
PEDAGOGICAL BASIS OF TEACHING THE SUBJECT OF CLASSIFICATION OF ANIONS BY ANALYTICAL GROUPS AND QUALITATIVE ANALYSIS

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This text details laboratory methods for qualitative analysis of Group I anions $(SO_4^{2-}, SO_3^{2-}, S_2O_3^{2-}, CO_3^{2-}, PO_4^{3-})$. It describes their characteristic reactions with reagents like BaCl₂, including the formation and solubility of precipitates. The agricultural significance of these anions is noted. A key focus is the systematic fractional separation method, which uses sequential acid treatment, selective precipitation, and redox reactions for reliable identification of anions in mixtures, forming the core of classical qualitative analysis.

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Group I Anions. The common group reagent for Group I anions is barium chloride (BaCl₂), which precipitates them only in a neutral or weakly alkaline medium. The Ba²⁺ cation forms salts with the first group anions that are sparingly soluble in water but readily soluble in dilute mineral acids (except for barium sulfate, BaSO₄).

Identifying Group I anions is of significant practical importance, as their compounds are widely used in agriculture. K₂SO₄ and (NH₄)₂SO₄ are components of mineral fertilizers. Copper(II) sulfate pentahydrate (CuSO₄·5H₂O) and iron(II) sulfate heptahydrate (FeSO₄·7H₂O) are used in agriculture for pest control in plants.

In soil, CaCO₃ and MgCO₃ are relatively more abundant compared to other carbonates, while carbonates of alkali metals are present in very small quantities. Calcium carbonate and dolomite (CaCO₃·MgCO₃) are used to neutralize acidic soils.

Soils also contain phosphates, with a portion existing in forms available for plant uptake. Phosphorus is an essential macroelement for plant nutrition, and its deficiency in soil is corrected by applying phosphate fertilizers. Most of these fertilizers are salts of phosphoric acid. For instance, phosphorite and apatite contain calcium phosphate, Ca₃(PO₄)₂.

Characteristic Reactions of the Sulfate Anion (SO₄²⁻). For the experiments, colorless aqueous solutions of well-soluble salts of sulfuric acid can be used.

Reaction with Barium Chloride (BaCl₂). The reagent reacts with SO₄²⁻ anions, forming a white crystalline precipitate of BaSO₄:

$$\begin{split} Na_2SO_4 + BaCl_2 &= BaSO_4 \downarrow + 2NaCl\\ SO_4^{2-} + Ba^{2+} &= BaSO_4 \downarrow \end{split}$$

Procedure: Place 4-5 drops of sodium sulfate solution into a test tube and add 4-5 drops of BaCl₂ solution. Within a minute, a white crystalline precipitate of BaSO₄ forms. Divide the precipitate into two parts and test its solubility in hydrochloric acid and alkali.

Reaction with Lead(II) Acetate (Pb(CH₃COO)₂). This reagent reacts with SO₄²⁻ anions, forming a white crystalline precipitate of PbSO₄:

$$\begin{split} Na_2SO_4 + Pb(CH_3COO)_2 &= PbSO_4 \downarrow + 2CH_3COONa \\ SO_4^{2-} + Pb^{2+} &= PbSO_4 \downarrow \end{split}$$

Procedure: To 4-5 drops of sodium sulfate solution in a test tube, add 3-4 drops of lead(II) acetate solution. An insoluble white crystalline precipitate forms, which does not dissolve in dilute acids but dissolves in alkalis (caustic alkalis).

Characteristic Reactions of the Sulfite Anion (SO₃²⁻). For the reactions, aqueous solutions of salts containing SO₃²⁻ are used.

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Reaction with Barium Chloride (BaCl₂). This reagent reacts with SO₃²⁻ anions in solution, forming a white precipitate of barium sulfite:

$$Na_2SO_3 + BaCl_2 = BaSO_3 \downarrow + 2NaCl$$

$$SO_3^{2-} + Ba^{2+} = BaSO_3$$

The formed precipitate dissolves in hydrochloric and nitric acids with the evolution of sulfur dioxide (SO₂):

$$BaSO_3 + 2HCl = H_2O + SO_2 \uparrow + BaCl_2$$

Procedure: Add 4-5 drops of sodium sulfite solution to a test tube, then add an equal volume of the reagent solution. A white precipitate forms. Dissolving the precipitate in acids results in the evolution of sulfur dioxide, which has a pungent smell resembling burning sulfur.

Reaction with Iodine Water. Sulfite anions are oxidized by iodine, reducing I₂ to I⁻ and decolorizing the brown iodine solution:

$$SO_3^{2-} + I_2 + H_2O = SO_4^{2-} + 2I^- + 2H^+$$

Procedure: Place 1-2 drops of iodine water into a test tube, then add 3-4 drops of the sulfite salt solution and 5 drops of H₂SO₄ solution. The brown color of the iodine solution disappears.

Note: The reaction can be carried out in neutral or acidic media. At pH < 7, the reaction proceeds completely. In an alkaline medium, the iodine color may fade due to a disproportionation reaction. The presence of other reducing or oxidizing ions in the solution can interfere with the reaction.

Reaction with Fuchsin Solution. In neutral solutions, the SO₃²⁻ anion reacts with the red color of the dye disappear fuchsin, causing to (decolorization). **Procedure:** Place one drop of fuchsin solution on a glass plate, then add one drop of a neutral solution of the sulfite salt. (Acidic solutions are neutralized with NaHCO₃, alkaline solutions by passing CO₂ gas until phenolphthalein becomes colorless). In the presence of SO₃²⁻, the fuchsin solution becomes colorless.

Characteristic Reactions of the Thiosulfate Anion (S₂O₃²⁻). For the experiments, an aqueous solution of Na₂S₂O₃ is used.

Reaction with Barium Chloride (BaCl₂). The reagent reacts with S₂O₃²⁻ ions in solution, forming a white precipitate of barium thiosulfate:

$$Na_2S_2O_3 + BaCl_2 = BaS_2O_3 \downarrow + 2NaCl$$

$$S_2O_3^{2-} + Ba^{2+} = BaS_2O_3 \downarrow$$

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Procedure: To 5-6 drops of sodium thiosulfate solution, add 8-10 drops of BaCl₂ solution. The formation of a white precipitate is observed.

Procedure Conditions:

The reaction occurs when an excess of BaCl₂ solution is added.

To induce precipitation, the inner wall of the test tube at the liquid interface is rubbed with a glass rod.

Reaction with Iron(III) Chloride. Fe³⁺ ions oxidize thiosulfate, forming a dark violet-colored complex $[Fe(S_2O_3)_2]^-$, which is unstable and decomposes within minutes, and the solution becomes colorless again.

Procedure: Place 2-3 drops of sodium thiosulfate solution into a test tube and add 1 drop of iron(III) chloride solution. An immediate deep violet color appears. This color disappears within 1-2 minutes, and the solution becomes colorless again.

Characteristic Reactions of the Carbonate Anion (CO₃²⁻). Experiments are conducted using colorless aqueous solutions of Na₂CO₃, K₂CO₃, or (NH₄)₂CO₃.

Reaction with Barium Chloride (BaCl₂). The reagent reacts with CO₃²⁻ anions in solution, forming a white precipitate of barium carbonate:

$$Na_{2}CO_{3}+BaCl_{2}=BaCO_{3}\downarrow+2NaCl$$

$$CO_3^{2-} + Ba^{2+} = BaCO_3 \downarrow$$

The formed precipitate dissolves in hydrochloric, nitric, and even acetic acids.

Procedure: To 4-5 drops of sodium carbonate solution, add 4-5 drops of BaCl₂ solution.

The formation of a white precipitate is observed.

Procedure Conditions:

The solution medium should be neutral or weakly alkaline.

The presence of SO_4^{2-} or SO_3^{2-} anions in the solution interferes with the reaction, as they also form white precipitates with Ba^{2+} cations.

Characteristic Reactions of the Phosphate Anion (PO₄³⁻/HPO₄²⁻)

For the experiments, a solution of sodium hydrogen phosphate (Na₂HPO₄) can be used.

Reaction with Barium Chloride (BaCl₂). The reagent reacts with the sodium hydrogen phosphate solution, forming a white precipitate of barium hydrogen phosphate:

$$Na_{2}HPO_{4}+BaCl_{2}=BaHPO_{4}\downarrow+2NaCl$$

$$HPO_4^{2-} + Ba^{2+} = BaHPO_4 \downarrow$$

Procedure: Take 4-5 drops of sodium hydrogen phosphate solution and add 2-3 drops of BaCl₂ solution to it. The formation of a white precipitate is observed.

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The BaHPO₄ precipitate dissolves in strong acids (except H₂SO₄) and also in acetic acid.

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Systematic Fractional Separation Method. One of the most effective methods in the qualitative analysis of anions is the systematic fractional (step-by-step) separation method. It is based on grouping anions according to their varying stability towards acids, alkalis, or oxidizing/reducing agents. The essence of the method is the sequential application of reactions that yield specific precipitates or gases under defined conditions, allowing for the identification of anions that do not react simultaneously.

The steps of the method are as follows:

- **1.Reaction with Strong Acids:** Anions like carbonates, sulfites, and nitrites, upon treatment with strong acids, release gases (CO₂, SO₂, NO), enabling their immediate identification.
- **2.Formation of Selective Precipitates with Cations:** For example, sulfates precipitate with Ba²⁺, carbonates with Ca²⁺, and halides with Ag⁺. In each step, the reaction conditions (pH, solution concentration) ensure clear differentiation between anions.
- **3.Oxidation-Reduction Reactions:** Anions such as nitrite, sulfite, and thiosulfate are sensitive to oxidizing agents and can be detected by color changes or gas evolution.
- **4.Final Test of the Residual Solution:** In the final stage, anions that have not reacted (e.g., phosphate, borate, fluoride) are identified using specific reagents.

The advantage of this method is that it allows for the sequential, orderly, and reliable identification of anions even in complex mixtures, and it fully aligns with the principle of classification into analytical groups.

Conclusion. Qualitative analysis of anions is one of the most important branches of analytical chemistry, requiring deep knowledge of reagents, the influence of medium conditions, and the principles of precipitate formation. The conducted experiments clearly demonstrated the specific reactions, solubility characteristics, and precipitate stability of sulfate, sulfite, thiosulfate, carbonate, phosphate, and silicate anions. The unique chemical transformations of each anion with specific reagents allow for their reliable differentiation from one another.

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