

EXPERIMENT

37

QUAL II. Pb²⁺, Sn⁴⁺(Sn²⁺), Cu²⁺, Bi³⁺

OBJECTIVE

- To identify the presence of Pb²⁺, Sn⁴⁺ (Sn²⁺), Cu²⁺, and/or Bi³⁺ in a mixture

INTRODUCTION

This second group of cations, in a generalized qualitative analysis scheme, includes more cations than what are addressed in this experiment. Any qualitative analysis text describes the procedure for separating and identifying these additional cations.

In a *total* qualitative analysis of a sample, most of the lead(II) cation is removed as the chloride precipitate (Experiment 36), but, because of its relatively high solubility, especially in warm water, some Pb²⁺ may remain in solution. Therefore, it is important that we address its presence in the Qual II cations as well.

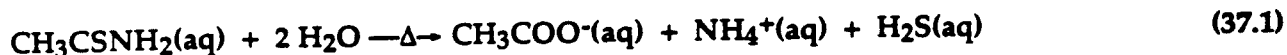
The analysis of Qual II cations requires good technique for their separation and confirmation, as well as a careful preparation and understanding of the procedure. If in following these steps, you only rely on a "cookbook" procedure, expect unexplainable results. Please read carefully the remainder of this Introduction, the Experimental Procedure, review your laboratory techniques, and complete the Prelaboratory Assignment before beginning the analysis—it will save you time and minimize frustration.

The sulfide salts of the Qual II cations are insoluble in solutions that are at least 0.3 M H⁺ (pH = 0.5). If the pH is greater than 0.5, sulfide precipitation of the Qual III cations (Experiment 38) is probable. Therefore, pH control is extremely important in the separation of these two groups.

		IIIA	IVA	VA
IB	IIB			
Cu ²⁺				As ³⁺
			Sn ²⁺ Sn ⁴⁺	Sb ³⁺
	Hg ²⁺		Pb ²⁺	Bi ³⁺

The cations of the Qual II group

Once the pH of the test solution is set at about 0.5, the sulfide ion is generated *in situ* in the form of $\text{H}_2\text{S}(\text{aq})$. The H_2S is *slowly* generated from the thermal hydrolysis of thioacetamide, CH_3CSNH_2 , in an acidic or basic solution.



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.

$\text{H}_2\text{S}(\text{aq})$ is a weak, diprotic acid ionizing slightly to produce the sulfide ion that is necessary for Qual II cation precipitation.



For a Qual II 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 the concept of LeChâtelier's Principle, a high H^+ concentration ($\text{pH} \approx 0.5$) shifts this equilibrium to the *left*, reducing sulfide concentration; a lower H^+ concentration (higher pH) shifts the equilibrium to the *right*, increasing the sulfide concentration. Hence, the pH or H_3O^+ controls the S^{2-} concentration.

Since the Qual II cations precipitate at a low pH, then only small amounts of sulfide ion are needed for their precipitation; this indicates that these cations have a low solubilities and also a small K_{sp} values, at least smaller than those for the Qual III cations.

Preparation of the Cations for Analysis

Stannous sulfide, SnS , is a gelatinous precipitate and therefore difficult to separate and identify. Therefore to begin the analysis, all stannous ion, Sn^{2+} , is oxidized to stannic ion, Sn^{4+} , by treating the sample with hot HNO_3 . Thioacetamide is then added, generating the sulfide ion that precipitates the four cations as SnS_2 , PbS , Bi_2S_3 , and CuS . The sulfide precipitate is separated from the supernatant liquid and the Qual II analysis is completed on the precipitate.

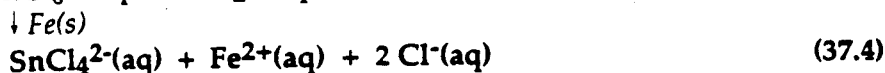
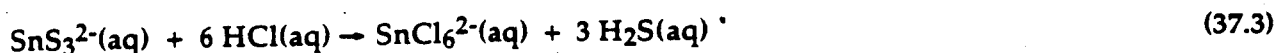
Tin Ion

SnS_2 , a yellow precipitate, is separated from the other sulfide precipitates by adding additional thioacetamide, but in a *basic* solution. The higher sulfide ion concentration¹ results in the formation of a soluble tin sulfide complex anion, SnS_3^{2-} , leaving PbS , Bi_2S_3 , and CuS as precipitates.

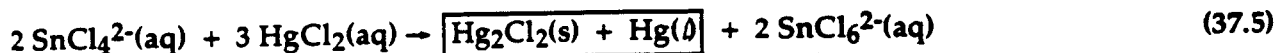


Conc HCl , added to the SnS_3^{2-} complex ion produces a soluble hexachloro complex of tin(IV), SnCl_6^{2-} , which when treated with iron metal reduces to a soluble tetrachloro complex ion of tin(II), SnCl_4^{2-} .

¹The lower H^+ concentration shifts the equilibrium in Equation 37.2 to the *right*.



The confirmatory test for the presence of tin in the sample is the appearance of a *grey-black precipitate* when mercuric chloride, HgCl_2 , is added to the solution containing the SnCl_4^{2-} ion.

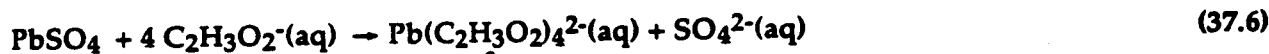


Dissolution of the Other Sulfide Precipitates

The PbS , Bi_2S_3 , and CuS precipitates (all black in color) are dissolved with hot HNO_3 . The hot HNO_3 oxidizes the sulfide ion in the precipitate to (free) elemental sulfur, forming $\text{NO}(\text{g})$ as its reduction product. The solution, containing the dissolved cations, Pb^{2+} , Bi^{3+} , and Cu^{2+} , is treated with H_2SO_4 and strongly heated to drive off any excess HNO_3 . Pb^{2+} forms a white precipitate, PbSO_4 .

Lead Ion

To confirm the presence of Pb^{2+} , the PbSO_4 is dissolved with an excess of $\text{C}_2\text{H}_3\text{O}_2^-$; this forms the $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_4^{2-}$ complex anion, which, when treated with CrO_4^{2-} , forms a *yellow* PbCrO_4 precipitate.



Copper Ion

The addition of aqueous NH_3 to a solution containing the remaining Bi^{3+} and Cu^{2+} cations precipitates Bi^{3+} as a white hydroxide, but complexes the Cu^{2+} as a soluble *deep-blue* $\text{Cu}(\text{NH}_3)_4^{2+}$ complex cation. This confirms the presence of Cu^{2+} in the solution.

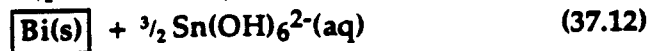
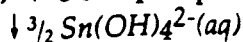
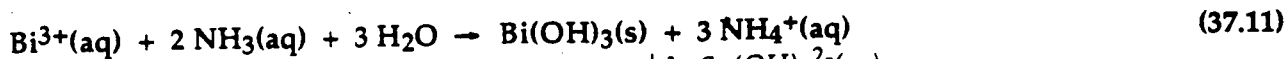


A second confirmatory test for the presence of Cu^{2+} is the addition of potassium hexacyanoferrate(II), $\text{K}_4[\text{Fe}(\text{CN})_6]$, producing a *red-brown precipitate* of $\text{Cu}_2[\text{Fe}(\text{CN})_6]$.



Bismuth Ion

The Bi^{3+} that precipitates in an ammoniacal solution to produce *white* bismuth hydroxide is dissolved and confirmed with the addition of *freshly prepared* sodium stannite, $\text{Na}_2\text{Sn}(\text{OH})_4$, in a basic solution. The Bi^{3+} ion is reduced to *black* bismuth metal, confirming the presence of bismuth in the sample.



As a guide to an understanding of the separation and identification of these four cations, complete the flow diagram on the Prelaboratory Assignment. Review the Preface to Qualitative Analysis for an understanding of the symbolism.

EXPERIMENTAL PROCEDURE

To become familiar with the identification of these cations, take a sample that contains the four cations and analyze it according to the procedure. At each numbered superscript (example, #1), STOP, and record on the Report Sheet. After each cation is confirmed, SAVE it in the test tube so that its appearance can be compared to that for your unknown sample.

If you are to analyze an unknown solution for the presence of the Qual II cations, place the sample in a 75-mm test tube alongside that which contains the known solution. As you progress through the procedure, perform the same test on both solutions and make comparative observations. Check (✓) the findings on the Report Sheet.

Before proceeding, review the techniques outlined in Dry Lab 7, Preface to Qualitative Analysis. The review of these procedures may expedite your analysis with fewer frustrations.

SAFETY AND DISPOSAL INFORMATION: Dispose of all test solutions and precipitates in the "Waste Metal Salts" container.

Caution: A number of concentrated and 6 molar acids and bases are used in the analysis of these cations. Handle each of these solutions with care. Read the Lab Safety section for instructions in handling acids and bases.

A. Preparation of the Cations for Analysis

1. **Oxidation of Tin and pH Adjustment.** To 2 mL of test solution in an evaporating dish—either the supernatant from Experiment 36, Part B.2 or a solution containing the four test cations—add 10-15 drops of 6 M HNO₃ (Caution!). Heat until a moist residue remains (Figure 37.1). Cool and add 1 mL of water. Add drops of 6 M NH₃ (Caution!) until the solution is basic to litmus.² Now make the solution acidic to litmus with drops of 6 M HCl; then add 2 more drops. This should adjust the pH of the solution to about 0.5. Transfer the solution to a 75-mm test tube. **CAUTION**

2. **Precipitation of Cations as Sulfides.** Add 10-15 drops of 1 M CH₃CSNH₂, heat in a hot water bath (= 95°C) (Figure 37.2) for several minutes, cool, and centrifuge. Test the solution for complete precipitation by repeating the thioacetamide addition to the supernatant. The precipitate contains the SnS₂, PbS, Bi₂S₃, and CuS salts; #1 the supernatant contains cations that do not precipitate under these conditions (on the advice of your laboratory instructor, save for Experiments 38 and 39).

²Review this technique for testing acidity and basicity.

3. **Wash the Precipitate.** Wash *twice* the precipitate³ with 0.1 M HCl, stir, and discard each washing.

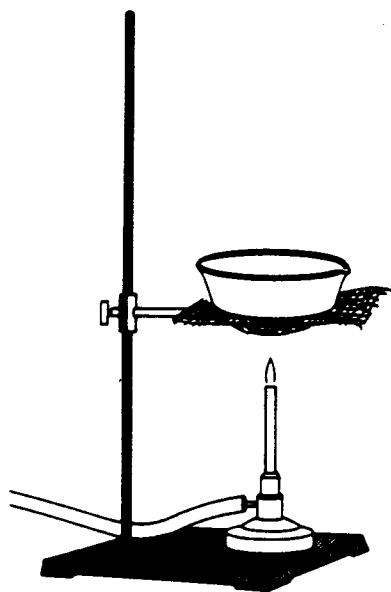


Figure 37.1. Heat the test solution to a moist residue

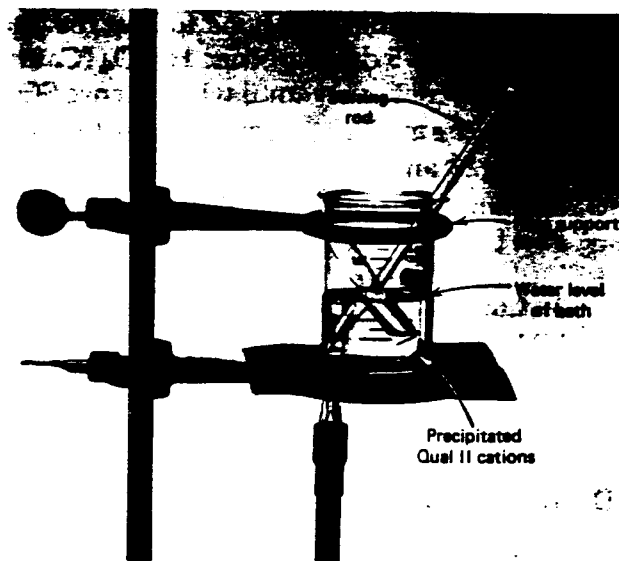


Figure 37.2. A hot water bath

B. Test for Tin Ion

1. **Dissolving the Tin Ion.** To the washed precipitate in Part A.3, add 2 mL of 6 M KOH and 3 drops of CH_3CSNH_2 solution. Heat the solution in a hot water bath ($\approx 95^\circ\text{C}$) for at least 5 minutes. While the solution is still warm, centrifuge and then decant the supernatant^{#2} into a 75-mm test tube. Save the precipitate for Part C.^{#3}

2. **Conversion to the Chloro Complex Ion.** Reacidify (to litmus) the supernatant with conc HCl (**Caution:** *Avoid inhalation or skin contact*); then add 6 more drops. Again heat in the hot water bath for 5 minutes.^{#4} Cool and add two *polished* 1-cm pieces⁴ of iron wire to this supernatant and reheat in the hot water bath for 3-5 minutes. Centrifuge and transfer the supernatant to another 75-mm test tube.

CAUTION

3. **Confirmatory Test.** To this supernatant,^{#5} add 5 drops of 0.2 M HgCl_2 . A *grey-black precipitate* confirms the presence of tin in the sample.^{#6}

³Review the procedure for washing a precipitate in Dry Lab 7, Preface to Qualitative Analysis.

⁴Remove the rust from the iron wire with 6 M HCl and then rinse thoroughly with distilled water.

C. Test for Lead Ion

1. **Dissolve the Cation Sulfides.** Add 15 drops of 6 M HNO₃ (**Caution!**) to the precipitate from Part B.1 and heat to boiling with a direct flame (**Caution: Read the technique for heating test tubes with a direct flame**) until the precipitates dissolve. Cool and centrifuge. Save the supernatant^{#7} and discard any free sulfur. **CAUTION**

2. **Separation of Lead Ion.** Transfer the supernatant to a crucible and set up an apparatus in the fume hood to heat the crucible with a direct flame (read Technique 12a). Add 3-5 drops of conc H₂SO₄ (**Caution: conc H₂SO₄ causes severe skin burns!**) and heat cautiously until white, dense SO₃ fumes appear. This is a very important step in the analysis.⁵ Cool, add 10-15 drops of water to the precipitate, which is PbSO₄,^{#8} and stir. Carefully transfer the solid-liquid suspension to a 75-mm test tube and centrifuge. Decant to and save the supernatant^{#9} in a 75-mm test tube for Part D. **CAUTION**

3. **Confirmatory Test.** Dissolve the PbSO₄ precipitate with 10 drops of 1 M NH₄C₂H₃O₂.^{#10} Heating may be required. Stir thoroughly and add 1 drop of 1 M K₂CrO₄. A *yellow precipitate*,^{#11} not solution, confirms the presence of Pb²⁺ in the sample.

D. Test for Copper Ion

1. **Confirmatory Test.** Add drops of conc NH₃ (**Caution: Avoid inhalation or skin contact!**) to the solution from Part C.2. The *deep-blue solution* confirms the presence of Cu²⁺ in the sample.^{#12} Centrifuge, decant the solution, and save the precipitate^{#13} for Part E. **CAUTION**

2. **A Second Confirmatory Test.** Acidify the supernatant from Part D.1 with 6 M HC₂H₃O₂ (**Caution!**). Add 3 drops of 0.2 M K₄[Fe(CN)₆]. A *red-brown precipitate* reconfirms the presence of Cu²⁺ ion.^{#14} **CAUTION**

E. Test for Bismuth Ion

1. **Preparation of Sodium Stannite.** Prepare a fresh Na₂Sn(OH)₄ solution by placing 2 drops of 1 M SnCl₂ in a 75-mm test tube, followed by drops of 6 M NaOH (**Caution!**) until the Sn(OH)₂ precipitate just dissolves. Agitate or stir the solution. **CAUTION**

2. **Confirmatory Test.** Add several drops of the Na₂Sn(OH)₄ solution to the precipitate from Part D.1. The immediate formation of a *black precipitate*^{#15} confirms the presence of the Bi³⁺ ion in the sample.

SAFETY AND DISPOSAL INFORMATION: Dispose of all test solutions and precipitates in the "Waste Metal Salts" container.

⁵PbSO₄ is soluble in a strongly acidic sulfuric acid solution due to the formation of HSO₄⁻. Heating the mixture until SO₃ fumes appear assures the removal of HNO₃ (Part C.1), of water (both have relatively low boiling points), and the decomposition of H₂SO₄ (H₂SO₄ → H₂O + SO₃ (g)) at its boiling point (338°C). This removes all sources of H⁺ and prevents the formation of HSO₄⁻.

PRELABORATORY ASSIGNMENT-EXPERIMENT 37

QUAL II. Pb^{2+} , $\text{Sn}^{4+}(\text{Sn}^{2+})$, Cu^{2+} , Bi^{3+}

Date _____ Lab Sec. ____ Name _____ Desk No. ____

1. a. Write the equilibrium equations for the SnS_2 , PbS , CuS , and Bi_2S_3 salts. Write the equilibrium expression (K_{sp}) for each salt and look up their K_{sp} values and color in your text book or other reference book, such as the CRC, *Handbook of Chemistry and Physics*.

	Equation	Equilibrium Expression	K_{sp} Value	Color
SnS_2				
PbS				
CuS				
Bi_2S_3				

- b. Calculate the molar solubility of each salt. Which salt is the least soluble? Which salt is the most soluble?

2. Which reagent converts Sn^{2+} to Sn^{4+} in preparation for the identification of the tin ion in the sample?

3. Write balanced redox equations for the oxidation of the PbS , CuS , and Bi_2S_3 salts with nitric acid. The redox products are elemental sulfur and nitric oxide, NO .

4. Which reagent separates Cu^{2+} from Bi^{3+} in solution?

5. What is the color of each?

a. $\text{Cu}(\text{NH}_3)_4^{2+}$ _____

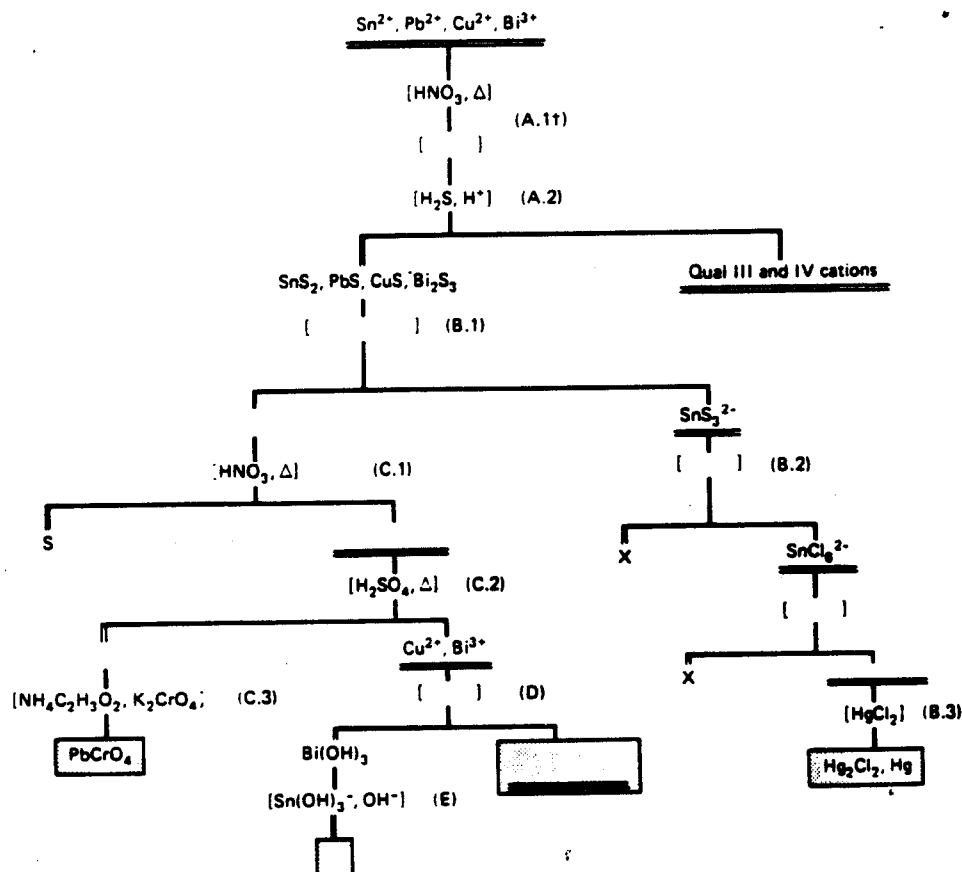
b. bismuth metal _____

c. a mixture of PbS and SnS_2 _____

6. Calculate the sulfide ion concentration in a saturated H_2S solution when the pH is 0.5. The concentration of H_2S in a saturated H_2S solution is about 0.1 mol/L.



7. Complete the following flow diagram for the Qual II cations.



†Refers to the Experimental Procedure, Part A.1.

REPORT SHEET - EXPERIMENT 37
QUAL II. Pb^{2+} , Sn^{4+} (Sn^{2+}), Cu^{2+} , Bi^{3+}

Date _____ Lab Sec. _____ Name _____ Desk No. _____

Procedure Number and Ion	Test Reagent or Technique	Observation (Color or General Appearance)	Chemical(s) Responsible for Observation	Equation(s) for Observed Reaction	Check (✓) if Observed in Unknown
#1		ppt			
#2 Sn^{4+} Sn^{2+}		spnt			
#3		ppt			
#4		spnt			
#5		spnt			
#6		ppt			<input type="checkbox"/>
#7 Pb^{2+}		spnt			
#8		ppt			
#9		spnt			
#10		spnt			
#11		ppt			<input type="checkbox"/>
#12 Cu^{2+}		spnt			<input type="checkbox"/>
#13		ppt			
#14		ppt			<input type="checkbox"/>
#15 Bi^{3+}		ppt			<input type="checkbox"/>

* ppt — precipitate; spnt—supernatant

Cations present in unknown: _____

Instructor's Approval: _____

Post Laboratory Questions

1. What happens in Part B.2 if the iron metal is *not* used in the procedure?
2. What happens in Part C.1 if 6 M HCl is substituted for 6 M HNO₃?
3. What happens in Part D.1 if NaOH is substituted for NH₃?
4. What happens if conc HCl is added to the precipitate in Part D.1?
5. If your unknown forms a yellow precipitate in Part A.2, identify the steps you would take to complete the Qual II analysis.
6. A student's unknown gives a blue solution but no white precipitate in Part D.1. What can be included?
7. Cite a reagent(s) that precipitates
 - a. Pb²⁺ but not Cu²⁺
 - b. Bi³⁺ but not Cu²⁺
 - c. Ag⁺ but not Bi³⁺
8. What reagent dissolves
 - a. SnS₂ but not CuS?
 - b. AgCl but not Bi₂S₃?