Experiment 5 Qualitative Analysis: Na^+, K^+, NH_4^+, Ag^+, Cu^{2+}, Bi^{3+}

Objective

Observe and utilize the chemical and physical properties of Na^+, K^+, NH_4^+, Ag^+, Cu^{2+}, and $Bi^{3+}$and separate and identify the presence of one or more of the cations, Na^+, K^+, NH_4^+, Ag^+, Cu^{2+}, Bi^{3+}, in an aqueous solution.

Equipment

- Bunsen burner and hose
- Wire loop
- Cobalt blue glass
- Glass stirring rod
- Evaporating dish
- Ring stand
- Iron ring
- Wire gauze
- Water bottle
- Watch glass
- 50-mL beaker
- 100-mL beaker
- Red and blue litmus paper

Chemicals

Reference solution containing cations: **Na^+, K^+, NH_4^+, Ag^+, Cu^{2+}, Bi^{3+}**.

Solid CaO or $Ca(OH)_2$, $(NH_4)_2CO_3$; conc NH_3, solutions of: 6.0 M HCl, 0.2 M NaCl, 0.2 M KCl, 6.0 M NaOH, 6.0 M NH_3, 6.0 M HNO_3, 6.0 M CH_3COOH, 0.2 M $K_4[Fe(CN)_6]$, 1.0 M $SnCl_2$.

Introduction

In identifying a particular cation in a mixture of cations, it would be ideal if we could detect each cation in the mixture by merely adding a specific reagent that would produce a characteristic color or precipitate; however, no such array of reagents has been developed. Instead, the cations must first be separated into groups having similar chemical properties; each group is then further divided until each ion is isolated. From there, the cation responds to a specific reagent to produce the characteristic color or precipitate for identification. The qualitative analysis of a mixture of cations requires such a plan of investigation.

The qualitative analysis of cations requires good laboratory technique for their **separation** and **confirmation**, as well as careful preparation and understanding of the procedure. We will approach this study as an experimental chemist: we will conduct some tests, write down our observations, and then write a balanced equation that agrees with our data.

As an introduction to the chemistry of the cations in this experiment, keep in mind the following:

- Na^+, K^+, and NH_4^+ salts are soluble.
- The chloride salt of Ag^+ is "insoluble".
- The sulfide salts of Cu^{2+} and Bi^{3+} are also considered "insoluble."

Thus, these ions can be separated from a large number of other cations.

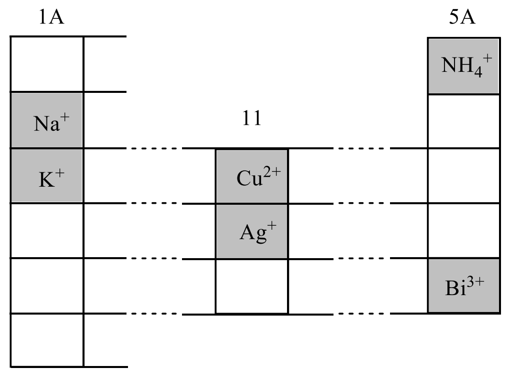


Figure 1 Cations of Qualitative Analysis Lab

Sodium and Potassium ions

Sodium and potassium ions form a very limited number of salts with low solubilities and only carefully controlled conditions provide confirmatory tests. However, both ions provide very sensitive, distinctive **flame tests**.

Sodium ions produces a characteristic, fluffy yellow flame. The color is so intense that it masks the color produced by other ions and is comparatively persistent.

Potassium ions can be detected also with a flame test in a sample. The flame is viewed through cobalt blue glass. The glass absorbs the intense yellow color of sodium but transmits the lavender color of the potassium flame. The lavender flame is of short duration. A comparative test of a solution known to contain only potassium ion is often necessary for the determination.

Ammonium ion

All ammonium salts are water soluble. The ammonium ion is a weak acid; its conjugate base is ammonia, which is a gas. When the pH of an aqueous solution of ammonium ion is increased, ammonia gas is evolved and is easily detected with red litmus.

To test for the ammonium ion, scientist take advantage of the following equilibrium:

$$\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq)$$

When a hydroxide ion (a common ion in the equilibrium) is added to a solution containing ammonium ion, this equilibrium shifts *left.* Heating drives *ammonia gas* from the system; its presence is detected using moist litmus paper (its odor is also frequently detected).

$$\Leftarrow \quad \text{shift left}$$
$$\mathrm{NH_3}(g) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq)$$
$$\uparrow \mathbf{OH}^-(aq)$$

Silver Ion

When hydrochloric acid is added to a solution containing Ag^+ ions, AgCl precipitates. A large concentration of the chloride ion must be avoided to prevent the formation of the soluble silver chloride complex anion:

$$\mathrm{AgCl}(s) + \mathrm{Cl}^-(aq) \rightleftharpoons [\mathrm{AgCl}_2]^-(aq)$$

In an ammoniacal solution, AgCl dissolves to form the $[\mathrm{Ag(NH_3)_2}]^+$ complex:

$$\mathrm{AgCl}(s) + \mathrm{NH_3}(aq) \rightleftharpoons [\mathrm{Ag(NH_3)_2}]^+(aq) + \mathrm{Cl}^-(aq)$$

The $[\mathrm{Ag(NH_3)_2}]^+$ ion is unstable in an acidic solution; H_3O^+reacts with NH_3 forming NH_4^+. The equilibrium shifts to the left and the AgCl re-forms as a *white precipitate.*

Separation of Copper (II) and Bismuth (III) Ions

The sulfide salts of Cu^{2+} and Bi^{3+} are insoluble in solutions with pH values as low as 0.5 (e.g., 0.3 M H_3O^+) and higher. If the pH is greater than 0.5, not only will the Cu^{2+} and Bi^{3+} sulfide salts precipitate but also other metal cations. Therefore, pH control is extremely important in the separation of Cu^{2+} and Bi^{3+} from OTHER cations. Once the pH of the test solution is set at about 0.5, the sulfide ion is generated *in situ* in the form of $H_2S(aq)$. The H_2S is *slowly* generated from the thermal hydrolysis of thioacetamide, CH_3CSNH_2.

$$\mathrm{CH_3CSNH_2}(aq) + 2\mathrm{H_2O}(l) \overset{\Delta}{\rightarrow} \mathrm{CH_3CO_2^-}(aq) + \mathrm{NH_4^+}(aq) + \mathrm{H_2S}(aq)$$

The slow generation of H_2S in solution minimizes the escape of this foul-smelling, highly toxic gas into the laboratory. When H_2S is produced slowly, more compact sulfide precipitates form, making them easier to separate by centrifugation. $H_2S(aq)$ is a weak. diprotic acid ionizing slightly to produce the sulfide ion that is necessary for Cu^{2+} and Bi^{3+} precipitation:

$$\mathrm{H_2S}(aq) + 2\mathrm{H_2O}(l) \rightleftharpoons 2\mathrm{H_3O^+}(aq) + \mathrm{S^{2-}}(aq)$$

Thioacetamide is added to an acidified solution of the cations to generate the sulfide ion. Copper(II) sulfide and bismuth(III) sulfide precipitate, and the supernatant solution contains the soluble cations. The CuS and Bi_2S_3 precipitates (both black in color) dissolve in hot HNO_3. The hot HNO_3 oxidizes the sulfide ion in the precipitates to elemental sulfur that further oxidizes to $SO_4^{2-}(aq)$, forming NO(g) as its reduction product. For CuS,

$$3\mathrm{CuS}(s) + 8\mathrm{H^+}(aq) + 8\mathrm{NO_3^-}(aq) \overset{\Delta}{\rightarrow} 3\mathrm{Cu^{2+}}(aq) + 3\mathrm{SO_4^{2-}}(aq) + 8\mathrm{NO}(g) + 4\mathrm{H_2O}(l)$$

For a Cu^{2+} or Bi^{3+} sulfide salt to precipitate, the product of the molar concentrations of the cation and sulfide ion in solution (the mass action expression for the salt) must exceed its K_{sp} value. Using LeChâtelier's principle, a high H_3O^+ concentration (pH ~ 0.5) shifts this equilibrium to the *left,* reducing the sulfide concentration. Hence, pH or H_3O^+controls the S^{2-} concentration. As the Cu^{2+} and Bi^{3+} cations precipitate at a low pH, only small amounts of sulfide ion are needed for their precipitation; these cations have low molar solubilities and also small K_{sp} values, at least smaller than other cations.

Copper ion

An alternative route for the separation of copper (II) and bismuth (III) ions, is the addition of aqueous ammonia NH_3 (ammonia dissolved in water, ammonium hydroxide, NH_4OH) to a solution containing the Bi^{3+} and Cu^{2+} cations. precipitates white bismuth hydroxide but complexes the Cu^{2+} as a soluble *deep blue* $[Cu(NH_3)_4]^{2+}$ *complex.* This confirms the presence of Cu^{2+} in the solution.

$$\mathrm{Bi^{3+}}(aq) + 3\mathrm{NH_3}(aq) + 3\mathrm{H_2O}(l) \rightarrow \mathrm{Bi(OH)_3}(s) + 3\mathrm{NH_4^+}(aq)$$

$$\mathrm{Cu^{2+}}(aq) + 4\mathrm{NH_3}(aq) \rightarrow \boxed{[\mathrm{Cu(NH_3)_4}]^{2+}(aq)}$$

A second confirmatory test for the presence of Cu^{2+} is the addition of potassium hexacyanoferrate(II), $K_4[Fe(CN)_6]$, which produces a *red-brown precipitate* of $Cu_2[Fe(CN)_6]$.

$$2[\mathrm{Cu(NH_3)_4}]^{2+}(aq) + [\mathrm{Fe(CN)_6}]^{4-}(aq) \rightarrow \boxed{\mathrm{Cu_2[Fe(CN)_6]}(aq)} + 8\mathrm{NH_3}(aq)$$

Bismuth Ion

The *white* bismuth hydroxide, $Bi(OH)_3(s)$, is dissolved and confirmed with the addition *of freshly prepared* sodium stannite, $Na_2Sn(OH)_4$, in a basic solution. The Bi^{3+} ion is reduced to *black* bismuth *metal,* confirming the presence of bismuth in the sample.

$$2\mathrm{Bi(OH)_3}(s) + 3[\mathrm{Sn(OH)_4}]^{2-}(aq) \rightarrow \boxed{2\mathrm{Bi}(s)} + 3[\mathrm{Sn(OH)_6}]^{2-}(aq)$$

As a guide to an understanding of the separation and identification of these six cations, carefully read the Experimental Procedure and then complete the flow diagram on the **Pre-Laboratory Assignment.**

Procedure

Procedure Overview: Two solutions are tested with various reagents in this analysis: (1) a **reference solution** containing all six of the cations and (2) an **unknown** test solution containing three of the cations. Comparative observations of the two solutions result in the identification of the cations in the test solution. All tests are qualitative; only identification of the cation(s) is required.

To become familiar with the separation and identification of cations, you will start with a sample that contains the six cations (**reference solution**) and analyze it according to the Experimental Procedure.

At each **[#]**, *stop* and record data on the Report Sheet. After the presence of a cation is confirmed, save the characteristic appearance of the cation in the test tube so that it can be compared with observations made in the analysis of your unknown test solution.

To analyze for cations in your test solution, place the test solution alongside the reference solution during the analysis. As you progress through the procedure, perform the same test on both solutions and make comparative observations. Check (**X**) the findings on the Report Sheet. Do not discard any solutions (but keep all solutions labeled) until the experiment is complete.

Contamination by trace amounts of metal ions in test tubes and other glassware lead to "unexplainable" results in qualitative analysis. Thoroughly clean all glassware with soap and tap water; rinse twice with tap water and twice with deionized water before use.

Caution: A number of 6 M acids and bases are used in the analysis of these cations. Handle each of these solutions with care.

A. Test for Sodium Ion

The Experimental Procedure is written for a single solution. If you are simultaneously identifying cations in *both* a reference solution *and* a test solution, adjust the procedure accordingly.

1. **Remove the Interfering Ions.** Place no more than 2 mL of the reference solution in an evaporating dish. Add solid CaO or $Ca(OH)_2$, (**Caution:** *avoid skin contact)* while stirring, until the solution is basic to litmus; add a slight excess of the solid and then a pinch of solid $(NH_4)_2CO_3$.
2. Heat the solution to a moist residue (**Figure 2a**) and allow the evaporating dish to cool. Add up to ~5 mL of deionized water, stir, and decant into a small beaker.

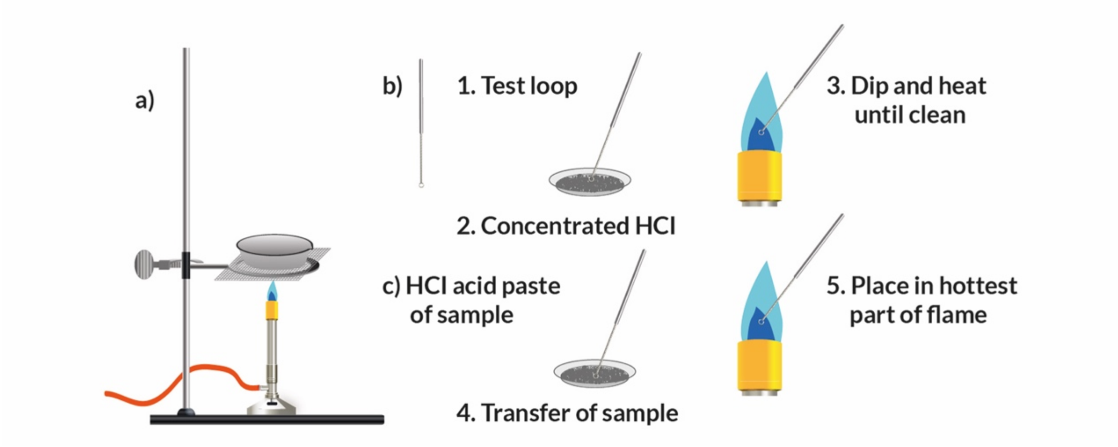


Figure 2 Proper cleaning of platinum wire.

3. **Confirmatory Test (C-TEST).** The flame test for sodium ion is reliable but also requires some technique. Clean the flame test wire by dipping it in 6.0 M HCl (**caution!**) and heating it in the hottest part of a Bunsen flame until the flame is colorless (**Figure 2b**). Repeat as necessary. Dip the flame test wire into the solution and place it in the flame (**Figure 2c**). A *brilliant yellow* persistent flame indicates the presence of sodium.**[1]** Conduct the sodium flame test on a 0.2 M NaCl solution for comparison.

B. Test for Potassium Ion

1. **Confirmatory Test.** Repeat **Part A.II**. A fleeting lavender flame confirms the presence of potassium. If sodium is present, view the flame through cobalt blue glass. Several trials are necessary as the test is judgmental. Conduct the potassium flame test on a 0.2 M KCl solution for comparison.**[2]**

C. Test for Ammonium Ion

1. **Prepare the Sample.** Transfer ~ 5 mL of the *original* reference solution to a 100-mL beaker, support it on a wire gauze, and heat until a moist residue forms (***do not evaporate to dryness!***). Moisten the residue with 1-2 mL of deionized water. Moisten a piece of red litmus paper and with water attach it to the convex side of a small watch glass (**Figure 3**). Cover the beaker with the convex side *down.*

2. **Confirmatory Test.** Add 1-2 mL of 6.0 M NaOH to the reference solution and very gently warm the mixture-*do not boil.* (**Caution: *Be careful not to let the* NaOH *come in contact with the litmus paper***)*.* A change in litmus from *red* to *blue* confirms ammonia.**[3]** The nose is also a good detector, but it is not always as sensitive as the litmus test.

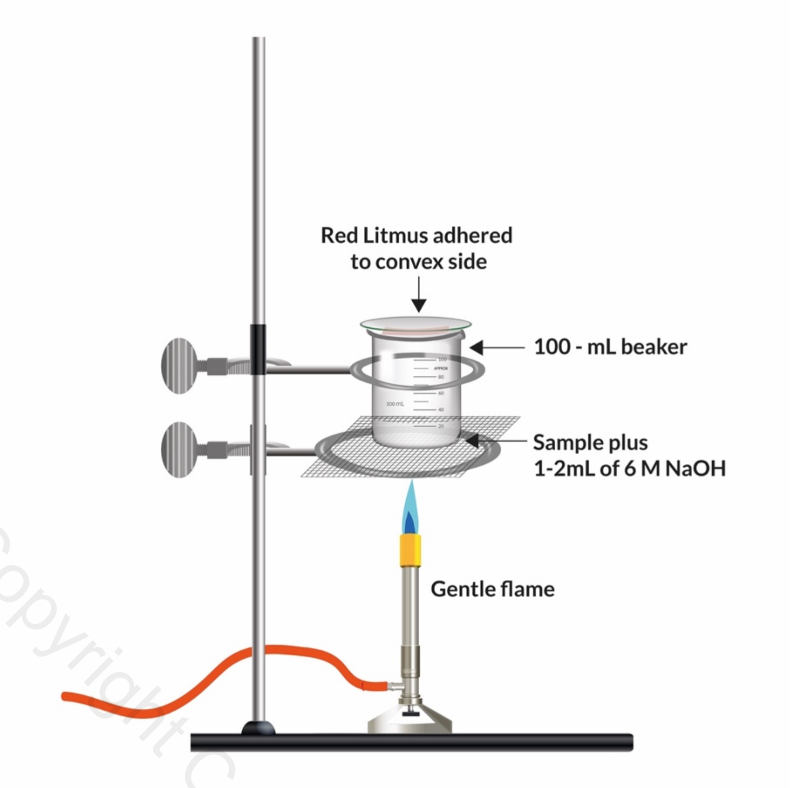


Figure 3 Absorbing NH_3 vapors on red litmus

Figure 4 Precipitation of Ag^+

D. Test for Silver Ion

1. **Precipitate the Silver Ion.** Place ~ 2 mL of the *original* reference solution in a small test tube, add 4-5 drops of 6.0 M HCl (**Figure 4**) until no further evidence of precipitation occurs.**[4]** (**Caution:** *Handle acid with care.)* Stir with a stirring rod and centrifuge the mixture. Test for complete precipitation by adding 1-2 additional drops of 6.0 M HCl. Ask your instructor about the safe operation of the

centrifuge. Decant and save the supernatant for **Part E**. Wash the precipitate with *5* drops of deionized water, centrifuge, and combine the supernatants.

2. **Confirmatory Test.** Dissolve the precipitate with 6.0 M NH_4OH (**caution!**).**[5]** Acidify the solution (check with litmus) with drops of 6.0 M HNO_3. (Caution: *Avoid skin contact; clean up spills immediately)*. A *white precipitate* confirms the presence of silver ion in the reference solution.

E. Test for Copper Ion

1. **Confirmatory Test.** Add drops of concentrated NH_4OH (**Caution**: *avoid inhalation or skin contact!)* to the solution from **Part D.I**. The *deep-blue* solution confirms the presence of Cu^{2+} in the sample.**[6]** Centrifuge, decant the solution, and save the precipitate **[8]** for Part F.
2. **A Second Confirmatory Test.** Acidify the supernatant from **Part E.I** with 6.0 M CH_3COOH (**caution**!). Add 3 drops of 0.2 M $K_4[Fe(CN)_6]$. A *red-brown precipitate* reconfirms the presence of Cu^{2+} ion.**[7]**

F. Test for Bismuth Ion

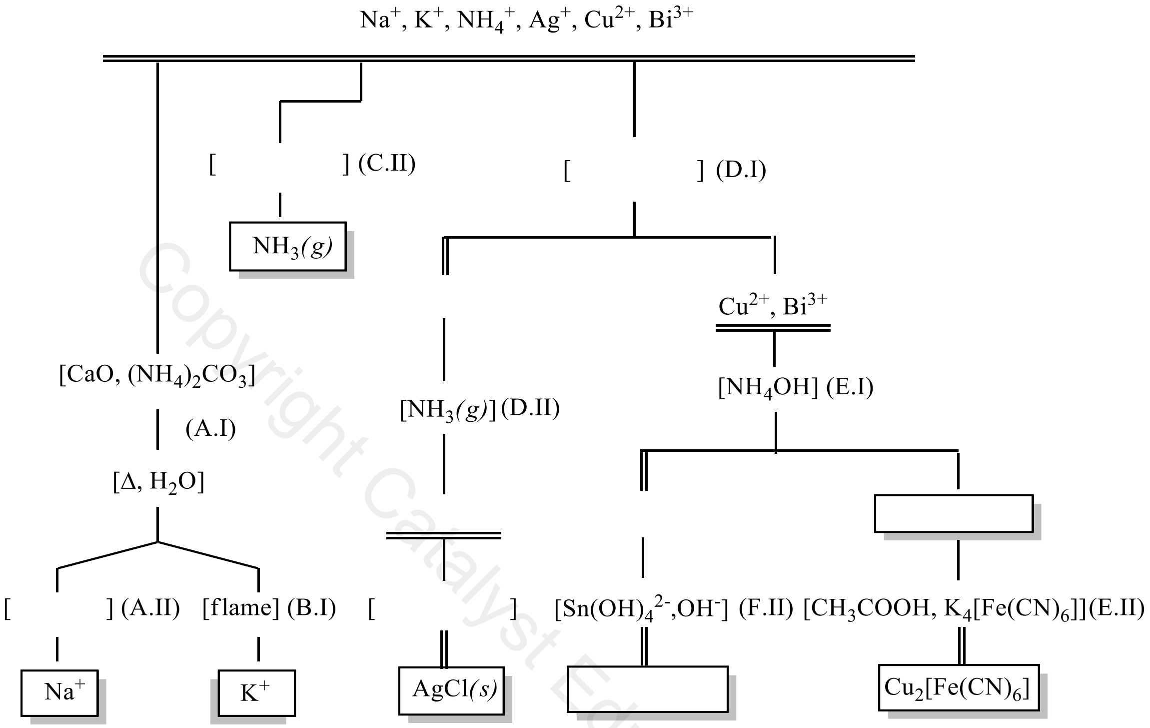
1. **Prepare the Sodium Stannite Solution.** Prepare a fresh $Na_2Sn(OH)_4$ solution by placing 2 drops of 1.0 M $SnCl_2$ in a small test tube, followed by drops of 6 M NaOH (**caution**!) until the $Sn(OH)_2$ precipitate just dissolves. Agitate or stir the solution.
2. **Confirmatory Test.** Add several drops of the $Na_2Sn(OH)_4$ solution to the precipitate from **Part E.I**. The immediate formation of a *black precipitate***[9]** confirms the presence of the Bi^{3+} ion in the sample.

Disposal*: Dispose of all test solutions and precipitates in the* ***"Waste Metal Salts"*** *container.*

CLEANUP*: Rinse each test tube twice with tap water. Discard each rinse in the* ***"Waste Metal Salts"*** *container. Thoroughly clean each test tube with soap and tap water; rinse twice with tap water and twice with deionized water.*

Pre-Laboratory Assignment

Following your procedure complete the following flow diagram before you attend the lab for the Qualitative analysis cations. Each square parenthesis represents a reactant, the box, a product and confirmation of the cation in the reference solution. It is important to note that a double horizontal line indicates that the ions on top of it are species in solution if the double lines are parallel is the formation of a precipitate.



Name: ____ Section: _________

Laboratory Instructor: ___________________________________ Date: ___/___/___

Report Sheet EXP5: Qualitative Analysis

Procedure Number and Ion	Test Reagent or Technique	Evidence of Chemical Change*	Chemical(s) Responsible for Observation	Check (**X**) if Observed in Unknown
[1] Na^+	Flame			[ ]
[2] K^+	Flame			[ ]
[3] NH_4^+				[ ]
Chemical Equation				
[4] Ag^+				[ ]
Chemical Equation				
[5] Ag^+ C-TEST				[ ]
Chemical Equation				
[6] Cu^{2+}				[ ]
Chemical Equation				
[7] Cu^{2+} C-TEST				[ ]
Chemical Equation				
[8] Bi^{3+}				[ ]
Chemical Equation				
[9] Bi^{3+} C-TEST				[ ]
Chemical Equation				

Cations present in **unknown** test solution number_______:

Instructor's approval: ____________________