Analytical Chemistry I laboratory
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QUALITATIVE ANALYSIS

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Acknowledgements

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Prof. Juan Peris Vicente

Classical analysis → **Procedure based on the use of chemical reactions → *Equilibria***

Instrumental analysis → **Physical and chemical propieties → *Instrumental***

❖ **Inorganic analysis**

❖ **Qualitative analysis (20 h)**

- **Presence/absence of analytes**
- **Identification assays: reactions involving the analyte - reactivity differences**

❖ **Quantitative analysis**

- **Analyte quantification**
- **Mesurar la quantitat de reactiu consumit o de producte generat → stoichiometry : titration/gravimetry**

Identification assay:

Chemical reaction or metallic cation reaction sequence

(pH/complex formation) evolving an observable characteristic

Analyte + Reagent → Product

(Redox/Complexes/Precipitacion/Acid-Base)

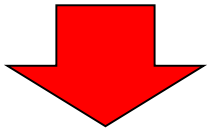
Shows a characteristic colour or shows luminescence

TEST SAMPLE **CONTROL** **BLANK**

They are not all reliable

SELECTIVITY **SENSITIVITY** **ROBUSTNESS**

- **Low selectivity on identification reactions**
- **Direct assays showing interferences:**
  - **Same reaction**
  - **Block the reaction**
  - **We can't see our target product**

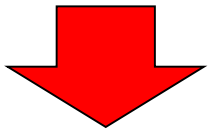


***Splitting into several groups*: Cationic single identification within each group:**

No interferences or easy elimination

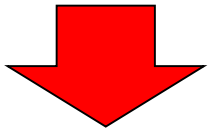
(pH change o complexes, heating…)

How can we separate our cations?



- Precipitate formation and separation of solid and the supernadant.

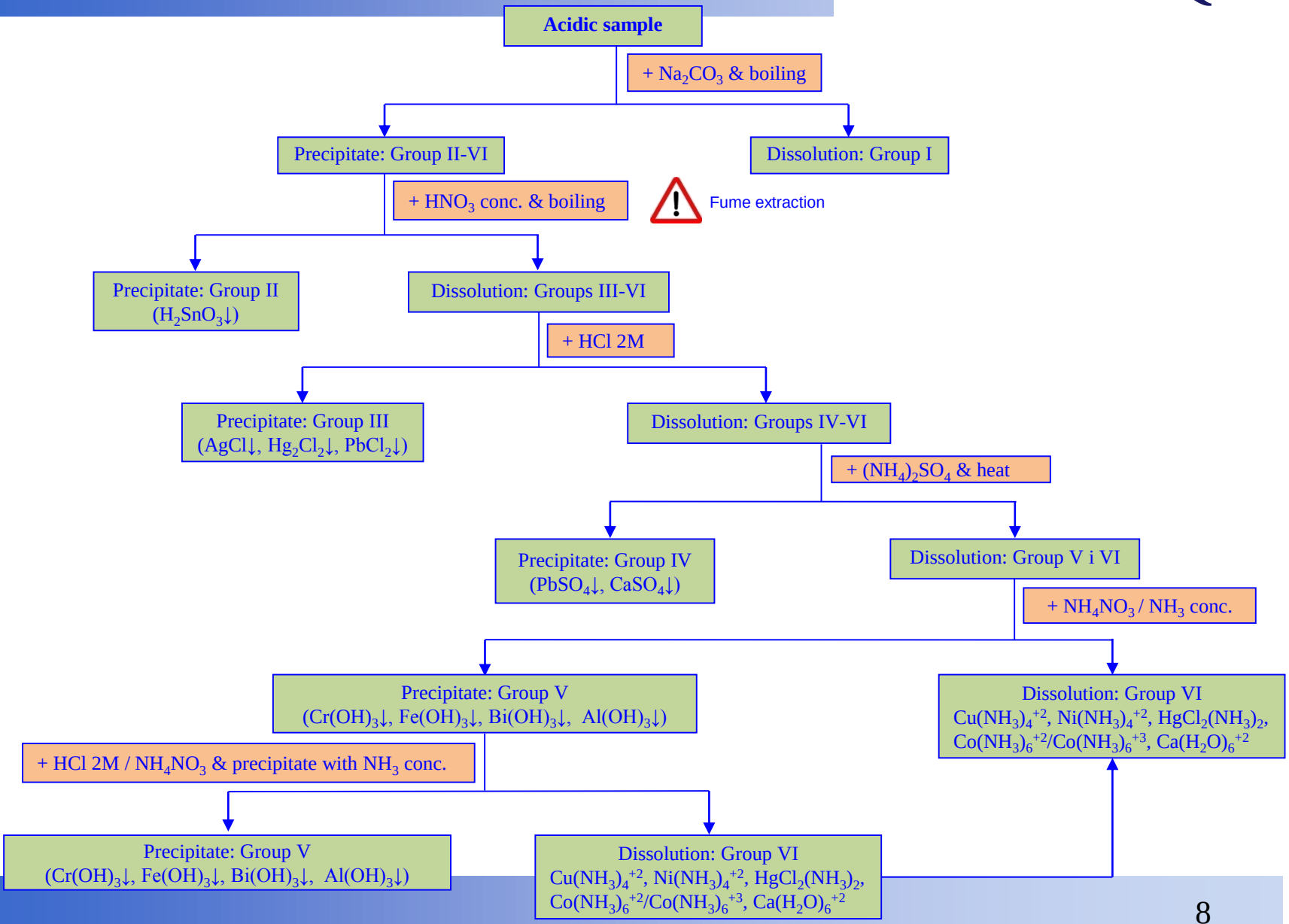
-Solubility differences of salts by using characteristics anions and specific media (pH, complex, redox, …)



ANALYTICAL SCHEME

Basis: A sequence of experimental operations that includes separation stages combined with identification stages of the analytes, designed for a large number of inorganic cations and anions.

AIM: To determine the presence of several cations in a sample of unknown composition, through the carbonate analytical scheme


Acidic sample
+ Na_2CO_3 & boiling
Precipitate: Group II-VI
Dissolution: Group I
+ HNO_3 conc. & boiling
Fume extraction
Precipitate: Group II
(H_2SnO_3↓)
Dissolution: Groups III-VI
+ HCl 2M
Precipitate: Group III
(AgCl↓, Hg_2Cl_2↓, $PbCl_2$↓)
Dissolution: Groups IV-VI
+ $(NH_4)_2SO_4$ & heat
Precipitate: Group IV
($PbSO_4$↓, $CaSO_4$↓)
Dissolution: Group V i VI
+ NH_4NO_3 / NH_3 conc.
Precipitate: Group V
($Cr(OH)_3$↓, $Fe(OH)_3$↓, $Bi(OH)_3$↓, $Al(OH)_3$↓)
Dissolution: Group VI
$Cu(NH_3)_4^{+2}$, $Ni(NH_3)_4^{+2}$, $HgCl_2(NH_3)_2$,
$Co(NH_3)_6^{+2}$/$Co(NH_3)_6^{+3}$, $Ca(H_2O)_6^{+2}$
+ HCl 2M / NH_4NO_3 & precipitate with NH_3 conc.
Precipitate: Group V
($Cr(OH)_3$↓, $Fe(OH)_3$↓, $Bi(OH)_3$↓, $Al(OH)_3$↓)
Dissolution: Group VI
$Cu(NH_3)_4^{+2}$, $Ni(NH_3)_4^{+2}$, $HgCl_2(NH_3)_2$,
$Co(NH_3)_6^{+2}$/$Co(NH_3)_6^{+3}$, $Ca(H_2O)_6^{+2}$

Experimental session organization

- **Session 1**

  Identification assays of I, II, III cation groups (each one per separate)

- **Session 2**

  Identification assays of IV and V +VI cation groups

- **Session 3**

  Cationic mixture test solution to perform the total analytical scheme (non-avaluable)

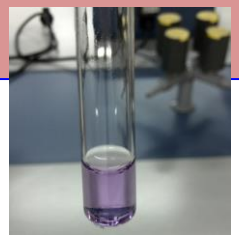
- **Session 4**

  Cationic mixture test solution to perform the total analytical scheme **(avaluable)**

- **Group I: Cr(VI) i As(III)**

Cr(IV) identification:

- Cromate to dicromate
- Peroxocròmic oxide formation
- Reduction to Cr(III) and complex formation with EDTA.

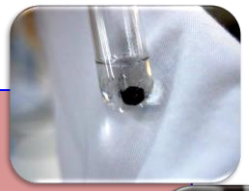


As(III) identification:

- Fleitmann assay

Fume extraction

- **Group II: Sn(IV)**



Sn(IV) identification:

- Amb sal mercúrica
- Reducció a hidrur i luminescència a la flama

- **Group III:** Ag(I), Pb(II) i Hg(I)

Group III

+ HCl 2M

Dissolution

Precipitate: Group III
$AgCl\downarrow$, $PbCl_2\downarrow$, $Hg_2Cl_2\downarrow$

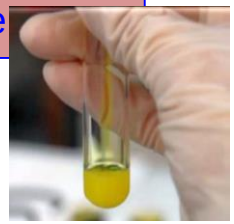
+ heat H_2O

Precipitate: $AgCl\downarrow$, $Hg_2Cl_2\downarrow$

+ NH_3 2M

Dissolution: Pb^{2+}

Pb(II) identification:
- With cromate



Precipitate: $Hg_2Cl_2\downarrow$

Hg (I) identification:
- Dismutation

Dissolució: $Ag(NH_3)_2^+$

Ag(I) identification:
- With KI
- With chloride

Chromium assays

$$2\ CrO_4^{2-}\ (groc)\ +\ 2\ H^+\ \leftrightarrows\ Cr_2O_7^{\ 2-}\ (ataronjat)\ +\ H_2O$$

$$Cr_2O_7^{2-} + 3\ H_2O_2\ + 2\ H^+ \rightarrow\ 2\ CrO(O_2)_2\ (blau) + 3H_2O$$

$$2\ CrO(O_2)_2 + 7\ H_2O_2 + 6\ H^+ \rightarrow 2\ Cr^{3+} + 7\ O_2 + 10\ H_2O$$

$$Cr_2O_7^{2-} + 3\ H_2O_2\ + 2\ H^+ \rightarrow\ 2\ CrO(O_2)_2\ (blau) + 3H_2O$$

$$2\ CrO(O_2)_2 + 7\ H_2O_2 + 6\ H^+ \rightarrow 2\ Cr^{3+} + 7\ O_2 + 10\ H_2O$$

$$Cr^{3+}\ (verd)\ +\ H_2Y^{2-}\ \leftrightarrows\ CrY^-\ (violeta)\ +\ 2\ H^+$$

Tin assays

$$3\ Sn^{4+} + 2\ Fe(0) + 12\ Cl^- \leftrightarrows 3\ Sn^{2+} + 2\ FeCl_6^{3-}$$

$$2\ Fe(0) + 6\ H^+ + 12\ Cl^- \leftrightarrows 2\ FeCl_6^{3-} + 3\ H_2\uparrow$$

$$Sn^{2+} + 2\ Hg^{2+} + 8\ Cl^- \leftrightarrows SnCl_6^{2-} + Hg_2Cl_2\downarrow \text{(blanc)}$$

$$Sn^{2+} + Hg^{2+} + 6\ Cl^- \leftrightarrows SnCl_6^{2-} + Hg(0)\downarrow \text{(negre)}$$

$$Zn^0 + 4\ Cl^- \rightarrow ZnCl_4^{2-} + 2\ e^-$$

$$2\ x \quad [\ H^+ + e^- \rightarrow H\ (naixent)\ ]$$

$$Zn^0 + 4\ Cl^- + 2\ H^+ \rightarrow ZnCl_4^{2-} + 2\ H\ (naixent)$$

$$Sn^{2+} + 4\ H\ (naixent) \rightarrow H_2Sn\uparrow + 2\ H^+$$

$$H_2Sn\uparrow + \tfrac{1}{2}\ O_2 \rightarrow SnO^* \rightarrow SnO + h\nu$$

Lead assays

$$Pb^{2+} + CrO_4^{2-} \leftrightarrows PbCrO_4 \downarrow \text{(groc)}$$

Mercury assays

$$Hg_2Cl_2 \downarrow \text{(blanc)} + 2\,NH_3 \rightarrow HgNH_2Cl \downarrow \text{(blanc)} + Hg(0) \downarrow \text{(negre)}$$

Silver assays

$$Ag(NH_3)_2^+ + I^- \leftrightarrows AgI \downarrow \text{(blanc groguenc)} + 2\,NH_3$$

$$Ag(NH_3)_2^+ + Cl^- + 2\,H^+ \leftrightarrows AgCl \downarrow \text{(blanc)} + 2\,NH_4^+$$

REAGENTS

- In droppers:
- A: General → 1 per couple
- B: especifics cation → 1 per couple
- C: especific anions →1 per 2 couples
- Do not contaminate the droppers
- Don’t introduce glass rods or droppers in the reagents
- Close the reagrent bottles
- Bring back to their place
- Wastes

GLASS MATERIAL USE

Short test tubes and assay plate: all the assays

- Write with glass marker

Large Test tubes: gas emission, splashes, dryness boiling, luminiscence, flame, save the test solution

Big glass: with wàter (bath haeting and clean droppers)

Little glass: Group I separation

Glass rod: take drops to pH measurements and mix

Test rod: take precipitates and regulate the water boiling process.

Ceramic porous plate: to improve the boiling process

Droppers:

- Take the supernatant after centrifugate

- Take volumes (20 drops → 1 mL) Semiquantitative !!

pH measurements:

pH paper indicator

CENTRIFUGE

- To take teh precipitate from the supernatant
- Only with thick glass test tubes
- Always with the same type of tubes (gruix de paret i longitud)
- Centrifuge must be equilibrated with tubes
- Centrifugate test tubes of different couples
- Do not open the centrifuge in using
- Check if supernatant must be saved of not.

WASH A PRECIPITATE

- In centrifuge test tubes
- MIX the precipitate with aqueous solution
- Shake until the precipitate is suspended.
- Centrifugate
- Take the supernatant and waste

HEATING

- Acelerate or produce som reactions

- Water heatin on heating plate (not with a flame)

- Little tubes or centrifuge tubes taken with clamps and introduced in water

-Always must be one studient during the process

- Boiling: begins when the water is boiling

- Let cool before take the material

- Turn off the heating plate

FLAME HEATING

- Only for specific cases, in gas fume: HNO_3 conc. treatment, As(III), Sn(IV) and Ca(II) luminescence.

- Take the test tube with long clmps

-Let cool before take the material

- Heat the test tube in the lateral part and taking care that there ins no one close to the tube.

- Close the gas when you finish.

GAS FUME

- **Processes with toxic gas release.**
- **Heating with possible splashes.**
- **Flame assays**
- **Assays: HNO_3 treatment, As(III), Sn(IV), Ca(II)**
- **HCl and HNO_3 conc. use**