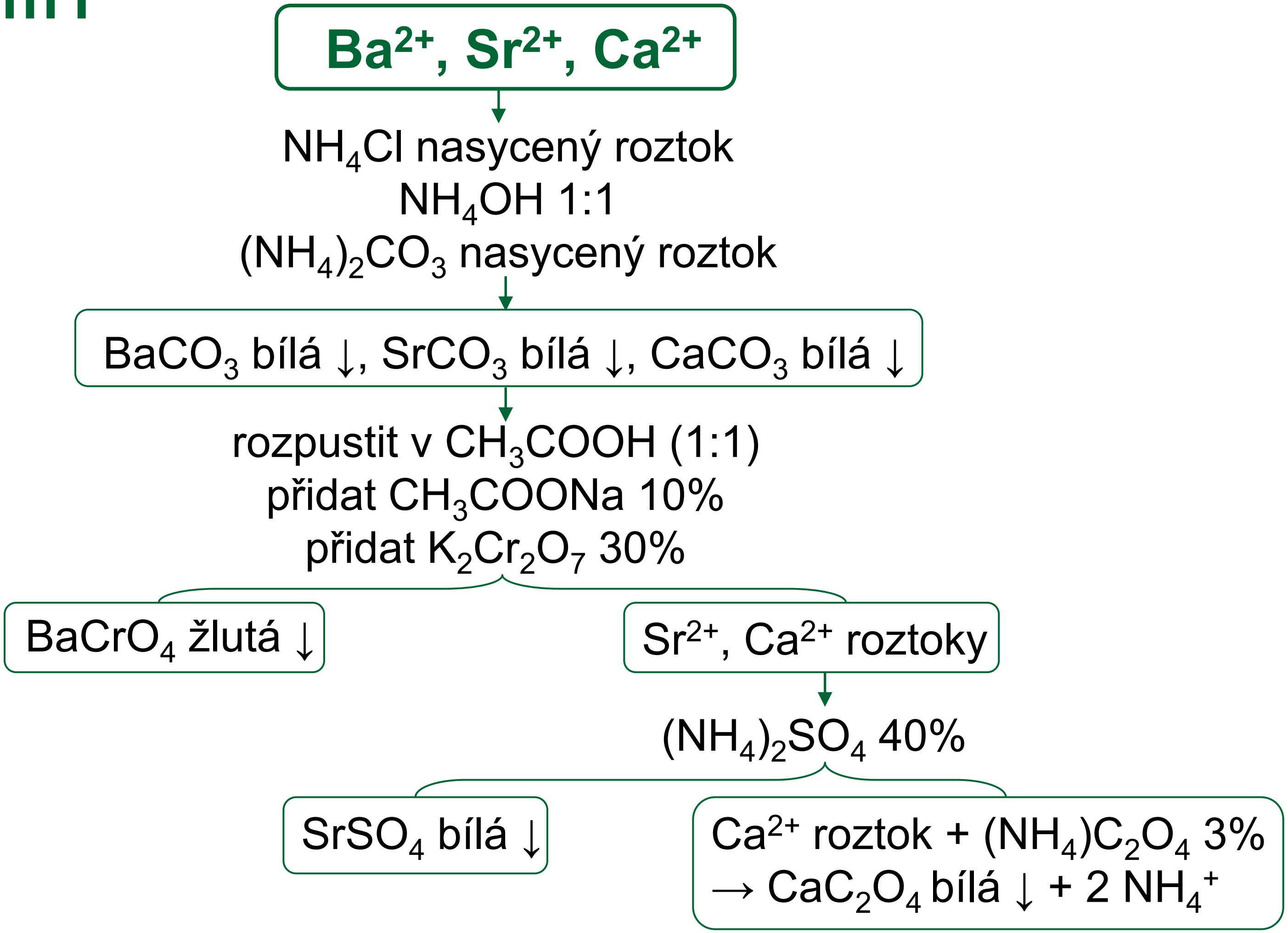
- **Co^{2+}**
  1. s thiokyanatanem vzniká modrý rozpustný komplex $[Co(SCN)_4]^{2-}$, extrakce např. do izoamylalkoholu, ruší Fe^{3+}, Bi^{3+} - maskování s F^-, Cu^{2+} tvoří hnědou sraženinu
  2. bezvodé soli jsou modré, hydratované růžové např.: $CoCl_2.6H_2O$, $Co(NO_3)_2.6H_2O$, $CoSO_4.7H_2O$
  3. $Co^{2+} + 2\ NH_3 + 2\ H_2O \rightarrow \downarrow$ světle modrá zásaditých solí, rozpouští se v nadbytku NH_3 na $[Co(NH_3)_4]^{2+}$, který oxiduje na $[Co(NH_3)_6]^{3+}$ (hnědý roztok)
  4. s 1-nitroso-2-naftolem vzniká červenohnědá sraženina chelátu CoL_3, ruší Cu^{2+}, Fe^{3+}, Hg^{2+}, Ni^{2+} - jejich cheláty se v 10% HCl rozloží

Selektivní reakce kationů Co^{2+}, Ni^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Al^{3+}, Zn^{2+}, Cr^{3+}

- **Mn^{2+}**
  1. oxidací v kyselých roztocích jodistanem za horka vzniká fialový MnO_4^-
  2. $Mn^{2+} + 2\ NH_3 + 3\ H_2O \rightarrow$ bílá ↓ zásaditých solí, v důsledku oxidace hnědne
  3. bezvodé soli jsou bezbarvé hydratované růžové: $MnSO_4.7H_2O$, $Mn(NO_3)_2.6H_2O$, $MnCl_2.4H_2O$

- **Ni^{2+}**
  1. s diacetylaldioximem (Čugajevovo činidlo) v amoniakálním prostředí vzniká růžově červená sraženina chelátu $Ni(DH)_2$
  2. $Ni^{2+} + 2\ NH_3 + 2\ H_2O \rightarrow$ ↓ zásadité soli, v nadbytku NH_3 vznik $[Ni(NH_3)_4]^{2+}$ modrý roztok
  3. hydratované soli Ni^{2+} jsou zelené, bezvodé jsou bezbarvé

Skupina kationtů kovů alkalických zemin



Ba^{2+}, Sr^{2+}, Ca^{2+}

↓

NH_4Cl nasycený roztok

NH_4OH 1:1

$(NH_4)_2CO_3$ nasycený roztok

↓

$BaCO_3$ bílá ↓, $SrCO_3$ bílá ↓, $CaCO_3$ bílá ↓

↓

rozpustit v CH_3COOH (1:1)

přidat CH_3COONa 10%

přidat $K_2Cr_2O_7$ 30%

$BaCrO_4$ žlutá ↓

Sr^{2+}, Ca^{2+} roztoky

↓

$(NH_4)_2SO_4$ 40%

$SrSO_4$ bílá ↓

Ca^{2+} roztok + $(NH_4)C_2O_4$ 3%

→ CaC_2O_4 bílá ↓ + 2 NH_4^+

Selektivní reakce alkalických kovů a kovů alkalických zemin

- **Li^+, Na^+, K^+, NH_4^+**
  - bezbarvé, dobře rozpustné soli; netvoří stabilní komplexy
  - plamenové zkoušky (ne NH_4^+) - zbarvení emisí alkal. kovů
  - reakce s organickými činidly

- **Ca^{2+}, Sr^{2+}, Ba^{2+}**
  - sraženiny: SO_4^{2-}, CrO_4^{2-}, OH^-, F^-, $C_2O_4^{2-}$, CO_3^{2-} rozpustnost:
    - SO_4^{2-}, CrO_4^{2-} : $Ca^{2+} > Sr^{2+} > Ba^{2+}$
    - OH^-, F^-, $C_2O_4^{2-}$: $Ca^{2+} < Sr^{2+} < Ba^{2+}$
    - CO_3^{2-} : $Ca^{2+} \approx Ba^{2+} < Sr^{2+}$

Selektivní reakce alkalických kovů a kovů alkalických zemin

- plamenové zkoušky – těkavé chloridy, Pt drát

Li^{2+} karmínově červená	670,0 nm
Na^{+} žlutá	589,6 a 589,0 nm
K^{+} fialová + červená	404,7 a 768,0 nm
Ca^{2+} cihlově červená	620,0 nm
Sr^{2+} červená + oranž.	674,7; 662,8 a 606,0 nm (oranž.)
Ba^{2+} zelená	531; 524 a 514 nm

Selektivní reakce alkalických kovů a kovů alkalických zemin

- **Li^+**
  1. LiCl je rozpustný v organických rozpouštědlech × chloridy Na, K, Ca a Ba, vhodné pro oddělení pro plamenovou zkoušku
- **Na^+**
  1. s octanem uranylo-zinečnatým v kyselině octové vzniká světle žlutá krystalická sraženina $NaMg(UO_2)_3(CH_3COO)_9.9H_2O$, ruší TK
- **K^+**
  1. s dipikrylaminem vzniká oranžovo-červená sraženina draselné soli hexanitrodifenylaminátu, ruší TK, NH_4^+
  2. s kyselinou pikrovou vzniká pikran draselný žlutá sraženina
- **NH_4^+**
  1. s Nesslerovým činidlem v alkalickém prostředí vzniká hnědá až žlutá sraženina;
     příprava Ness. činidla: $HgCl_2 + 2KI \rightarrow HgI_2 \ldots + 2KI \rightarrow [HgI_4]^{2-}$;
     v NaOH reakce $[HgI_4]^{2-} + NH_4^+ \rightarrow Hg_2I_3NH_2$ ruší všechny kationty, které se srážejí v alkalickém prostředí

Selektivní reakce alkalických kovů a kovů alkalických zemin

- **Mg^{2+}**
  1. s Magnezonem (4-nitrobenzen azorezorcin nebo 4-nitrobenzenazo-1-naftol) v NaOH tvoří modrou sraženinu chelátu; slepý pokus: žlutá → fialová v roztoku (acidobazický indikátor); modrý chelát – zbarvení při adsorpci na $Mg(OH)_2$
  2. s thiazolovou (titanovou) žlutí vzniká červená sraženina; slepý pokus dává žlutý až oranžový roztok
  3. s 8-hydroxichinolinem v alkalickém prostředí vzniká žlutá sraženina (jehličky)
- **Ca^{2+}**
  1. s kyselinou šťavelovou ve slabě kyselém prostředí vzniká bílá krystalická sraženina šťavelanu vápenatého; Neruší Sr^{2+}, Ba^{2+}, alkalické kovy, ruší TK - odstranění s MgO
- **Sr^{2+}**
  1. žlutá sraženina s K_2CrO_4 po oddělení TK, ruší Ca^{2+}, na rozdíl od Ba^{2+} se nesráží Sr^{2+} ve 2 mol.l^{-1} kys. octové
- **Ba^{2+}**
  1. sráží se s K_2CrO_4 ve 2 mol.l^{-1} HAc, v neutr./ alkal. prostředí, sráží se 1 mol.l^{-1} H_2SO_4