Introduction

The aim of Exercise 9 is to analyze three inorganic salts (one of them poorly soluble) - and detect both cation and anion, which are two components of each salt, belonging to the groups mentioned below:

- **Group I cations**: Ag⁺, Hg₂²⁺, Pb²⁺
- **Group IIA cations**: Pb₂⁺, Hg₂²⁺, Cu²⁺, Cd²⁺, Bi³⁺
- **Group III cations**: Fe³⁺, Mn₂⁺, Cr³⁺, Co²⁺, Ni²⁺, Zn²⁺, Al³⁺
- **Groups IV and V cations**: Ca²⁺, Ba²⁺, Sr²⁺, Mg²⁺, Na⁺, K⁺, NH₄⁺
- **Group I anions**: Cl⁻, Br⁻, I⁻, [Fe(CN)₆]⁴⁻, [Fe(CN)₆]³⁻
- **Groups II and V anions**: NO₂⁻, CH₃COO⁻, NO₃⁻, MnO₄⁻
- **Group III anions**: SO₃²⁻, CO₃²⁻, C₂O₄²⁻, BO₃³⁻, C₄H₄O₆²⁻
- **Group IV and VI anions**: PO₄³⁻, S₂O₃²⁻, CrO₄²⁻, SO₄²⁻

The qualitative analysis of single salt consists of preliminary research and analysis of cation and anion separately. For this purpose, the salt must be dissolved in some suitable solvent to prepare a clear and transparent solution.

All inorganic salts can be divided into soluble in water and insoluble in water and the solubility depends strongly on the composition of the salt (cation and anion). Of course, there are some rules which are helpful in prediction of whether the salt will dissolve in water and they are presented in the table below:

<table>
<thead>
<tr>
<th>SOLUBLE SALTS</th>
<th>Na⁺, K⁺, and NH₄⁺ ions form <em>soluble salts</em> for instance NaCl, KNO₃, (NH₄)₂SO₄, Na₂S, K₂CO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>nitrates NO₃⁻ form <em>soluble salts</em>, for instance Cu(NO₃)₂, Fe(NO₃)₃, Ca(NO₃)₂</td>
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<tr>
<td>acetates CH₃COO⁻ form <em>soluble salts</em>, for instance Co(CH₃COO)₂, Ba(CH₃COO)₂, CH₃COOK</td>
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<tr>
<td>chlorides Cl⁻, bromides Br⁻, and iodides I⁻ generally form <em>soluble salts</em>, except the salts of the Pb²⁺, Hg²⁺, Ag⁺, and Cu⁺ ions</td>
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<tr>
<td>sulfates SO₄²⁻ generally form <em>soluble salts</em>, except BaSO₄, SrSO₄, and PbSO₄, which are insoluble, and Ag₂SO₄, CaSO₄, and Hg₂SO₄, which are slightly soluble</td>
<td></td>
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<table>
<thead>
<tr>
<th>INSOLUBLE SALTS</th>
<th>sulfides S²⁻ are usually <em>insoluble</em>, except Na₂S, K₂S, (NH₄)₂S, MgS, CaS, SrS, and BaS</th>
</tr>
</thead>
<tbody>
<tr>
<td>chromates CrO₄²⁻ are usually <em>insoluble</em>, except Na₂CrO₄, K₂CrO₄, (NH₄)₂CrO₄, MgCrO₄</td>
<td></td>
</tr>
<tr>
<td>phosphates PO₄³⁻ and carbonates CO₃²⁻ are usually <em>insoluble</em>, except salts of the Na⁺, K⁺, and NH₄⁺ ions</td>
<td></td>
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<tr>
<td>sulfates SO₄²⁻ of the salts BaSO₄, SrSO₄, and PbSO₄ are insoluble, and Ag₂SO₄, CaSO₄, and Hg₂SO₄, which are slightly soluble</td>
<td></td>
</tr>
<tr>
<td>chlorides Cl⁻, bromides Br⁻, and iodides I⁻ of the salts of the Pb²⁺, Hg₂²⁺, Ag⁺, and Cu⁺ ions</td>
<td></td>
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<tr>
<td>all carbonates are insoluble except those of sodium, potassium, and ammonium</td>
<td></td>
</tr>
</tbody>
</table>
There are two main steps in preliminary research:

1. **Solubility test** - which always begins with dissolving the sample in distilled water. In the first attempts are made at room temperature and then solutions are warmed up until the boiling point of solvent, due to the lack of solubility. If the salt is not soluble in water, the following solvents are used one after another in a systematic order:
   - diluted CH$_3$COOH
   - diluted HCl
   - concentrated HCl
   - diluted HNO$_3$
   - concentrated HNO$_3$
   - *aqua regia* - mixture of concentrated HCl and HNO$_3$ acids in ratio 3:1
   - strong bases

The form and color of analyzed salt may suggest its solubility and the presence of particular ions like Cu$^{2+}$ (blue), Ni$^{2+}$ (green), Mn$^{2+}$ (light pink), Co$^{2+}$ (rose), Cr$^{3+}$ (green or purple), CrO$_4^{2-}$ and Fe$^{3+}$ (yellow), MnO$_4^{-}$ (purple) and then the solution of dissolved salt should also be colored. The crystalline form of the salt suggests its good solubility in water, whereas the powder form of a salt indicates its poor solubility in water. Also, if dissolving any salt in water is followed by appearance of gelatinous residue, different from starting one, it may imply salt hydrolysis. For instance, this is observed with Bismuth salts.

2. **Checking pH of the solution** - to specify the acidity or basicity of an aqueous solution, which gives an initial orientation about the type of the salt:
   - neutral pH is observed for salts of strong acids and strong bases or salts of weak acids and weak bases (NaCl, NH$_4$NO$_2$);  
   - basic pH is observed for salts of strong bases and weak acids (CH$_3$COOK, Na$_2$CO$_3$);  
   - acidic pH is observed for salts of weak bases and strong acids (NH$_4$NO$_3$, MgSO$_4$), as well as acid salts (KHSO$_4$).

**Identification of salt samples**

Student must identify three unknown solid salts. Two of them are soluble in water, the third is insoluble in water. Nevertheless, each simple salt is composed of one cation and one anion and they have to be identified. Therefore, some helpful procedure is given below to follow:

1. Take a look at the sample - specify its form (crystal or powder) and color (colorless, white or other). Remember that hydrated copper(II) salts and anhydrous cobalt salts are blue, hydrated iron(II), chromium(III), nickel(II) salts are green, hydrated cobalt salts are red, calcium(II), zinc(II) or cadmium(II) nitrates or sulfates are white.
2. Take a small amount of salt to a clean test tube and dissolve it in a small amount (5-10 mL) of distilled water.

If the sample dissolves in water, the obtained solution can be diluted with additional amount of distilled H$_2$O and it is ready for cation and anion identification. However, it is still worth checking the pH of the solution (important information given in Introduction part). Then, you can start with cation identification. For this purpose:
3. Take small amount of obtained solution and start the analysis with the use of the group reagent. As a first, use HCl as the 1st group reagent. The occurrence of the precipitate points at the presence of the cation from the 1st group cations. The lack of the precipitate means, that cation belongs to another group (II, III, IV or V). Therefore, the reactions with other group reagents (procedures described in book entitled “Selected Topics in General and Inorganic Chemistry” part C) should be conducted.

4. Confirmation of the group to which cation belongs, should be followed by characteristic reactions to identify specific cation (exercises 1-4).

After identification of the cation you can start the determination of the anion (exercises 5-8).

Example of the analysis

**Sample 1**
1. Visual test – white crystalline powder
2. Solubility in water – soluble
3. Cation identification:
   a) number of the group:
      1st group reagent (HCl solution) – no precipitate
      2nd group reagent (HCl / H₂S aq) – black precipitate – means, that cations belongs to the 2nd group
   
   **Conclusion** – the salt is white, so Pb(II) and Hg(II) ions are under consideration
   
   b) characteristic reactions:
      for Pb(II): reaction with KI, K₂CrO₄ or diluted H₂SO₄ – yellow precipitate obtained in reaction with KI and K₂CrO₄ and white precipitate with H₂SO₄
      for Hg(II): drop of the analyzed solution placed on the copper plate – no reaction
   
   **Conclusion: Sample contains Pb²⁺ ions**

4. Anion identification
   a) number of the group: reactions with AgNO₃aq and BaCl₂aq

   Observation: no precipitate with AgNO₃ and BaCl₂

   **Conclusion – the salt is white, so CH₃COO⁻, NO₂⁻ and NO₃⁻ are the only possible anions**

   b) characteristic reactions:
      for CH₃COO⁻: reaction with solid KHSO₄ – detection of acetic acid odor (vinegar odor)
      for NO₂⁻ and NO₃⁻: the reaction with Mohr’s salt in the presence of diluted and concentrated H₂SO₄, respectively – no reaction

   **Conclusion – CH₃COO⁻ is present in the analyzed salt**

   **Final conclusions: Sample 1 is Pb(CH₃COO)₂**
Sample 2
1. Visual test – green powder
2. Solubility in water – insoluble
3. Solubility in CH₃COOHaq – soluble
4. Solubility in diluted HCl - soluble
3. Cation identification:
   a) number of the group
      1ˢᵗ group reagent (HCl solution) – no precipitate
      2ⁿᵈ group reagent (HCl / H₂S aq) – no precipitate
      3ʳᵈ group reagent (solutions of NH₃, NH₄Cl and H₂Saq) – REMEMBER that the salt was dissolved in the acid, so the obtained solution has acidic pH. Therefore, the reaction with the 3ʳᵈ group reagent must be followed in excess of NH₃ and NH₄Cl to obtain alkaline solution (check the pH with indicator paper)

   Observation – the appearance of black precipitate

Conclusion – the salt is green, so Ni(II) ion is the most probable one

   b) characteristic reactions for Ni(II): the reaction with dimethylglyoxime (HDMG) in the presence of NH₃ solution

   Observation – the appearance of characteristic rose-red precipitate

Conclusion: Sample contains Ni²⁺ ions

4. Anion identification
   a) Dissolution of salt sample is accompanied by the release of colorless gas

Conclusion – the salt contains CO₃²⁻ anions which are decomposed and carbon dioxide gas is released, visible as gas bubbles

Final conclusions: Sample 2 is NiCO₃