

Qualitative Analysis of an Inorganic Mixture

ABSTRACT

Students are given a mixture of two salts (up to two different cations and two anions) and required to identify the cations and ions in the mixture. The students are given a series of tests to perform, including precipitation, redox, and physical (colour, flame emission) tests, all of which are qualitative and can be done with standard glassware (test tubes, bunsen burners, etc.). Cations are from d-, s-, and p-block elements; cation tests are hierarchical to eliminate/choose cations by solubility groups. Anion tests are individual.

Equipment

No special equipment required. Some tests should be done in a fumehood. Test tubes, spatulae, beakers, etc.

Safety Hazards

No particular hazards. Utilizes an H₂S reagent which is smelly/toxic, some metals and reagents are toxic and/or environmentally hazardous. Ether (highly flammable) is used. Halogenated solvents are considered carcinogenic.

Year Level: 2nd year introductory inorganic
Student time required: 9-10 hours; three 3-hour lab periods minimum, probably four is better
Instructor time required: initial set-up in week one, preparing samples and solutions ~10 hours??
subsequent weeks - negligible

Technician notes? Available upon request
Study question solutions? Available upon request
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Chemistry 2351: Inorganic Chemistry I Laboratory Manual

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Experiment One:

Qualitative Analysis of an Inorganic Mixture

In this experiment, the student will learn how to test for inorganic cations and anions, then identify the contents of an unknown mixture.

CAUTION: When the lab manual instructs you to run a test in the fumehood, do so! Many of the tests and reagents will emit toxic and/or vile smelling gasses!

Introduction

Inorganic chemicals have enormous industrial and commercial importance. For example, the single largest chemical produced in the world is sulfuric acid. Therefore, being able to identify and to understand the reactivity of inorganic species is important, and is the topic of this experiment. Naturally, some of these chemical tests are obsolete in terms of identifying unknowns (many would be superseded by spectroscopic or mass spectrometric instrumental analyses). However, the chemistry used in these tests are a compendium of the common reactions - acid/base, precipitation, and redox reactions - that are still used commonly in industrial and academic settings.

In your lab book, you will need to make a table for your observations. Careful observations are the key to understanding the reactions and identifying the unknown. We suggest the following style:

Operation	Observation	Deduction
flame test	white powder gives orange flame	Na ⁺ and/or Ca ²⁺

The operation is the experimental procedure. Observation is a list of everything you noticed - evolution of gas, precipitation, dissolution, colours, etc. Deduction is what you can conclude from the test.

The reporting of your experimental results should allow conclusion of what your unknown mixture is. Once you have deduced a formulation for your unknown, (if time permits) you can test it by obtaining the components from the lab instructor and doing the test on the known species. In addition, you will have the opportunity to perform all the tests on known compounds before you start working on your unknown. Take advantage of the opportunity because every chemist has a different “touch” and your neighbour’s test result may look slightly different from your own.

Unknowns will be made up of two cations and one or two anions. The following species are possible:

Cations: Na⁺, K⁺, Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺, Cr³⁺, Mn²⁺, Fe^{2+ or 3+}, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Ag⁺, Sn²⁺, Pb²⁺, NH₄⁺
Anions: Cl⁻, Br⁻, I⁻, NO₃⁻, S²⁻, HPO₄²⁻, SO₄²⁻, S₂O₃²⁻, CrO₄²⁻

Techniques

1. Unless otherwise stated, use 10-20 mg of solids (this is the amount that will balance on the tip of a spatula). If you wish to “calibrate” your spatula, use the analytical balance, but do not weigh things each time - it takes too long!
2. Unless otherwise states, use test tubes. You can calibrate the test tubes and droppers by measuring with graduated cylinders. Use of grad cylinders each time is time-consuming.
3. Use a glass rod, or tap the side of the test tube with your finger, for mixing. **DO NOT** shake with a thumb over the top! Even if wearing gloves, some of the materials are quite toxic, acidic, etc., and some can pass through the glove material.
4. Be clean! Contamination could lead to false positive and/or ambiguous results. Remember that your skin has NaCl, for example, which is one of the possible unknown compounds!
5. “Warm” = place sample in a beaker of hot water. “Heat” = gentle heating with Bunsen burner. Remember to point tubes away from yourself and others!

Experimental Procedure

PART 1: PHYSICAL PROPERTIES

- (a) Look carefully at the sample. Colours and consistency can tell you something about the compound. The following cations will often have the following colours

Alkali and alkaline metal salts are usually colourless

Cr (+3) deep green; (+6) bright orange/yellow

Mn²⁺ very faint blush pink

Fe (+2) pastel green; (+3) yellow to brown

Co²⁺ purple or brown

Ni²⁺ pale green

Cu²⁺ blue if ligated (*e.g.* with water), white otherwise

- (b) Flame tests: moisten the end of a platinum wire and dip into the salt you are testing. Heat the wire in a Bunsen burner. Common flame colours are:

Na⁺ street-lamp orange

K⁺ lilac

Ca²⁺ could be brick red or orange like Na⁺

Sr²⁺ bright red

Ba²⁺ light green

Sn²⁺ light bluish (could look like K⁺)

Pb²⁺ no colour, but salt may melt into a blob and fall onto bench

- (c) Ammonium salts will often have a distinctive odour.

PART II: CATIONS

- (a) Prepare a solution of your unknown by putting 0.02 g of sample in a test tube and add one of the solvents below. If it does not dissolve, warm it. If it still does not dissolve, discard and try the next solvent. Proceed down this list in order, stopping when you find one that works.
NOTE: you will need 1 g of solid for Part III so make sure you set some aside!!
- (i) 1 mL of distilled water
 - (ii) 1 mL of dilute HCl
 - (iii) 10 drops of conc. HCl, heat with care, then dilute
 - (iv) 8 drops of conc. HCl and 1 drop of conc. HNO₃
 - (v) 1 mL of dilute HNO₃ (if sample immediately dissolves, boil to nearly to dryness and add 1 mL of water)
 - (vi) 1 mL of conc. nitric. Proceed as for (v). Caution: be careful with heating, make sure it is in the fumehood.
- (b) *Choosing a cation group.* Once you have a solution, follow the flow chart to determine the group to which your cation belongs. These groups are not periodic groups, but rather groups with similar solubilities. These are done sequentially, using the same solution throughout. Once a group is chosen, perform the confirmatory tests for that group.

Group I = Ag⁺, Pb²⁺

Group II = Cu²⁺, Sn²⁺

Group III = Fe²⁺, Fe³⁺, Cr³⁺

Group IV = Mn²⁺, Co²⁺, Ni²⁺, Zn²⁺

Group V = Ca²⁺, Sr²⁺, Ba²⁺

Group VI = Na⁺, K⁺, NH₄⁺, Mg²⁺

Group I Add 1 mL of dilute HCl (if no HCl used as solvent). Cool and scratch inside of tube with glass rod and wait at least 1 min.

Centrifuge. A precipitate indicates Group I

If no ppt, proceed to Group II.

SUMMARY OF GROUP SEPARATIONS

To a solution of the cation, add HCl					
ppt: AgCl PbCl ₂	Solution, ions of: Na, K, Mg, Ca, Sr, Ba, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sn, (Pb)*, NH ₄				
	Add "H ₂ S"				
	ppt: CuS, SnS, PbS		Solution, ions of: Na, K, Mg, Ca, Sr, Ba, Cr, Mn, Fe, Co, Ni, Zn, NH ₄		
	add (NH ₄) ₂ S _x		Add NH ₄ Cl and NaOH		
	ppt: CuS PbS	soln: (NH ₄) ₂ SnS ₃	ppt: Fe(OH) ₃ Cr(OH) ₃	Solution, ions of: Na, K, Mg, Ca, Sr, Ba, Mn, Co, Ni, Zn, NH ₄	
			Add "H ₂ S"		
		ppt: MnS CoS NiS ZnS	Solution, ions of: Na, K, Mg, Ca, Sr, Ba, NH ₄		
		Add (NH ₄) ₂ CO ₃			
		ppt: CaCO ₃ SrCO ₃ BaCO ₃	Solution, ions of: Na, K, Mg, NH ₄		
I	II		III	IV	VI

* Since PbCl₂ has some solubility in water, it will ppt in Group I and the remnants will ppt in Group II

SUMMARY OF PRECIPITATES FROM PRELIMINARY TESTS FOR CATIONS

group	metal and sol ⁿ colour	group reagent	group ppt	colour
I	silver lead	dil. HCl	chloride	white white
II	copper - blue soln (lead) tin	H ₂ S and HCl	sulfide	black black dark. brown
III	iron - green-yellow soln chromium - deep green soln	NH ₄ ⁺ and OH ⁻	hydroxide	red-brown green or mauve
IV	manganese cobalt - pink soln nickel - green soln zinc	H ₂ S and OH ⁻	sulfide	pink black black white or grey
V	calcium strontium	(NH ₄) ₂ CO ₃	carbonate	white no ppt

Group II Take two drops of the solution from Group I. Add 10 drops water, add a few drops of “H₂S” (aqueous thioacetamide) solution and warm. **KEEP THIS SOLUTION IN THE FUMEHOOD!!** (the entire lab with know if you don't!!)

Centrifuge. A precipitate indicates Group II.

No ppt: Discard **IN HOOD!** Go on to Group III.

If the test gives a copious ppt (should be coloured), dilute sample in Erlenmeyer to 6 mL. Warm and add a few more drops of “H₂S”. Decant, centrifuge and retain solid for confirmatory tests. If you haven't yet found your second cation, it may be in the liquid - boil to remove H₂S (gently! in the hood!) and proceed to Group III test.

NOTE: A small amount of black flecks usually indicates PbS. This is generally only an indication of Pb contamination, especially if you found Pb²⁺ in Group I.

Group III Add 2 drops of conc. HNO₃ and boil, then add 1 mL of 2 M NH₄Cl solution. Dilute to 5 mL (in a flask) and add 50% NH₃ until alkaline (red litmus).

Centrifuge (will need more than one tube). A ppt indicates Group III. **CAREFUL:** these ppt's might be transparent! Save ppt for confirmatory tests.

No ppt, go on to Group IV.

Group IV Warm sample and add a few drops of “H₂S” (**HOOD!**).

If a ppt forms, warm and add more “H₂S.” Mix well and centrifuge. A ppt indicates Group IV. Save ppt for confirmatory tests.

Note: If the solution is not colourless, bring to a boil and centrifuge again. The brown is colloidal NiS that should ppt with this second treatment.

No ppt, proceed to Group V.

Group V Boil down to 1 mL (**HOOD!**). (see note under Group IV, above) Transfer to a test tube and add 1 mL of ammonium carbonate solution. Warm (do not boil!). Scratch and let stand for 5 min.

Centrifuge. A ppt indicates Group V.

The solution will contain any Group VI cations you have. If you haven't found your two unknown cations by this point, you'll have to do the confirmatory tests for Group VI.

- (c) *Confirmatory tests for cations.* These tests are performed on the ppt you isolated in each group test. They will show which specific member of the group you have.

Group I Wash ppt with cold water. Add 2 mL of water and warm well. Centrifuge.

<p><u>ppt</u>: add 1 mL dilute NH_3, warm ppt dissolves, add dil. HNO_3</p> <p>white ppt: SILVER</p>	<p><u>solution</u>: divide into 2 samples (i) add dil. acetic acid and K_2CrO_4 solⁿ (ii) add KI solution</p> <p>yellow ppt in each case: LEAD</p>
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Group II Wash ppt with hot water. Add a few drops of ammonium sulfide solution and warm.

<p><u>if ppt doesn't dissolve</u>: warm ppt with 1 mL water and 10 drops of conc. HNO_3. Centrifuge. Add 50% NH_3 to solⁿ until a slight excess.</p> <p>Blue solution: COPPER</p>	<p><u>if ppt dissolves</u>: add 2 mL conc. HCl and centrifuge. Add HgCl_2 solⁿ to test solⁿ.</p> <p>white ppt: TIN</p>
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Group III Wash ppt with water. Warm with 1 mL of NaOH and 1 mL of H₂O₂ until effervescence ceases. Centrifuge.

<p><u>ppt</u>: red-brown = Fe dissolve rest of ppt in 2 mL dil. HCl. Add potassium <u>ferricyanide</u> blue solⁿ: IRON</p> <p>test original substance with potassium <u>ferricyanide</u> blue solⁿ: FERROUS no blue: FERRIC</p>	<p><u>solution</u>: acidify with acetic acid; add lead acetate solⁿ yellow ppt: CHROMIUM</p>
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Group IV Wash group ppt with water. Mix ½ mL dil. HCl and 1 mL of water and pour onto ppt. Mix well (do not warm). Centrifuge.

<p><u>to ppt</u>: heat with ½ mL conc. HCl and a crystal of KClO₃; divide into portions for testing</p> <p>to one portion, add dil. NH₃ until alkaline, then 2 drops of dimethyl glyoxime pink ppt: NICKEL</p> <p>to another portion, add equal volumes of acetone and KCNS blue solution: COBALT</p>	<p><u>to solⁿ</u>: boil to expel H₂S. Add 2 drops of H₂O₂ and then NaOH until there is excess. Warm, then cool and centrifuge</p> <p>Brown ppt: MANGANESE to confirm: fuse small amount of ppt on porcelain with KNO₃ and K₂CO₃ green mass: MANGANESE</p> <p>Soak filter paper in soln; add tiny drop of cobalt nitrate soln; ignite in crucible green ash: ZINC</p>
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Group V Divide group ppt into 2 parts

To one part of group ppt, dissolve by pouring in 2 mL of warm dil. acetic acid. Add 50% NH₃ until alkaline. Add 1 mL ammonium oxalate solⁿ. Stir and stand.
White ppt: CALCIUM

Wash the other part with 50% ethanol (*aq*). Dissolve ppt in 1 drop of 4 M CH₃COOH and 5 drops water. Add 1 drop 2 M sulfuric acid and 4 drops of ethanol. Centrifuge and moisten residue with HCl and do flame test.
Crimson flame: STRONTIUM
Green flame: BARIUM

- Group VI Boil off ammonia in crucible, add ½ mL of water.
- (i) to a portion (few drops) add a few drops of 50% ammonia and 1 mL of sodium phosphate soln. Stir and stand.
white ppt: MAGNESIUM
 - (ii) to another portion (few drops), add an equal volume of zinc uranyl acetate soln. Scratch and stand
slight white ppt: SODIUM (check with flame test!)
 - (iii) evaporate the rest of the solution in a crucible - heat until no more fumes are seen. When cool, dissolve residue in 1 mL dil. acetic acid. Add 1 mL of cold (freshly made) sodium cobaltinitrite. Stir.
yellow ppt: POTASSIUM (check with flame test!)
 - (iv) to a small portion of your original solution, add conc. NaOH and warm gently. Place a moistened piece of red litmus over the top of the test tube.
red litmus turns blue: AMMONIUM
caution: NO₃⁻ anion may give a false positive

PART III: ANIONS

Take 1 g of the unknown solid, add sodium carbonate solution (you will need up to 8 mL at the end of this procedure) and boil gently (in beaker of hot water) for a few minutes. Centrifuge and retain the solution. This is the test solution for anions.

- CHLORIDE To 1 mL of the test solution, add 6 M nitric acid until solution is slightly acidic, then add 10 drops of 0.1 M AgNO₃. A white ppt is AgCl. The ppt should be soluble in conc. NH₃ (aq).
- BROMIDE or IODIDE Acidify 3 drops of the test solⁿ with 2 M sulfuric acid, add 1 drop of 5% NaClO, and a few drops of CH₂Cl₂ and mix vigorously. Brown in the CH₂Cl₂ layer is Br₂, purple in the CH₂Cl₂ is I₂.
- SULFATE To 1 mL of the test solⁿ, add 6 M HCl until solⁿ is acidic. Add 10 drops of BaCl₂ soln. White ppt is BaSO₄.
- SULFIDE To 1 mL of the test solⁿ add dilute HCl and sodium nitro-prusside. A violet solⁿ indicates the presence of S²⁻.
- THIOSULFATE Take 6 drops of the test solⁿ, add 2 M sulfuric acid and 0.5 mL of 1% AgNO₃ solⁿ. A creamy-yellow ppt turning brown, then black on warming, indicates S₂O₃²⁻.
- CHROMATE To 1 mL of the test solⁿ, add dilute HCl and 2 drops of H₂O₂. A blue colour that

fades rapidly indicates CrO_4^{2-} . (To verify, you can repeat this test in the fumehood adding 10 drops of ether - the ether layer should retain the blue colour.)

HYDROPHOSPHATE To 1 mL of the test solution, add conc. nitric acid ammonium molybdate (1 mL). Stand in hot water. A yellow ppt indicates a phosphate species (this will work for PO_4^{3-} , HPO_4^{2-} , and H_2PO_4^-).

NITRATE Almost all metal salts of nitrate are soluble, so a redox reaction must be used to verify nitrate. Combine 1 mL of the test solⁿ and 1 mL of 4 M NaOH solⁿ. Add a piece of aluminium foil. Ammonia will evolve in the presence of nitrate. Test by holding moistened litmus paper over the neck of the flask. The ammoniac smell should be obvious as well.

Final Report

For your report, you will need to fill in the question sheet at the end of this lab. You will have to identify your unknown (remember to write down your unknown number!) and give reasons for your assignment. These reasons will include detailed observations, including your path through the group tests and specific observations in the confirmatory test and any other physical observations (flame test, etc.). (The following would *not* acceptable as a justification: "Confirmatory test for X positive.") Finally, you will have to supply the chemical reactions of the test reactions you did. Of course, if no obvious reaction took place, it probably means that no reaction took place at all! Just supply reactions for which you saw a chemical change (colour, ppt, gas evolution, etc.). Precipitation reactions are the most common - use your K_{sp} tables from your 1st year text as a reference source. Redox reactions are also possible, as discussed in class.

Remember: unknowns will have 2 cations and either 1 or 2 anions.

References/Bibliography:

For purposes of the lab writeup, you might want to use:

General information: Miessler and Tarr, Inorganic Chemistry, 3rd Edition (2351 text)
Zumdahl and Zumdahl, Chemistry, 8th Edition (1110/1130 text)

redox chemistry: Wulfsberg, Inorganic Chemistry (library course reserve)

specific tests: Vogel, Textbook of Macro and Semimicro Qualitative Inorganic Analysis, 5th edition (library reserve, QD 81 V87 1979)
Lagowski and Sorum, Introduction to Semimicro Qualitative Analysis, 3rd edition (library reserve, QD 81 S71)
Slowinski and Masterton, Qualitative Analysis and the Properties of Ions in Aqueous Solution (Aisley has a copy of this)

CHEMISTRY 2351 REPORT SHEET
Experiment One:
Qualitative Analysis of an Inorganic Mixture

NAME: _____

DATE: _____

UNKNOWN NUMBER: _____

My unknown mixture contains the following cations: _____

My unknown mixture contains the following anion(s): _____

ANION #1

Justification:

Confirmatory test reaction:

ANION #2 (if present)

Justification:

Confirmatory test reaction:

Experiment 1 Report Sheet

NAME: _____

Cation #1:

Justification:

Group test reaction(s):

Confirmatory test reaction(s):

Cation #2:

Justification:

Group test reaction(s):

Confirmatory test reaction(s):